Physical Chemistry III

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Chapter 1

Statistical Thermodynamics

1.1 Introduction

Statistical mechanics deals with the understanding and prediction of the macroscopic properties of a system from the knowledge of its microscopic components. Classical thermodynamics defines macroscopic properties (internal energy, entropy, etc.) and provides relations between them, but the magnitude of these quantities must be measured experimentally. Because classical thermodynamics does not know about atoms or molecules, the value of a thermodynamic property cannot be predicted from the composition of the system alone. The goal of statistical mechanics is to predict the macroscopic properties of a system using information about its microscopic behavior: molecular geometries, energy levels, intermolecular interaction strengths, etc.

The part of statistical mechanics that studies systems at equilibrium is called **statistical thermodynamics**, and it provides useful results for understanding fundamental laws of chemistry. Non-equilibrium statistical mechanics, which is considerably more complex, is an active field of research, and can be used to predict transport properties and to model chemical reactions. We will focus on systems at equilibrium only. Statistical thermodynamics can be used to study many systems of chemical interest including gases, liquids, electrolytic solutions, adsorption and reactivity of molecules on surfaces, magnetic solids, and the behavior of biological macromolecules (e.g. protein folding). It is also useful in computational chemistry, where it provides recipes to predict the properties of a macroscopic system from quantum chemical calculations.

Statistical thermodynamics is built on a microscopic description of the system's components. This description can be founded on classical mechanics or quantum mechanics. In the classical variant, which was developed by Maxwell, Boltzmann, and Gibbs in the late 19th century, the state of the system is described by the position and momentum of all its particles, and its evolution in time is given by Hamilton's equations (a reformulation of Newton's laws of motion that is invariant under a change of coordinates). This classical formalism is correct in the **classical limit**, where the energy available to the system greatly exceeds the separation between energy levels.

It is often the case that chemical systems are not at the classical limit, and therefore classical statistical thermodynamics fails to explain experimental results. Particularly egregious examples of this fact, like the inability to predict the heat capacity of solids at low temperature, were contributing factors in the development of quantum theory. In those instances, taking into account the fact that the energy levels of the system are quantized is essential for a correct qualitative description of experimental phenomena. We will focus on the quantum mechanical version of statistical thermodynamics, which describes the state of the system using a wavefunction and its time evolution with the time-dependent Schrödinger equation. Quantum statistical thermodynamics tends to be mathematically simpler than the classical version, and the former tends to reproduce the results of the latter in the high-temperature limit.

Regardless of the microscopic description used to represent its energy levels, the number of molecules in the system is generally in the order of Avogadro's number. Therefore, a complete description of the state and evolution of a given system is unfeasible. The power of statistical thermodynamics is in the use of probabilistic methods to calculate macroscopic properties from averages of microscopic properties of a system, without having to explicitly solve its equation of motion. To simplify even further, we will mostly focus in the next chapter on systems of non-interacting molecules, which leads to simple derivations of important chemical results. The application of statistical thermodynamics is not limited to molecules and can be used to describe other types of particles or quasi-particles such as harmonic vibrations in a crystal (phonons), photons, and others.

1.2 Macrostates and Microstates

In the following, we use the term **system** to refer to a thermodynamic system with measurable macroscopic properties such as volume, temperature, pressure, etc. The **macrostate** of the system is the set of macroscopic variables that determine its thermodynamic state. The number and nature of the variables that determine the macrostate of a system depend on its characteristics. For a instance, a homogeneous isolated system is characterized by its volume (V), energy (E) and number of particles (N). The macrostate of a mixture of gases inside a vessel with heat-conducing, impermeable, rigid walls (a closed system) is determined by its volume (V), temperature (T), and the number of moles of each of its components (n_1, n_2,...).

For simplicity, let us first consider a homogeneous closed system, with macrostate given by N, V, and temperature (T). Since the volume and the interactions between the particles are known, we can, in principle, solve the time-independent Schrödinger equation for the whole system, which yields the set of all possible quantum states accessible to it. (Of course, with N in the order of Avogadro's number, this is an impossible task in practice.)

$$\mathcal{H}\Psi_i = E_i\Psi_i \tag{1.1}$$

We sort the states of the system in order of increasing energy ($E_0 \leq E_1 \leq \ldots$) as well as the corresponding eigenfunctions (Ψ_0, Ψ_1,...). Note that the time-independent Schrödinger equation is completely determined by the number of particles, the volume, and the interactions between the particles, and therefore the energies depend on N and V ($E_i(N,V)$) but not on temperature.

The particular microscopic (quantum) state that a system occupies is called its **microstate**. Each of the solutions of the Schrödinger equation above is a possible microstate of the system. For a macroscopic system, there are very many different microstates compatible with a given macrostate. To illustrate this point, let us consider an isolated system (macrostate given by N, V, and E) containing an ideal monoatomic gas like, for instance, neon atoms. Because it is ideal, the neon atoms do not interact with each other and the state of the whole system is, in principle, determined by the enumeration of the states each individual atom occupies.

The molecular energy levels can usually be separated into translational, rotational, vibrational, and electronic. Being an atom, neon does not have vibrational or rotational energy levels and, because it is a noble gas, the excited electronic energy levels are not significantly populated at room temperature. Therefore, only the translational energy levels are available to the atoms in this system. For each neon atom, the translational states are determined by three translational quantum numbers (n_x, n_y, and n_z), and the associated energies are:

$$E_{n_x,n_y,n_z} = \frac{(n_x + n_y + n_z)^2 h^2}{8mL^2} \tag{1.2}$$

where each of the quantum numbers is an integer greater than zero. Therefore, the microstate of this system is determined by approximately $3N_A$ numbers (N_A = Avogadro's number), while its macrostate is given only three values (N, V, and E). Furthermore, there are very many combinations of molecular states (n_x, n_y, and n_z) that, when the energies of the corresponding atoms are summed, give the system's total energy (E). Note also that the index i that runs over the system's states in Eq. 1.1 is actually a very complex composite of very many individual quantum numbers.

Question: In a system composed of three non-interacting distinguishable harmonic oscillators of frequency ω, how many microstates correspond to an energy level $E = 15/2\hbar\omega$?

The energy of a quantum harmonic oscillator is:

$$E = (n + 1/2)\hbar\omega$$

where $n = 0, 1, \ldots$. If the quantum numbers of the three oscillators are n_1, n_2, and n_3, then the total energy of the system is:

$$E = \left(n_1 + n_2 + n_3 + \frac{3}{2}\right)\hbar\omega$$

and therefore the number of microstates is the number of solutions of the equation:

$$\left(n_1 + n_2 + n_3 + \frac{3}{2}\right)\hbar\omega = \frac{15}{2}\hbar\omega$$

$$n_1 + n_2 + n_3 = 6$$

where each n_i can be any integer ≥ 0. The number of microstates is:

$$\left(\!\!\binom{3}{6}\!\!\right) = \binom{8}{6} = \frac{8!}{6!2!} = 28$$

The number of microstates associated with a particular energy level E of the system is called the **degeneracy**, and denoted $g(E)$ or g_E (alternatively, a unique quantum number can be used instead of E to label the level). The distinction between the **energy levels** of a system (determined by a particular value of the energy, E) and the **state** of a system (there are $g(E)$ states, all with energy E) is important, and can be applied to the system as a whole or to individual molecules. For instance, in a rigid rotor the energy level given by quantum number J, with energy:

$$E_J = hc\tilde{B}J(J+1) \tag{1.3}$$

has a degeneracy of $2J + 1$. This happens because there is an additional quantum number m_J associated to one of the components of the angular momentum operator that does not enter the energy expression. If the rigid rotor is in an energy level given by J, with energy E_J, then there are $2J + 1$ states because m_J can take integer values between $-J$ and J. The $2J + 1$ states belong to the E_J energy level, and therefore its degeneracy is $g(E_J) = g_J = 2J + 1$.

Question: What is the degeneracy of level $n = 3$ in the hydrogen atom? (assume spinless electron)

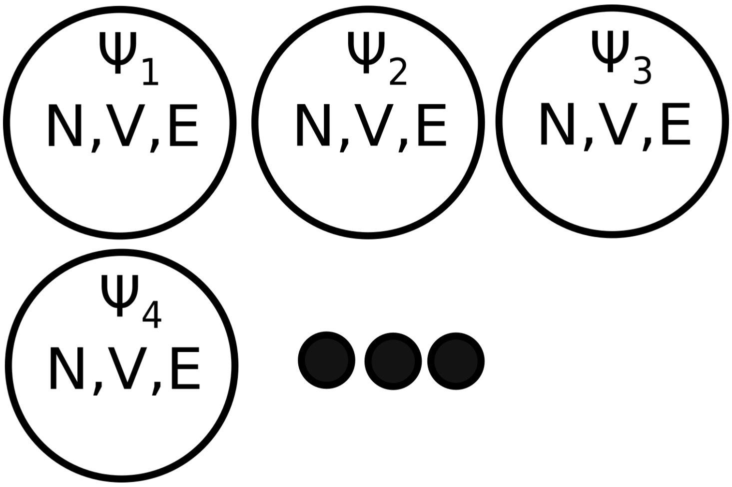


Figure 1.1: An example of a (microcanonical) ensemble. All systems in the ensemble have number of particles N, volume V, and energy E, but they are in different quantum states (Ψ_1, Ψ_2,...).

The energy of a hydrogen atom is given by:

$$E_n = -\frac{1}{2n^2}$$

in atomic units (Hartree). The energy levels are determined by quantum number $n = 1, 2, \ldots$. There are two additional quantum numbers that do not appear in the energy expression, associated with the electron's angular momentum: $l = 0, \ldots, n-1$ and $m = -l \ldots l$. For $n = 3$, we can have:

- $l = 0$ and $m = 0$ ($3s_0$).
- $l = 1$ and $m = -1, 0, 1$ ($3p_{-1}$, $3p_0$, $3p_1$).
- $l = 2$ and $m = -2, -1, 0, 1, 2$ ($3d_{-2}$, $3d_{-1}$, $3d_0$, $3d_1$, $3d_2$).

for a total of nine states. The degeneracy is $g(n = 3) = 9$.

1.3 Ensembles

The goal in statistical thermodynamics is to calculate the thermodynamic properties of a system starting from a microscopic description of its components. We distinguish two kinds of thermodynamic properties: mechanical and non-mechanical. A **mechanical property** can be defined without using the concept of temperature. An example of a mechanical property is pressure (p), which can be calculated as an average of the number of molecular collisions with the walls of the container over time. Other mechanical properties include the volume (V), and the internal energy (U). A system in a given microstate has a well-defined value for every mechanical property. A **non-mechanical property** involves temperature in its definition. For example, the entropy (S) or the Gibbs free energy (G). Non-mechanical properties are statistical in nature and cannot be defined for a single microstate.

A fundamental concept in statistical thermodynamics is that of an **ensemble** (ensemble means "collection"). An ensemble is a very large collection of replicas of the thermodynamic system under study, all in the same macrostate. For instance, let us assume a homogeneous isolated system whose macrostate is given by its volume V, number of particles N, and energy E. Then, we replicate this system $\tilde{N}$ times. Since all systems in the ensemble share the same macrostate, the ensemble as a whole has energy $\tilde{E} = \tilde{N}E$ and volume $\tilde{V} = \tilde{N}V$. However, each of the systems in the ensemble can be in any of the $g(E)$ microstates compatible with this macrostate. This ensemble (called a microcanonical ensemble) is illustrated in Figure 1.1.

There are two fundamental postulates in statistical thermodynamics:

- The **principle of equal a priori probabilities** states that all microstates with the same energy are represented an equal number of times in the ensemble. Since the number of systems in the ensemble is very large, this is equivalent in statistical terms to stating that a system with energy E is equally likely to be in any of the $g(E)$ possible microstates. Although they have the same energy, in general each of the $g(E)$ microstates has a different value for the other various mechanical properties of the system.
- The **ensemble postulate** states that the time average of a mechanical property is equal to the average over systems in the ensemble. By applying this postulate, we can identify quantities calculated as an average over the ensemble with the corresponding thermodynamic property, experimentally measured as a time average ($\langle E\rangle = U$, $\langle p\rangle = p$,...).

These postulates are proposed as axioms and verified *a posteriori* by reproducing experimental observations.

Different ensembles are possible depending on the type of system and the macrostate variables used to specify its thermodynamic state. The choice of which particular ensemble to use is dictated by experimental conditions and mathematical convenience. An ensemble like the one above composed of isolated systems (macrostate given by N, V, and E) is called a **microcanonical ensemble**. An ensemble that comprises closed systems with impermeable rigid walls, which can exchange heat (but not matter) with each other and the environment, is called a **canonical ensemble** (canonical means “in common practice”). In the canonical ensemble, the macrostate variables are N, V, and T. Conceptually, a canonical ensemble can be visualized as a very large heat bath in which all the replicas of the system are submerged. The replicas exchange energy with the bath and with each other, and all of them are in thermal equilibrium. The canonical ensemble is the most useful one in practice, and we will focus almost exclusively on it. Another ensemble that is occasionally useful is the **grand canonical ensemble**, in which all the systems have permeable walls and can exchange both matter and energy with each other (i.e. composed of open systems). In this ensemble, the macrostate of each system is given by V, T, and the **chemical potential** μ, which measures the stability of the component within the system (or, equivalently, its tendency to escape to other systems).

1.4 Occupations and Distributions

We focus now on a canonical ensemble. This ensemble comprises $\tilde{N}$ systems and all systems are in the same macrostate given by the number of molecules N, the volume V, and the temperature T (i.e. all systems are in thermal equilibrium with a heat bath at temperature T). The ensemble is thermally insulated from the rest of the universe and, therefore, it is itself an isolated system with energy $\tilde{E}$.

Same as in the previous section, the Schrödinger equation for each system is determined by the volume (V), the number of particles (N), and the interactions between them. The Schrödinger equation can be solved, in principle, to find the available quantum states and their associated energies for the system. Let us assume that the energies of these states are sorted in ascending order: $E_0 \leq E_1 \leq E_2 \leq \ldots$. Note that, because we are considering states instead of levels, some of these energies may be repeated. We define a **configuration** of the ensemble as the specific assignment of states to each particular system:

System	1	2	3	4	...
State	Ψ_2	Ψ_1	Ψ_0	Ψ_2	...
Energy	E_2	E_1	E_0	E_2	...

The **occupation number** a_i of a state i is the number of ensemble systems that occupy that particular state. Since the systems in a canonical ensemble do not have a fixed energy (because E is not a macrostate variable), a given system at any time can be in any of all its possible states, although some are more probable than others. Therefore, we can list the occupation numbers:

State	0	1	2	3	...
Energy	E_0	E_1	E_2	E_3	...
Occupation number	a_0	a_1	a_2	a_3	...

and, in principle, there are no restrictions regarding the possible values any a_i can take.

The set of occupation numbers of the ensemble $\boldsymbol{a} = \{a_i\}$ is called its **distribution**. In order to be valid, a distribution must satisfy the constraint:

$$\sum_i^{\text{states}} a_i = \tilde{N} \tag{1.4}$$

since all systems in the ensemble must occupy one, and only one, state at any given time. In addition, the state of each system changes constantly over time as it exchanges energy with the heat bath. However, because the ensemble itself is an isolated system, it cannot gain or lose energy. This is an additional constraint on what constitutes a valid distribution:

$$\sum_i^{\text{states}} a_i E_i = \tilde{E} \tag{1.5}$$

In both of these equations, the sum runs over all possible states of the system, and E_i is the energy of state i. (Remember that i can be a composite of very many individual quantum numbers.)

The specification of all states for all systems in the ensemble (its configuration) can be thought as a microstate of the ensemble, which is itself an isolated system. Because the energy of the ensemble is a constant ($\tilde{E}$), all configurations of the ensemble are equally probable by the principle of equal a priori probabilities. A given distribution is associated with many of these configurations and, since all configurations are equally probable, the probability of a given distribution is proportional to the number of ways in which this distribution can be generated. This is similar to the probabilities in an experiment in which two dice are thrown and the resulting values are added. Obtaining a 2 or a 12 is difficult because there is only one way of generating those number (i.e. a 1 or a 6 in each die). In comparison, obtaining a 7 is much more likely because there are more ways in which this value can be obtained (1+6 or 2+5 or 3+4).

To further illustrate this point, let us consider a simple chemical example. We have a system with only two possible states: 0 and 1. (This may sound like a contrived example but two-state systems are often used as models for atomic magnetism in materials science.) We further assume that the ensemble contains only three systems. Because we only have two states, there are only two occupation numbers: a_0 and a_1. The sum of the two occupation numbers must be equal to 3 because of the number constraint on the valid distributions (Eq. 1.4). Therefore, the only possible distributions are $\{3, 0\}$, $\{2, 1\}$, $\{1, 2\}$, and $\{0, 3\}$. We now consider how probable each of these distributions are by counting their number of configurations:

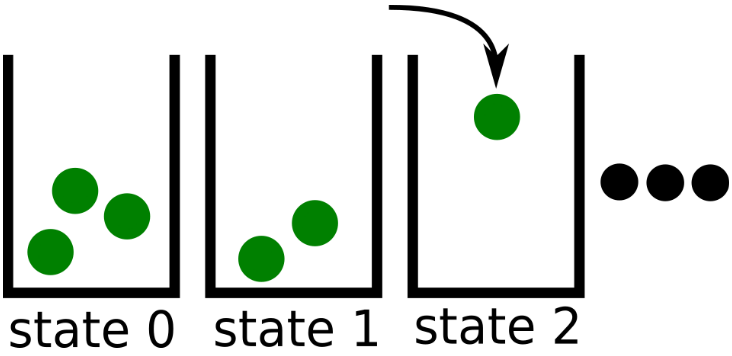


Figure 1.2: The states of the system are represented as bins. State 0 is the ground state (E_0), state 1 is the first excited state, etc. The ensemble systems, represented as green circles, fill the bins from left to right.

Configuration			Distribution
System 1	System 2	System 3	
0	0	0	$\{3,0\}$
1	0	0	$\{2,1\}$
0	1	0	"
0	0	1	"
1	1	0	$\{1,2\}$
1	0	1	"
0	1	1	"
1	1	1	$\{0,3\}$

Each row in the table is a configuration of the ensemble and all of them are equally probable (by the principle of equal a priori probabilities). Therefore, the distributions $\{1,2\}$ and $\{2,1\}$ are three times as likely to occur than $\{3,0\}$ and $\{0,3\}$.

We now define the **weight of a distribution**, $W(\boldsymbol{a})$, as its number of configurations, i.e., the number of ways in which that distribution can be obtained. From the discussion above, the weight of a distribution is directly proportional to the likelihood of its appearing in the ensemble. In the example above, the weights of the four distributions are $W(\{3,0\}) = 1$, $W(\{2,1\}) = 3$, $W(\{1,2\}) = 3$, and $W(\{0,3\}) = 1$.

The weight of a distribution can be calculated for a general canonical ensemble. In an ensemble with $\tilde{N}$ systems, the weight of distribution $\boldsymbol{a} = \{a_0, a_1, \ldots\}$ is:

$$W(\boldsymbol{a}) = \frac{(\sum_i^{\text{states}} a_i)!}{a_0!a_1!a_2!\ldots} = \frac{\tilde{N}!}{a_0!a_1!a_2!\ldots} \tag{1.6}$$

where the sum runs over states of the system. This is the expression of a **multinomial distribution** with equal probabilities. (The right-hand-side of Eq. 1.6 is sometimes called a multinomial coefficient, $(a_0, a_1, \ldots)!$.)

This formula is derived as follows. We want to calculate the ways in which a distribution $\boldsymbol{a} = \{a_0, a_1, \ldots\}$ can be obtained. We represent all possible states of the system as bins into which we classify the systems in the ensemble, and we sort the bins in increasing order of energy. This is illustrated in Figure 1.2. We assign all $\tilde{N}$ systems to bins in order of increasing energy (first the E_0 bin, then the E_1 bin, etc.) such that we end up with a_0 systems in the first bin, a_1 systems in the second bind, and so on. At the beginning, we pick one system and put it in the first available bin with lowest-energy. There are $\tilde{N}$ ways of picking this first system. Then, we pick the next system and bin it in the next available low-energy bin. There are $\tilde{N}-1$ ways of choosing this second system. Continuing, there are $\tilde{N}!$ ways of choosing the systems for distribution in the bins from low to high energy. However, the same distribution would be obtained if we swap the order in which any of the a_0 systems inside the first bin were chosen. Therefore, we need to divide by $a_0!$ to prevent over-counting. Applying the same reasoning to all other bins, we arrive at the formula above. Note that this procedure is correct only because the systems are distinguishable (i.e. they can be labeled).

As an example, we can apply the $W(\boldsymbol{a})$ formula to the example with three systems and two states above. There are three systems ($\tilde{N} = 3$) and two possible states (only $a_0!$ and $a_1!$ in the denominator). Therefore:

$$W(\{3,0\}) = \frac{3!}{3! \times 0!} = 1 \qquad W(\{2,1\}) = \frac{3!}{2! \times 1!} = 3$$
$$W(\{1,2\}) = \frac{3!}{1! \times 2!} = 3 \qquad W(\{0,3\}) = \frac{3!}{0! \times 3!} = 1$$

which agrees with our previous result.

1.5 Finding the Most Probable Distribution

1.5.1 Definition

The weights of all possible distributions in the ensemble can be used to carry out ensemble averages and, using the ensemble postulate, identify these averages with the thermodynamic properties of the system. For a given distribution $\boldsymbol{a}$, we denote the occupation of state i in that particular distribution as $a_i(\boldsymbol{a})$ (i.e. the $\boldsymbol{a}$ distribution is $\{\ldots, a_i, \ldots\}$). If $W(\boldsymbol{a})$ is proportional to the probability of distribution $\boldsymbol{a}$ happening ($p(\boldsymbol{a})$),

$$p(\boldsymbol{a}) = \frac{W(\boldsymbol{a})}{\sum_{\boldsymbol{a}} W(\boldsymbol{a})} \tag{1.7}$$

then the average occupation number is:

$$\langle a_i \rangle = \sum_{\boldsymbol{a}} p(\boldsymbol{a}) a_i(\boldsymbol{a}) = \frac{\sum_{\boldsymbol{a}} W(\boldsymbol{a}) a_i(\boldsymbol{a})}{\sum_{\boldsymbol{a}} W(\boldsymbol{a})} \tag{1.8}$$

The probability that a system is the in state i is the average occupation number for that state divided by the number of systems in the ensemble:

$$p_i = \frac{\langle a_i \rangle}{\tilde{N}} = \frac{1}{\tilde{N}} \frac{\sum_{\boldsymbol{a}} W(\boldsymbol{a}) a_i(\boldsymbol{a})}{\sum_{\boldsymbol{a}} W(\boldsymbol{a})} \tag{1.9}$$

Since each state has a well-defined value for each mechanical property, the average over the ensemble of a mechanical property M is:

$$\langle M \rangle = \sum_{i}^{\text{states}} p_i M_i \tag{1.10}$$

where M_i is the value of that property for state i. We can now identify these mechanical properties calculated as ensemble averages with the corresponding thermodynamic quantities. For instance, the average energy is:

$$\langle E \rangle = \sum_{i}^{\text{states}} p_i E_i \tag{1.11}$$

where E_i is the energy of state i. By the ensemble postulate, these quantities are identified with the corresponding quantities in classical thermodynamics. In the last equation, $\langle E \rangle = U$.

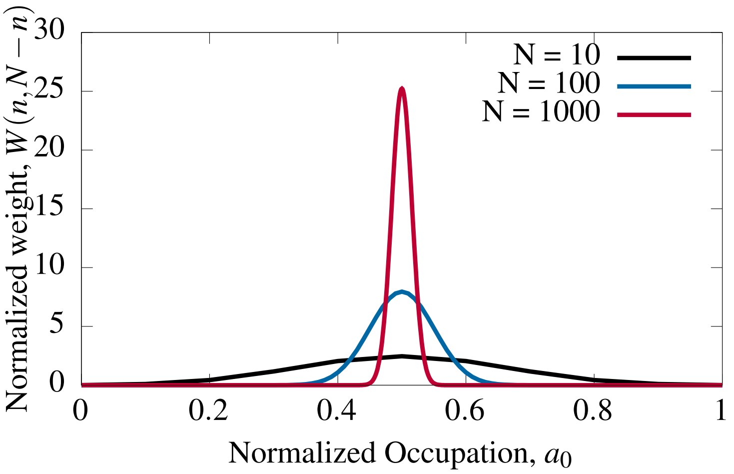


Figure 1.3: Normalized distribution weight for a two-state system ($W(n, N-n)$) as a function of the occupation of the first state (a_0). The three curves show the effect of increasing the number of states. This plot shows corresponds to the outcomes of a binomial distribution $B(n, 1/2)$ as a function of n increases. The mean and standard deviation of this binomial distribution are $n/2$ and $\sqrt{n}/2$, respectively.

For ensembles with a very large number of systems, the average in Eqs. 1.9 and 1.10 can be simplified because there is a distribution that is overwhelmingly more probable (i.e. has a much higher weight) than all the others. We call this the **dominant** or **most probable distribution**, denoted by $\boldsymbol{a}^*$. To illustrate why this is the case, we go back to our two-state example and consider what happens when we increase the number of systems ($\tilde{N}$). Because only two states are present, there are two occupation numbers only, related by the constraint (Eq. 1.4):

$$a_0 + a_1 = \tilde{N} \tag{1.12}$$

so if we assign $a_0 = n$, then $a_1 = \tilde{N} - n$. The possible distributions in this system are given by $\{n, \tilde{N} - n\}$, with $n = 0, \ldots, \tilde{N}$. The corresponding weights (Eq. 1.6) are:

$$W(\{n, \tilde{N} - n\}) = \frac{\tilde{N}!}{a_0! a_1!} = \frac{\tilde{N}!}{n!(\tilde{N} - n)!} = \binom{\tilde{N}}{n} \tag{1.13}$$

The weight of a distribution in a two-state system is a binomial coefficient involving the number of systems and the occupation of either of them.

Figure 1.3 shows the shape of the (normalized) weight as a function of the occupation number n. As the number of systems ($\tilde{N}$) increases, the weight becomes more and more sharply peaked around the half-occupation point, which is the mean of a binomial distribution. As $\tilde{N}$ increases, the weight of the distribution with $n = \tilde{N}/2$ becomes much higher than the others. Since our ensemble is a virtual construct, we can have as many systems in it as we want, and therefore we can consider the $\tilde{N} \to \infty$ limit, in which only the weight of the $\tilde{N}/2$ distribution will be non-zero.

Question: In the two-state system example from above, calculate the distribution weights for an ensemble with $\tilde{N} = 4$ and $\tilde{N} = 5$ systems, and find the ratio between the probability of the most and least probable distributions.

In the four-system case, $\tilde{N} = 4$), the possible distributions are $\{4, 0\}$, $\{3, 1\}$, $\{2, 2\}$, $\{1, 3\}$, and

$\{0,4\}$. The weights are:

$$W(\{4,0\}) = W(\{0,4\}) = \frac{4!}{4! \times 0!} = 1 \qquad W(\{2,2\}) = \frac{4!}{2! \times 2!} = 6$$
$$W(\{1,3\}) = W(\{3,1\}) = \frac{4!}{1! \times 3!} = 4$$

In the five-system case, $\tilde{N} = 5$, the possible distributions are $\{5,0\}$, $\{4,1\}$, $\{3,2\}$, $\{2,3\}$, $\{1,4\}$, and $\{0,5\}$. The corresponding weights are:

$$W(\{5,0\}) = W(\{0,5\}) = \frac{5!}{5! \times 0!} = 1 \qquad W(\{1,4\}) = W(\{4,1\}) = \frac{5!}{4! \times 1!} = 5$$
$$W(\{2,3\}) = W(\{3,2\}) = \frac{5!}{2! \times 3!} = 10$$

So, putting all the results together, in $\tilde{N} = 3$, we have that the most probable distribution is 3 times more likely to appear than the least probable one. In $\tilde{N} = 4$ and $\tilde{N} = 5$ this ratio increases to 6, and 10, respectively.

A real system has, in general, many more than two states. In a canonical ensemble comprising real systems, the same principle applies: As $\tilde{N}$ increases, the distribution weights (Eq. 1.6) center around the most probable distribution ($\boldsymbol{a}^*$). In the limit of $\tilde{N} \to \infty$, the ensemble will be invariably found in the dominant distribution because its weight is much higher than the others distributions:

$$W(\boldsymbol{a}^*) \gg W(\boldsymbol{a} \neq \boldsymbol{a}^*) \tag{1.14}$$

This result, which we will verify a posteriori by calculating the ensemble fluctuations (Section 1.6) simplifies the calculation of ensemble averages because the properties of the ensemble reduce to those obtained from the most probable distribution. The average occupation number for state i (Eq. 1.8) becomes:

$$\langle a_i \rangle = \frac{\sum_{\boldsymbol{a}} W(\boldsymbol{a}) a_i(\boldsymbol{a})}{\sum_{\boldsymbol{a}} W(\boldsymbol{a})} \approx \frac{W(\boldsymbol{a}^*) a_i(\boldsymbol{a}^*)}{W(\boldsymbol{a}^*)} = a_i(\boldsymbol{a}^*) \tag{1.15}$$

The probability of finding a system in state i (Eq. 1.9) simplifies to the fraction of ensemble systems in that state (p_i^*) in the most probable distribution, because all terms other than the one corresponding to $W(\boldsymbol{a}^*)$ are negligible.

$$p_i = \frac{1}{\tilde{N}} \frac{\sum_{\boldsymbol{a}} W(\boldsymbol{a}) a_i(\boldsymbol{a})}{\sum_{\boldsymbol{a}} W(\boldsymbol{a})} \approx \frac{1}{\tilde{N}} \frac{W(\boldsymbol{a}^*) a_i(\boldsymbol{a}^*)}{W(\boldsymbol{a}^*)} = \frac{a_i(\boldsymbol{a}^*)}{\tilde{N}} = p_i^* \tag{1.16}$$

Note that this value is also the probability of finding a system in state i if picked at random from the ensemble. Likewise, the calculation of mechanical properties (Eq. 1.10) is also simplified, and becomes an average over the most probable distribution:

$$\langle M \rangle = \sum_i^{\text{states}} p_i^* M_i \tag{1.17}$$

For instance, for the energy:

$$\langle E \rangle = \sum_i^{\text{states}} p_i^* E_i = U \tag{1.18}$$

In view of this result, the problem of calculating ensemble averages (and therefore the prediction of thermodynamic properties of the system) reduces to finding the occupation of each state in the most probable distribution. To do this, we want to maximize the weight

($W(a_0, a_1, \ldots)$, Eq. 1.6) as a function of all the occupation numbers a_i. In order to do this, we take the derivative of W with respect to each occupation number and make it equal to zero:

$$\frac{\partial W(\boldsymbol{a})}{\partial a_i} = 0 \tag{1.19}$$

Then, we solve these equations to find the occupation numbers in the dominant distribution, a_i^*. However, this problem is complicated by the fact that not all possible a_i result in a valid distribution. As discussed above, there are two constraints imposed by the fixed number of systems in the ensemble (Eq. 1.4) and the conservation of the ensemble energy (Eq. 1.5):

$$\sum_i^{\text{states}} a_i = \tilde{N} \tag{1.20}$$

$$\sum_i^{\text{states}} a_i E_i = \tilde{E} \tag{1.21}$$

Therefore, we want to carry out a constrained maximization of $W(\boldsymbol{a})$.

1.5.2 Lagrange's Method of Undetermined Multipliers

To maximize a function under constraints, we use **Lagrange's method of undetermined multipliers**. In the most general case, we have a scalar function that depends on n variables

$$f(x_1, \ldots, x_n) = f(\boldsymbol{x}) \tag{1.22}$$

and we want to maximize (or minimize) this function subject to m constraints given by the following equations:

$$g_k(x_1, \ldots, x_n) = g_k(\boldsymbol{x}) = 0 \quad ; \quad k = 1, \ldots, m \tag{1.23}$$

To maximize $f(\boldsymbol{x})$ under the $g_k(\boldsymbol{x})$ constraints, we define an auxiliary function, called the **Lagrangian function** ($\mathcal{L}$):

$$\mathcal{L}(x_1, \ldots, x_n, \lambda_1, \ldots, \lambda_m) = f(x_1, \ldots, x_n) + \sum_{k=1}^{m} \lambda_k g(x_1, \ldots, x_n) \tag{1.24}$$

where the m new variables λ_k are the **Lagrange multipliers**. A point $(x_1^*, \ldots, x_n^*, \lambda_1^*, \ldots, \lambda_m^*)$ maximizes the Lagrangian function if the following $m + n$ equations hold:

$$\frac{\partial \mathcal{L}}{\partial x_i}(\boldsymbol{x}^*, \boldsymbol{\lambda}^*) = \frac{\partial f}{\partial x_i}(\boldsymbol{x}^*) + \sum_{k=1}^{m} \lambda_k^* \frac{\partial g_k}{\partial x_i}(\boldsymbol{x}^*) = 0 \quad \text{for all } i \tag{1.25}$$

$$\frac{\partial \mathcal{L}}{\partial \lambda_j}(\boldsymbol{x}^*, \boldsymbol{\lambda}^*) = g_j(\boldsymbol{x}^*) = 0 \quad \text{for all } j \tag{1.26}$$

The point that maximizes the Lagrangian function ($\boldsymbol{x}^*$) is a maximum of $f(\boldsymbol{x})$ subject to the constraints $g_k(\boldsymbol{x}^*) = 0$ for all k.

The optimal multipliers that maximize the Lagrangian function (λ_k^*) are usually meaningful. In general, the constraints imposed on the function $f(\boldsymbol{x})$ are given by expressions such as $g(\boldsymbol{x}) = c$, where c is a constant. The corresponding Lagrangian is:

$$\mathcal{L} = f(\boldsymbol{x}) + \lambda(g(\boldsymbol{x}) + c) \tag{1.27}$$

(The sign of the c term is irrelevant.) The value of the Lagrangian at the maximum ($\boldsymbol{x}^*$) is equal to the value of the function we are maximizing, since all constraints are satisfied at $\boldsymbol{x}^*$:

$$\mathcal{L}(\boldsymbol{x}^*, \boldsymbol{\lambda}^*) = f(\boldsymbol{x}^*) + \lambda^*(g(\boldsymbol{x}^*) + c) = f(\boldsymbol{x}^*) = M^* \tag{1.28}$$

If we take the value of c as a parameter, then the optimal values $\boldsymbol{x}^*$ that maximize the Lagrangian and the maximum value of the Lagrangian M^* can both be viewed as a function of c, $\boldsymbol{x}^*(c)$ and $M^*(c)$. Since:

$$\frac{\partial \mathcal{L}}{\partial c} = \lambda \tag{1.29}$$

then it is possible to show that:

$$\frac{dM^*}{dc}(c) = \lambda^*(c) \tag{1.30}$$

Hence, the Lagrange multiplier associated with the constraint $g(\boldsymbol{x}) = c$ gives the rate of change of the function undergoing maximization with the value of the constraining parameter c, at its maximum point. In the case we are interested in, we want to maximize the weight of a distribution (Eq. 1.6) as a function of all the state occupations a_i subject to the particle number (Eq. 1.20) and energy (Eq. 1.21) constraints. Therefore, the Lagrange multipliers associated to these two constraints will give the rate of change of the distribution weight as a function of the number of particles and the energy in the system, respectively.

Going back to the problem of maximizing weights, instead of performing the constrained maximization of the distribution weight (W) as a function of the occupations, we will use the logarithm of the weight ($\ln W$). This is equivalent to maximizing W directly, since:

$$\frac{\partial \ln W}{\partial a_i} = \frac{1}{W}\frac{\partial W}{\partial a_i} \tag{1.31}$$

and $\frac{\partial \ln W}{\partial a_i} = 0$ if and only if $\frac{\partial W}{\partial a_i} = 0$. (Unless $W = 0$, which is not possible since no valid distribution has exactly zero weight because there must be at least one way to obtain it). From Eq. 1.6, the logarithm of the weight is:

$$\ln W = \ln\left[\left(\sum_i^{\text{states}} a_i\right)!\right] - \sum_i^{\text{states}} \ln\left(a_i!\right) \tag{1.32}$$

We now discuss an approximation to $N!$ when N is very large that simplifies further calculations.

1.5.3 Stirling's Approximation

The factorial $f(n) = n!$ is a function that increases very quickly with n. For instance, $100! = 9.3 \times 10^{157}$. In statistical thermodynamics we deal with factorials of very large numbers, in the order of Avogadro's number ($6.022 \times 10^{23}\,\text{mol}^{-1}$). To handle those calculations, we must make use of approximate formulas that accurately describe the scaling of these quantities.

The formula involving factorial scaling that is most useful in statistical thermodynamics is **Stirling's approximation**. It states:

$$\ln N! = N \ln N - N \tag{1.33}$$

which is valid when N is very large. The use of this approximation is justified by replacing the logarithm sum with an integral:

$$\ln N! = \sum_{n=1}^{N} \ln n \approx \int_1^N \ln n dn \tag{1.34}$$

and then solving the integral by parts ($u = \ln n$, $dv = dn$):

$$\ln N! \approx n \ln n|_1^N - \int_1^N n\frac{1}{n}dn = N\ln N \cancel{- 1\ln 1} - (N-1) \approx N\ln N - N \tag{1.35}$$

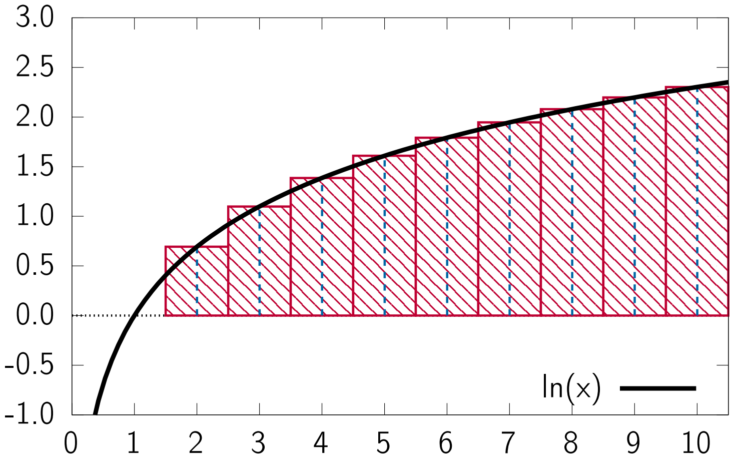


Figure 1.4: Graphical representation of the error in approximating a sum with an integral. The area between the positive part of the black curve and the x-axis is $\int_0^N \ln n dn$. The area in the striped rectangles is $\sum_{n=0}^{N} \ln n$. As N increases, the relative difference between the two areas (i.e. the relative error from this approximation) decreases.

Replacing the sum by the integral is appropriate because N is very large and the integrand ($\ln n$) does not change very quickly with n for large values of n (see Figure 1.4). This approximation will be of use later on, when we will use in cases when differences between energy levels are small compared to the available energy in the system. By the same reasoning, the final 1 term can be neglected when compared to N. The error from applying Stirling's approximation grows at a rate of less than $\alpha \ln N$, where α is a scalar constant. For N in the order of N_A, $\ln N_A \approx 54.8$, which is negligible compared to N_A itself. Hence, the application of Stirling's approximation gives excellent results.

1.5.4 Maximization of the Weight

Applying Stirling's approximation to both terms in Eq. 1.32, we find:

$$\begin{aligned}\ln W &= \ln\left[\left(\sum_i a_i\right)!\right] - \sum_i \ln(a_i!)\\ &= \left(\sum_i a_i\right)\ln\left(\sum_i a_i\right) - \left(\sum_i a_i\right) - \left(\sum_i a_i \ln a_i - a_i\right) \qquad (1.36)\end{aligned}$$

where the i index runs over system states.

The Lagrangian function for the constrained maximization of the distribution weight is:

$$\mathcal{L}(a_0, a_1, \ldots, \alpha, \beta) = \ln W(a_0, a_1, \ldots) + \alpha\left(\sum_i^{\text{states}} a_i - \tilde{N}\right) - \beta\left(\sum_i^{\text{states}} a_i E_i - \tilde{E}\right) \qquad (1.37)$$

where α and β are the Lagrange multipliers. (We choose the $-$ sign in the β term for later convenience. It makes no difference to the maximization.) Maximization of this Lagrangian as a function of a_i, α, and β gives (Eqs. 1.25 and 1.26):

$$\frac{\partial \ln W}{\partial a_i} + \alpha - \beta E_i = 0 \tag{1.38}$$

$$\sum_i^{\text{states}} a_i - \tilde{N} = 0 \tag{1.39}$$

$$\sum_i^{\text{states}} a_i E_i - \tilde{E} = 0 \tag{1.40}$$

where differentiation with respect to α and β simply recovers the constraints. The derivative of the weight logarithm is calculated from Eq. 1.36. The derivative of the first term is:

$$\begin{aligned}
\frac{\partial\left[\left(\sum_k a_k\right)\ln\left(\sum_k a_k\right)\right]}{\partial a_i} &= \cancelto{1}{\frac{\partial\left(\sum_k a_k\right)}{\partial a_i}} \ln\left(\sum_k a_k\right) + \left(\sum_k a_k\right)\frac{\partial \ln\left(\sum_k a_k\right)}{\partial a_i} \\
&= \ln\left(\sum_k a_k\right) + \left(\sum_k a_k\right)\frac{1}{\left(\sum_k a_k\right)}\cancelto{1}{\frac{\partial\left(\sum_k a_k\right)}{\partial a_i}} \\
&= \ln\left(\sum_k a_k\right) + 1 = \ln\tilde{N} + 1
\end{aligned} \tag{1.41}$$

Note the sum indices are "dummy" (we can change their symbol to k, similar to how we can change the symbol of the integration variable in an integral).

And the derivative of the second term in Eq. 1.36 is:

$$\frac{\partial \sum_k^{\text{states}} a_k \ln a_k}{\partial a_i} = \ln a_i + a_i \frac{\partial \ln a_i}{\partial a_i} = \ln a_i + a_i \frac{1}{a_i} = \ln a_i + 1 \tag{1.42}$$

where all terms other than the one corresponding to a_i are zero when taking the derivative. Combining the two results, we have that the occupations for the dominant distribution (a_i^*) are:

$$\frac{\partial \ln W}{\partial a_i} = \ln\tilde{N} + 1 - (\ln a_i^* + 1) = -\ln\frac{a_i^*}{\tilde{N}} \tag{1.43}$$

And substitution in Eq. 1.38 leads to the following expression for the occupations a_i^*:

$$-\ln\frac{a_i^*}{\tilde{N}} + \alpha - \beta E_i = 0 \tag{1.44}$$

Rearranging:

$$\frac{a_i^*}{\tilde{N}} = e^{\alpha - \beta E_i} \tag{1.45}$$

Now we try to assign meaning to the Lagrangian multipliers α and β in this expression. The α multiplier is easily understood. Using the particle number constraint (Eq. 1.20), we have:

$$\tilde{N} = \sum_k^{\text{states}} a_k^* = \sum_k^{\text{states}} \tilde{N} e^{\alpha - \beta E_k} = \tilde{N} e^{\alpha} \sum_k^{\text{states}} e^{-\beta E_k} \tag{1.46}$$

from where we find that:

$$e^{\alpha} = \frac{1}{\sum_k e^{-\beta E_k}} \tag{1.47}$$

and substituting in Eq. 1.45, we find that the occupations at the dominant distribution are given by:

$$p_i^* = \frac{a_i^*}{\tilde{N}} = e^{\alpha} e^{-\beta E_i} = \frac{e^{-\beta E_i}}{\sum_k e^{-\beta E_k}} \tag{1.48}$$

which is the expression for the **Boltzmann distribution**.

The Boltzmann distribution gives the probability of a system occupying state i (with energy E_i) as a function of the macrostate variables of a closed system (N, V, and T). From the knowledge of the different quantum mechanical states for a system, the Boltzmann distribution allows us to predict the probability of each of these states and their contribution to the ensemble averages. We will justify later in this chapter that the β parameter is equal to $\frac{1}{k_B T}$, where k_B is Boltzmann's constant and T is the temperature of the system. (Note again that the energies in Eq. 1.48 are functions of the volume and number of particles but not of temperature.) The Boltzmann distribution says that, for a fixed temperature, the probability that a system will be in state i decreases exponentially with its energy (E_i). In addition, increasing the temperature means that higher energy levels become accessible to the system.

Using the Boltzmann distribution and Eq. 1.17, we can now calculate the ensemble average of any mechanical property, which we identify with the corresponding thermodynamic property in the system. For instance, the internal energy is:

$$U = \langle E \rangle = \sum_k^{\text{states}} p_k^* E_k = \frac{\sum_k E_k e^{-\beta E_k}}{\sum_k e^{-\beta E_k}} \tag{1.49}$$

Likewise, if a system is in state j, its pressure is:

$$p_j = -\left(\frac{\partial E_j(N,V)}{\partial V}\right)_N \tag{1.50}$$

and therefore the thermodynamic pressure of the system calculated as the ensemble average is:

$$p = \langle p \rangle = -\sum_k^{\text{states}} p_k^* \left(\frac{\partial E_j}{\partial V}\right)_N = -\frac{\sum_k \left(\frac{\partial E_j}{\partial V}\right)_N e^{-\beta E_k}}{\sum_k e^{-\beta E_k}} \tag{1.51}$$

The denominator in all these expressions is the same. It is called the **(canonical) partition function**:

$$Q(N,V,\beta) = \sum_k^{\text{states}} e^{-\beta E_k} \tag{1.52}$$

Different ensembles have different expressions for the partition function. As we shall see, the partition function plays an essential role in statistical thermodynamics because it is the bridge between the microscopic properties of the system and its macroscopic thermodynamic variables.

Note that in all these expressions the sum over states can be replaced by a sum over energy levels by introducing the degeneracy of each level. The partition function is:

$$Q(N,V,\beta) = \sum_k^{\text{levels}} g_k e^{-\beta E_k} \tag{1.53}$$

and the probability of a level is the sum of the probabilities of all states in that level:

$$p_i^* = \frac{g_i e^{-\beta E_i}}{Q} \tag{1.54}$$

where in this case i is an energy level and g_i is its degeneracy. In the same way, the ensemble averages can be calculated with a sum over levels instead of over states.

Question: For a system with three energy levels, $E_n = n\epsilon$, $n = 0, 1, 2$, and degeneracies $g_0 = 1$, $g_1 = 3$, and $g_2 = 5$, calculate the canonical partition function, the probability of each level, and the internal energy of the system.

The canonical partition function is:

$$Q(N,V,\beta) = \sum_k^{\text{levels}} g(E_k)e^{-\beta E_k} = 1\times e^{-\beta\times 0\epsilon} + 3\times e^{-\beta\times 1\epsilon} + 5\times e^{-\beta\times 2\epsilon} = 1 + 3\times e^{-\beta\epsilon} + 5\times e^{-2\beta\epsilon}$$

The probability of each level is:

$$\begin{aligned} p_0 &= \frac{1\times e^{-\beta\times 0\epsilon}}{Q} = \frac{1}{Q} \\ p_1 &= \frac{3\times e^{-\beta\times 1\epsilon}}{Q} = \frac{3e^{-\beta\epsilon}}{Q} \\ p_2 &= \frac{5\times e^{-\beta\times 2\epsilon}}{Q} = \frac{5e^{-2\beta\epsilon}}{Q} \end{aligned}$$

and the internal energy is obtained as the average energy calculated over the ensemble:

$$\begin{aligned} U = \langle E\rangle = \sum_k^{\text{levels}} p_k E_k &= \frac{1\times 0\epsilon + 3e^{-\beta\epsilon}\times 1\epsilon + 5e^{-2\beta\epsilon}\times 2\epsilon}{Q} \\ &= \frac{3\epsilon e^{-\beta\epsilon} + 10\epsilon e^{-2\beta\epsilon}}{Q} \end{aligned}$$

1.5.5 Entropy and the Interpretation of β

In the discussion above we have seen that the Lagrange multipliers are related to the change in the maximum of the function (in this context, $\ln W$ for the most dominant distribution) as a function of the constant parameters in the applied constraints (α for the particle number constraint and β for the energy constraint). We now interpret β by applying this concept. The first way of doing this is by identifying equivalent microscopic and macroscopic relations between ensemble averages and thermodynamic quantities.

Differentiating the energy (Eq. 1.49) with respect to the system volume, we have:

$$\begin{aligned} \left(\frac{\partial\langle E\rangle}{\partial V}\right)_{N,\beta} &= \frac{\left(\sum_k \frac{\partial E_k}{\partial V}e^{-\beta E_k} - \beta\frac{\partial E_k}{\partial V}E_k e^{-\beta E_k}\right)\sum_k e^{-\beta E_k} + \beta\left(\sum_k E_k e^{-\beta E_k}\right)\left(\sum_k \frac{\partial E_k}{\partial V}e^{-\beta E_k}\right)}{\left(\sum_k e^{-\beta E_k}\right)^2} \\ &= -\langle p\rangle + \beta\langle pE\rangle - \beta\langle E\rangle\langle p\rangle \end{aligned} \tag{1.55}$$

where we have used the pressure of state k (Eq. 1.50) is:

$$p_k = -\left(\frac{\partial E_k}{\partial V}\right)_{V,\beta} \tag{1.56}$$

and the corresponding average pressure (equivalent to the thermodynamic pressure of the system) is:

$$\langle p\rangle = \frac{\sum_k p_k e^{-\beta E_k}}{\sum_k e^{-\beta E_k}} \tag{1.57}$$

Taking the derivative of the pressure average with respect to β, we have:

$$\begin{aligned} \left(\frac{\partial\langle p\rangle}{\partial\beta}\right)_{N,V} &= \frac{\left(-\sum_k p_k E_k e^{-\beta E_k}\right)\left(\sum_k e^{-\beta E_k}\right) + \left(\sum_k E_k e^{-\beta E_k}\right)\left(\sum_k p_k e^{-\beta E_k}\right)}{\left(\sum_k e^{-\beta E_k}\right)^2} \\ &= -\langle pE\rangle + \langle E\rangle\langle p\rangle \end{aligned} \tag{1.58}$$

Combining Eq. 1.58 and Eq. 1.55, we have:

$$\left(\frac{\partial\langle E\rangle}{\partial V}\right)_{N,\beta} = -\langle p\rangle - \beta\left(\frac{\partial\langle p\rangle}{\partial\beta}\right)_{N,V} \tag{1.59}$$

Let us try to arrive at the equivalent in classical thermodynamics using the equivalent thermodynamic quantities ($U = \langle E\rangle$ and $p = \langle p\rangle$). The fundamental thermodynamic relation for the internal energy in a homogeneous system is:

$$dU = TdS - pdV + \mu dN \tag{1.60}$$

$$\left(\frac{\partial U}{\partial V}\right)_{N,T} = T\left(\frac{\partial S}{\partial V}\right)_{N,T} - p = T\left(\frac{\partial p}{\partial T}\right)_{N,V} - p \tag{1.61}$$

where we have used the Maxwell relation:

$$\left(\frac{\partial S}{\partial V}\right)_{N,T} = \left(\frac{\partial p}{\partial T}\right)_{N,V} = -\frac{\partial^2 A}{\partial T\partial V} \tag{1.62}$$

Now we use the chain rule to express the temperature derivative as a derivative with respect to $1/T$:

$$\frac{\partial p}{\partial T} = \frac{\partial p}{\partial(1/T)}\frac{\partial(1/T)}{\partial T} = -\frac{1}{T^2}\frac{\partial p}{\partial(1/T)} \tag{1.63}$$

Hence, we have:

$$\left(\frac{\partial U}{\partial V}\right)_{N,T} = -p - \frac{1}{T}\left(\frac{\partial p}{\partial(1/T)}\right)_{N,V} \tag{1.64}$$

Comparing this equation and Eq. 1.59, we infer that:

$$\beta = \frac{\text{constant}}{T} = \frac{1}{k_BT} \tag{1.65}$$

The constant $k_B = 1.380\,648\,8 \times 10^{-23}$ J/K is **Boltzmann's constant**, and it is equal to the gas constant R divided by Avogadro's number N_A ($R = k_BN_A$).

We now justify the same result in a different way in order to arrive at the definition of entropy. Let us consider a reversible process in which we very slowly change the volume and temperature of the systems in the ensemble: $V \to V + dV$ and $T \to T + dT$. Since the volume of the systems is changing and the energies depend on the volume, we have that for each state $E_i \to E_i + dE_i$ and also, because the temperature is changing, $\beta \to \beta + d\beta$, while N is fixed. The change in the logarithm of the canonical partition function is:

$$\left(\frac{\partial \ln Q}{\partial\beta}\right)_{E_i} = \frac{1}{Q}\left(\frac{\partial Q}{\partial\beta}\right)_{E_i} = \frac{-\sum_i E_ie^{-\beta E_i}}{Q} = -\langle E\rangle \tag{1.66}$$

$$\left(\frac{\partial \ln Q}{\partial E_i}\right)_{\beta,E_{j\neq i}} = \frac{1}{Q}\left(\frac{\partial Q}{\partial E_i}\right)_{\beta,E_{j\neq i}} = \frac{-\beta e^{-\beta E_i}}{Q} = -\beta p_i^* \tag{1.67}$$

from where the differential of the partition function logarithm is:

$$d(\ln Q) = \left(\frac{\partial \ln Q}{\partial\beta}\right)_{E_i} d\beta + \sum_i\left(\frac{\partial \ln Q}{\partial E_i}\right)_{\beta,E_{j\neq i}} dE_i = -\langle E\rangle d\beta - \beta\sum_i p_i^* dE_i \tag{1.68}$$

Rearranging:

$$d(\ln Q) + \langle E\rangle d\beta = -\beta\sum_i p_i^* dE_i \tag{1.69}$$

From where we have that:

$$d(\ln Q + \beta\langle E\rangle) = d(\ln Q) + \beta d\langle E\rangle + \langle E\rangle d\beta = \beta d\langle E\rangle - \beta\sum_i p_i^* dE_i \tag{1.70}$$

If the ensemble has a_i systems in state E_i and we modify their energies by dE_i, then the (reversible) work done on the ensemble is:

$$\delta\tilde{w}_{\text{rev}} = \sum_i a_i^* dE_i \tag{1.71}$$

and the average reversible work per system is:

$$\delta\langle w_{\text{rev}}\rangle = \frac{\delta\tilde{w}_{\text{rev}}}{\tilde{N}} = \sum_i p_i^* dE_i \tag{1.72}$$

from where, applying the first law of thermodynamics, we find that the average reversible heat per system is:

$$\delta\langle q_{\text{rev}}\rangle = d\langle E\rangle - \sum_i p_i^* dE_i \tag{1.73}$$

Combining this result with Eq. 1.70, we arrive at:

$$d(\ln Q + \beta\langle E\rangle) = \beta\delta\langle q_{\text{rev}}\rangle \tag{1.74}$$

The left-hand side of this equation is an exact differential and, therefore, so is $\beta\delta\langle q_{\text{rev}}\rangle$. This implies that β is an integrating factor for δq_{rev} and from the second law of thermodynamics we have that:

$$\beta = \frac{\text{constant}}{T} = \frac{1}{k_B T} \tag{1.75}$$

which is the same result as before. (See V. C. Weiss, "The uniqueness of Clausius' integrating factor", *Am. J. Phys.* **8** (2006), 699 for an in-depth discussion of this topic. This material can be found in the virtual campus.) More importantly, the left-hand-side of Eq. 1.74 is dS/k_B and so we find:

$$\frac{S}{k_B} = \ln Q + \beta\langle E\rangle + \text{constant}$$

$$S = k_B \ln Q + \frac{\langle E\rangle}{T} \tag{1.76}$$

The constant is chosen as zero to agree with the conventional entropies in classical thermodynamics.

Two final notes. First, from the definition of the internal energy (Eq. 1.49), we have that:

$$dU = d\langle E\rangle = \underbrace{\sum_i E_i dp_i^*}_{\delta q_{\text{rev}}} + \underbrace{\sum_i p_i^* dE_i}_{\delta w_{\text{rev}}} \tag{1.77}$$

so we ascribe the mechanical (reversible) work ($-pdV$) to the change in the energy of the states keeping the occupations fixed and the (reversible) heat (TdS) as a change in the occupations keeping the energies fixed.

Second, the entropy in Eq. 1.76 can also be interpreted as follows. If, as it is usually the case, we have a system where the energy levels essentially form a continuum, we can define a density of states function $g(E)$ that represents the number of energy levels per energy interval, and then calculate the partition function as an integral instead of a sum:

$$Q = \sum_k g_k e^{-\beta E_k} \approx \int g(E) e^{-\beta E} dE \tag{1.78}$$

As we have seen before, the probability that the system has an energy in the vicinity of $\langle E\rangle = U$ is extremely high, so we can approximate this integral as:

$$Q \approx \int g(E)e^{-\beta E}dE \approx g(\langle E\rangle)e^{-\beta\langle E\rangle}\Delta E \tag{1.79}$$

where ΔE is a narrow energy range (see Section 1.6 for an estimate of how narrow this range is). With this, we can rewrite the entropy (Eq. 1.76) as:

$$S = k_B \ln Q + \frac{\langle E\rangle}{T} = k_B \ln\left[g(E)\Delta E\right] - \frac{\langle E\rangle}{T} + \frac{\langle E\rangle}{T} = k_B \ln\left[g(E)\Delta E\right] \tag{1.80}$$

The quantity $\Omega = g(E)\Delta E$ is adimensional and roughly represents the number of states accessible to the system at that temperature. Therefore, the entropy is the logarithm of the number of states available to the system:

$$S = k_B \ln \Omega \tag{1.81}$$

which is **Boltzmann's equation**. This equation, which is strictly correct only in a microcanonical ensemble (i.e. for isolated systems), is the basis for the common interpretation of the entropy as a measure of disorder. Consider an isolated system at equilibrium containing N particles of an ideal gas in a volume V with energy E. If we put this system in contact with a vacuum chamber with volume V, the gas expands into the vacuum spontaneously because the number of microstates associated with the gas occupying the full $2V$ container is much higher than the original volume V. The process in which the gas goes back to its original volume is energetically feasible (because the gas is ideal) but extremely unlikely.

1.5.6 Contributions to the Partition Function

The canonical partition function is a fundamental quantity in statistical thermodynamics:

$$Q = \sum_k^{\text{states}} e^{-\beta E_k} = \sum_k^{\text{states}} e^{-E_k/k_BT} = \sum_k^{\text{levels}} g_k e^{-E_k/k_BT} \tag{1.82}$$

contains one term in the sum for every state in the system. The canonical partition function is an adimensional quantity.

Let us assume for now that the ground state has zero energy, $E_0 = 0$. The terms that enter the partition function go to zero when $E_k \gg k_BT$ and to one if $E_k \ll k_BT$. If we consider all the terms comprising the sum as ordered in energy, at any given temperature, we will have a sum of ones (for the first few terms for which $E_k \ll k_BT$), then values between 0 and 1 when $E_k \approx k_BT$, and finally a number of zeros, corresponding to the states for which $E_k \gg k_BT$. At very low temperature, only the first few levels will be non-zero and, at exactly $T = 0$, the partition function is equal to the degeneracy of the ground state. Conversely, in the high-temperature limit ($T \to \infty$), many states give a contribution of one to the partition function. Therefore, when the ground-state has zero energy, Q is an estimate of how many states of the system are significantly populated at the given N, V, and T. The quantity k_BT, which has units of energy and determines the occupation of the system states, is often called the **thermal energy**.

If the temperature is so high that the separation between adjacent levels is much smaller than k_BT, then the energy levels behave like a continuum, and we arrive at the classical limit. Because the difference between energy levels is much smaller than k_BT, the terms in the sum change very slowly and we can approximate the sum with an integral:

$$Q = \sum_k^{\text{states}} e^{-\beta E_k} \approx \int e^{-\beta E_k} dk \tag{1.83}$$

In the next sections, we will see that this procedure often facilitates the calculation of the partition function but it is important to remember that this is only valid in the high-temperature (classical) limit.

1.5.7 The Third Law of Thermodynamics

Equation 1.76 gives the entropy in terms of the partition function and its derivatives up to a constant. The choice of this constant is arbitrary but by convention it is set to zero. Therefore, the entropy is calculated as:

$$S = k_B \ln Q + \frac{\langle E \rangle}{T} \tag{1.84}$$

The entropy from Eq. 1.84 in the limit $T \to 0$ can be easily found. Unpacking the expression results in:

$$S = k_B \ln \left(\sum_i^{\text{levels}} g_i e^{-E_i/k_BT} \right) + \frac{1}{T} \frac{\sum_i^{\text{levels}} g_i E_i e^{-E_i/k_BT}}{\sum_i^{\text{levels}} g_i e^{-E_i/k_BT}} \tag{1.85}$$

where the sum in this case runs over energy levels. Extracting the ground-state energy from both terms, we rearrange to have:

$$\begin{aligned}
S &= k_B \ln \left(e^{-E_0/k_BT} \sum_i g_i e^{-(E_i-E_0)/k_BT} \right) + \frac{1}{T} \frac{\cancel{\left(e^{-E_0/k_BT}\right)} \sum_i g_i E_i e^{-(E_i-E_0)/k_BT}}{\cancel{\left(e^{-E_0/k_BT}\right)} \sum_i g_i e^{-(E_i-E_0)/k_BT}} \\
&= -\frac{E_0}{T} + k_B \ln \left(\sum_i g_i e^{-(E_i-E_0)/k_BT} \right) \\
&+ \frac{1}{T} \frac{\sum_i g_i (E_i - E_0) e^{-(E_i-E_0)/k_BT} + E_0 \sum_i g_i e^{-(E_i-E_0)/k_BT}}{\sum_i g_i e^{-(E_i-E_0)/k_BT}} \\
&= -\cancel{\frac{E_0}{T}} + k_B \ln \left(\sum_i g_i e^{-(E_i-E_0)/k_BT} \right) + \frac{1}{T} \frac{\sum_i g_i (E_i - E_0) e^{-(E_i-E_0)/k_BT}}{\sum_i g_i e^{-(E_i-E_0)/k_BT}} + \cancel{\frac{E_0}{T}} \\
&= k_B \ln \left(\sum_i g_i e^{-(E_i-E_0)/k_BT} \right) + \frac{1}{T} \frac{\sum_i g_i (E_i - E_0) e^{-(E_i-E_0)/k_BT}}{\sum_i g_i e^{-(E_i-E_0)/k_BT}}
\end{aligned} \tag{1.86}$$

Because i runs over levels, the $E_i - E_0$ terms are all strictly positive except for $i = 0$, for which this quantity is exactly zero. This means that in the limit $T \to 0$, we have:

$$\lim_{T \to 0} e^{-(E_i-E_0)/k_BT} = 0 \text{ for all } i > 0 \tag{1.87}$$

and the same limit is equal to 1 for $i = 0$ because $E_i - E_0 = 0$. In the $T \to 0$ limit of Eq. 1.86, the denominator in the second term tends to g_0 and the numerator tends to zero (the first term in the numerator sum is zero because $E_i - E_0 = 0$ and the others are zero because the exponential vanishes). This creates a 0/0 indeterminate form in the second term, and application of L'Hôpital's rule results in the whole of the second term vanishing in the limit $T \to 0$. (This is easy to see because the exponential goes to zero much more quickly than the T in the denominator.) In contrast, the first term in the argument to the logarithm survives and we have:

$$S_0 = \lim_{T \to 0} S = k_B \ln g_0 \tag{1.88}$$

where g_0 is the degeneracy of the ground state.

The thermodynamically stable form of most chemical substances at temperatures approaching absolute zero is a perfect crystal with $g_0 = 1$ (an exception is liquid helium, which does not crystallize, even at zero temperature), so their entropy is zero. This agrees with the conventions regarding entropy in classical thermodynamics, where all elements in their condensed phases are assigned a conventional entropy of zero. It has been experimentally observed that the ΔS of any isothermal process involving ordered crystalline substances tends to zero as $T \to 0$ (this is **Nernst's heat theorem**, also known as the **third law of thermodynamics**). Combined with the convention for zero entropy of the elements, this implies that the entropy of all ordered substances at $T = 0$ is also zero. Therefore, the conventional entropy defined in classical thermodynamics and the entropy calculated using statistical thermodynamics agree, which justifies our previous choice of zero as the integration constant (Eq. 1.76).

1.6 Fluctuations

We have justified that the dominant distribution is so much more probable than the others that ensemble averages can be calculated using exclusively this distribution. The actual thermodynamic properties of the systems in the ensemble (other than those that determine the macrostate) are constantly fluctuating and we want to quantify how large these fluctuations are, in order to verify our dominant distribution hypothesis. For instance, let us consider a canonical ensemble and the fluctuations in the internal energy of each system. To do this, we use the probabilities associated to the system's states to calculate the variance in the energy:

$$\sigma_E^2 = \langle (E - \langle E \rangle)^2 \rangle = \langle E^2 \rangle - \langle E \rangle^2 = \sum p_i E_i^2 - \left(\sum p_i E_i \right)^2 \tag{1.89}$$

where p_i is the probability of a system being in state i:

$$p_i = \frac{e^{-\beta E_i}}{Q} \tag{1.90}$$

and E_i is the corresponding state energy. (We drop the $*$ in p_i^* from now on.) The variance is calculated easily:

$$\begin{aligned} \langle E^2 \rangle &= \sum p_i E_i^2 = \frac{1}{Q} \sum_i E_i^2 e^{-\beta E_i} = -\frac{1}{Q} \frac{\partial}{\partial \beta} \sum_i E_i e^{-\beta E_i} = -\frac{1}{Q} \frac{\partial}{\partial \beta} \left(\langle E \rangle Q \right) \\ &= -\frac{1}{Q} \left(\frac{\partial \langle E \rangle}{\partial \beta} Q + \frac{\partial Q}{\partial \beta} \langle E \rangle \right) = -\frac{\partial \langle E \rangle}{\partial \beta} - \frac{\partial \ln Q}{\partial \beta} \langle E \rangle \end{aligned} \tag{1.91}$$

Now, we know that (Eq. 1.66):

$$\frac{\partial \ln Q}{\partial \beta} = -\langle E \rangle \tag{1.92}$$

and also (compare to Eq. 1.102):

$$\frac{\partial \langle E \rangle}{\partial \beta} = \frac{\partial \langle E \rangle}{\partial T} \frac{\partial T}{\partial \beta} = -k_B T^2 \frac{\partial \langle E \rangle}{\partial T} \tag{1.93}$$

Therefore, substituting these two results in Eq. 1.91 we have:

$$\langle E^2 \rangle = k_B T^2 \frac{\partial \langle E \rangle}{\partial T} + \langle E \rangle^2 \tag{1.94}$$

From where the variance is:

$$\sigma_E^2 = \langle (E - \langle E \rangle)^2 \rangle = k_B T^2 \frac{\partial \langle E \rangle}{\partial T} = k_B T^2 C_V \tag{1.95}$$

where we have used the definition of the constant-volume heat capacity:

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V \tag{1.96}$$

To give an order of magnitude to the energy fluctuations, we can consider one mole of a monoatomic gas, which has, as we will see in later sections:

$$\langle E\rangle = U = \frac{3}{2}N_A k_B T \tag{1.97}$$

$$C_V = \frac{3}{2}N_A k_B \tag{1.98}$$

and therefore the ratio between the standard deviation and the average energy is:

$$\frac{\sigma_E}{\langle E\rangle} = \frac{\sqrt{k_B T^2 C_V}}{\langle E\rangle} = \frac{\sqrt{k_B T^2 \times \frac{3}{2}N_A k_B}}{\frac{3}{2}N_A k_B T} = \frac{1}{\sqrt{\frac{3}{2}N_A}} = 1.05\times 10^{-12} \tag{1.99}$$

which is a very small value. Note that the energy fluctuations decrease with the square root of the number of particles, confirming *a posteriori* the validity of the dominant distribution assumption.

The fluctuations in the thermodynamic properties of a system are important when studying some phenomena. A well known example is the effect atmospheric gas density fluctuations have on the scattering of light by a substance as a function of the incident wavelength. This scattering explains the blue color of the sky. Another example is the cloudiness of a gas/liquid or liquid/liquid mixture at the critical point (“critical opalescence”), which is also caused by density fluctuations.

1.7 The Thermodynamic Connection

The canonical partition function Q is a function of the macrostate variables for the canonical ensemble (N, V, and T):

$$Q(N,V,T) = \sum_i e^{-E_i(N,V)/k_B T} \tag{1.100}$$

The importance of the partition function is that it can be calculated from microscopic quantities and, once its value is known as a function of all macrostate variables, it completely determines the macroscopic behavior of the system. The partition function can be used to calculate any thermodynamic property of the system and also the probability of the system being in any of its possible states.

As we have seen, the calculation of thermodynamic quantities is done via ensemble averages. For instance, the internal energy (U) of the system is equated to the average over the ensemble systems of their corresponding energies, $\langle E\rangle$:

$$U = \langle E\rangle = \sum_i p_i E_i = \frac{\sum_i E_i e^{-\beta E_i}}{Q} \tag{1.101}$$

We have also seen (Eq. 1.66) that the internal energy can be written as a derivative of the canonical partition function with respect to β or, equivalently, with respect to temperature:

$$U = -\frac{\partial \ln Q}{\partial \beta} = -\frac{\partial \ln Q}{\partial T}\frac{\partial T}{\partial \beta} = -\frac{\frac{\partial \ln Q}{\partial T}}{\frac{\partial(1/k_B T)}{\partial T}} = k_B T^2 \frac{\partial \ln Q}{\partial T} \tag{1.102}$$

The same procedure can be applied to find the thermodynamic pressure in terms of derivatives of the partition function:

$$\begin{aligned}
Q &= \sum_i e^{-\beta E_i} \\
\frac{\partial Q}{\partial V} &= \sum_i -\beta\left(\frac{\partial E_i}{\partial V}\right) e^{-\beta E_i} = \beta \sum_i p_i e^{-\beta E_i} \\
\frac{\partial \ln Q}{\partial V} &= \frac{1}{Q}\frac{\partial Q}{\partial V} = \beta \frac{\sum_i p_i e^{-\beta E_i}}{Q} = \beta \langle p \rangle
\end{aligned} \tag{1.103}$$

from where we find that the system pressure is:

$$p = \langle p \rangle = k_B T \left(\frac{\partial \ln Q}{\partial V}\right) \tag{1.104}$$

In addition, we know that the entropy is (Eq. 1.84):

$$S = k_B \ln Q + \frac{\langle E \rangle}{T} = k_B \ln Q + k_B T \frac{\partial \ln Q}{\partial T} \tag{1.105}$$

By combining these results, it is possible to show that all other thermodynamic quantities in the system can be calculated in terms of the partition function. One of them in particular, the Helmholtz free energy (A), has a very simple expression:

$$A = U - TS = U - T\left(\frac{U}{T} + k_B \ln Q\right) = -k_B T \ln Q \tag{1.106}$$

This is because A is the thermodynamic potential corresponding to the canonical ensemble.

A **thermodynamic potential** is a state function that represents the thermodynamic state of the system. If a thermodynamic potential is completely known as a function of its **natural variables**, then all thermodynamic quantities in the system can be calculated. Which thermodynamic potential corresponds to which natural variables is given by the corresponding statement of the second law, and they are apparent in the corresponding fundamental thermodynamic relation. For example, in the case of a closed system with rigid walls, the natural variables are V and T and the associated thermodynamic potential is the Helmholtz free energy, $A(V,T) = U - TS$. The second law in this case states that at constant T and V the Helmholtz free energy is a minimum when the system attains thermodynamic equilibrium, and the fundamental relation for A is written in terms of its natural variables (dV and dT).

Let us see how knowledge of $A(V,T)$ allows the calculation of all other thermodynamic properties. The fundamental relation is:

$$dA = -pdV - SdT \tag{1.107}$$

so we can get the pressure and the entropy from the derivatives:

$$p = -\left(\frac{\partial A}{\partial V}\right)_T \tag{1.108}$$

$$S = -\left(\frac{\partial A}{\partial T}\right)_V \tag{1.109}$$

The first of these equations gives the pressure as a function of volume and temperature, the **equation of state**. From these two relations, we can build all the other state functions:

$$G = A + pV = A - V\left(\frac{\partial A}{\partial V}\right)_T \tag{1.110}$$

$$U = A + TS = A - T\left(\frac{\partial A}{\partial T}\right)_V \tag{1.111}$$

$$H = U + pV = A - T\left(\frac{\partial A}{\partial T}\right)_V - V\left(\frac{\partial A}{\partial V}\right)_T \tag{1.112}$$

Table 1.1: List of common types of ensembles, associated macrostate variables, system types, partition functions, and thermodynamic potentials. $g(N, V, E)$ is the degeneracy for energy level E in an isolated system with N particles and volume V. μ is the chemical potential.

Ensemble	Macrostate	System	Partition Function	Therm. Potential
Microcanonical	N, V, E	isolated	$\Omega = g(N, V, E)$	
Canonical	N, V, T	closed, rigid walls	$Q = \sum_i e^{-\beta E_i}$	$A = -k_BT \ln Q$
Isothermal-isobaric	N, T, p	closed, flexible walls	$\Delta = \sum_{V,i} e^{-(E_{i,V}+pV)/k_BT}$	$G = -k_BT \ln \Delta$
Grand canonical	V, T, μ	open	$\Xi = \sum_{N,i} e^{-(E_{i,N}-N\mu)/k_BT}$	$pV = k_BT \ln \Xi$

and, from these, all other thermodynamic properties such as heat capacities, bulk moduli, the thermal expansion coefficient, and others. Other thermodynamic potentials as a function of their natural variables are $G(p, T)$, $U(S, V)$, and $H(S, p)$. In statistical thermodynamics, thermodynamic potentials are important because the potential corresponding to the macrostate variables of an ensemble always has a particularly simple relationship with its partition function. A list of types of ensembles and their associated partition functions and thermodynamic potentials is shown in Table 1.1.

Finally, note that if we consider a reversible process on a closed system in which the number of particles in the system changes, we have:

$$dA = -SdT - pdV + \mu dN \tag{1.113}$$

from where we can show that the chemical potential of the system can also be calculated in terms of the canonical partition function:

$$\mu = \left(\frac{\partial A}{\partial N}\right)_{V,T} = -k_BT\left(\frac{\partial \ln Q}{\partial N}\right)_{V,T} \tag{1.114}$$

This expression can be easily extended to each substance in a system with multiple components, just by replacing μ with μ_i and N with N_i, where i is one of the components. (Note that this definition of chemical potential is slightly different from the usual, where the derivative is taken with respect to the number of moles, n.)

In summary, to calculate the thermodynamic properties of a system in the canonical ensemble, we follow these steps:

1. Solve the Schrödinger equation for the system to obtain all possible quantum states of the system (Ψ_i) and their associated energies E_i.
2. With these, calculate the canonical partition function (Eq. 1.52).
3. Use the partition function and its derivatives to obtain the thermodynamic properties of the system like the internal energy (Eq. 1.102), pressure (Eq. 1.104), entropy (Eq. 1.105), Helmholtz free energy (Eq. 1.106), and chemical potential (Eq. 1.114).

Chapter 2

Thermodynamics of Ideal Gases

2.1 Systems with Non-Interacting Particles

The results in the previous chapter regarding the calculation of thermodynamic properties from the canonical partition function are completely general: they are valid for any closed system. However, calculating the partition function without further approximations is generally unfeasible.

A very important case in which the partition function of a system can be greatly simplified is when the particles that comprise the system are non-interacting. This is the case, for instance, in an ideal gas or in an ideal dilute solution. Since the particles do not interact with each other, the total energy of a system in state i (with energy E_i) is given by the sum of the corresponding molecular energies:

$$E_i = \sum_{n}^{\text{molecs}} \epsilon_i(n) \tag{2.1}$$

where the sum runs over all the molecules in the system and $\epsilon_i(n)$ is the energy of molecule n in the system's state i. The canonical partition function is written as:

$$Q = \sum_{i}^{\text{states}} e^{-\beta E_i} = \sum_{i}^{\text{states}} e^{-\beta(\epsilon_i(1)+\epsilon_i(2)+\ldots+\epsilon_i(N))} \tag{2.2}$$

If the molecules are non-interacting and distinguishable (i.e. we can label the molecules such that two molecules in the same state are not interchangeable), then the sum over all states of the system can be replaced by N sums over all the possible molecular states of each molecule:

$$Q = \sum_{i_1}^{\text{mol. states}} \ldots \sum_{i_N}^{\text{mol. states}} e^{-\beta(\epsilon_{i_1}+\ldots+\epsilon_{i_N})} \tag{2.3}$$

where ϵ_{i_1} is the energy of molecule 1 in molecular state i_1, etc. This sum can be factorized into contributions from each of the molecules:

$$Q = \left(\sum_{i_1}^{\text{mol. states}} e^{-\beta\epsilon_{i_1}}\right) \ldots \left(\sum_{i_N}^{\text{mol. states}} e^{-\beta\epsilon_{i_N}}\right) \tag{2.4}$$

and, since the molecules are identical, these factors are all the same, so we have that the canonical partition function is written:

$$Q = q^N \tag{2.5}$$

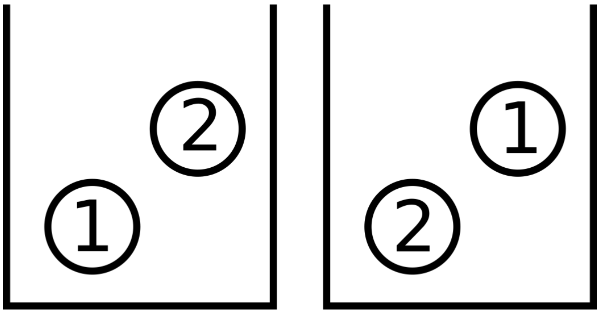


Figure 2.1: In this hypothetical system, there are only two molecules, one is state 1 and the other in state 2. The two situations depicted are different states of the system if the molecules are distinguishable, but the same state if they are not.

where q is the **molecular partition function**:

$$q(V,T) = \sum_{i}^{\text{mol. states}} e^{-\beta\epsilon_i} \tag{2.6}$$

The sum in the molecular partition function runs over all available states in the molecule (compare to Q where the sum runs over states in the system). Equation 2.5, however, is seldom used because the assumption that molecules are distinguishable is often not realistic. For instance, in a gas or a liquid, the molecules are constantly exchanging positions and therefore the state of the system is not specified by the state of each molecule but rather but how many molecules occupy each molecular state (see Figure 2.1). If the molecules are not distinguishable, it is not possible to go from Eq. 2.2 to Eq. 2.3, and the canonical partition function (Eq. 2.5) contains much fewer terms. In contrast, molecules in a crystalline solid are distinguishable, because they do not interchange and can be labeled by their position in the crystal. In addition, note that for two molecules to be indistinguishable they must at least be chemically identical. For instance, an Ar atom and a Ne atom are never indistinguishable.

To illustrate the relation between molecular distinguishability and the partition function, we consider a simple example: three molecules and two energy states with energies 0 and 1. At first, we consider the molecules distinguishable and we label them A, B, and C. The list of states in this system and the associated energies are:

ϵ_A	ϵ_B	ϵ_C	Total energy (E)
0	0	0	0
1	0	0	1
0	1	0	1
0	0	1	1
0	1	1	2
1	0	1	2
1	1	0	2
1	1	1	3

The canonical partition function is calculated as:

$$\begin{aligned} Q &= \sum_{i=1}^{8} e^{-\beta E_i} = e^{-0\beta} + 3e^{-1\beta} + 3e^{-2\beta} + e^{-3\beta} \\ &= e^{-0\beta}e^{-0\beta}e^{-0\beta} + 3e^{-1\beta}e^{-0\beta}e^{-0\beta} + 3e^{-1\beta}e^{-1\beta}e^{-0\beta} + e^{-1\beta}e^{-1\beta}e^{-1\beta} \\ &= \underbrace{(e^{-0\beta} + e^{-1\beta})}_{q^A} \times \underbrace{(e^{-0\beta} + e^{-1\beta})}_{q^B} \times \underbrace{(e^{-0\beta} + e^{-1\beta})}_{q^C} = q^3 \end{aligned} \tag{2.7}$$

where the molecular partition function in this case is:

$$q = e^{-0\beta} + e^{-1\beta} \tag{2.8}$$

If, on the other hand, we consider that the three molecules are indistinguishable then, for instance, $\{\epsilon_A = 1, \epsilon_B = 0, \epsilon_C = 0\}$, $\{\epsilon_A = 0, \epsilon_B = 1, \epsilon_C = 0\}$, and $\{\epsilon_A = 0, \epsilon_B = 0, \epsilon_C = 1\}$ represent the exact same state in the system (one molecule with energy 1 and two molecules with energy 0). Therefore, the list of unique states in the system is:

ϵ_A	ϵ_B	ϵ_C	Total energy (E)
0	0	0	0
1	0	0	1
1	1	0	2
1	1	1	3

where now we are not counting the states that are redundant. The canonical partition function contains four terms, one for each distinct state of the system:

$$Q = e^{-0\beta} + e^{-1\beta} + e^{-2\beta} + e^{-3\beta} \tag{2.9}$$

Note that Q contains fewer terms than in the distinguishable case and that, if the particles are indistinguishable, then Q cannot be written as a simple product of molecular partition functions.

To calculate the partition function for N indistinguishable particles, we first consider the case in which all molecules occupy different molecular states, with energies ϵ_1 to ϵ_N. Because the particles are indistinguishable and all molecules occupy different states, any permutation of those N state assignments to the molecules will yield the same state for the system. Therefore, the sum in Eq. 2.3 contains $N!$ equal terms that, when the particles are indistinguishable, represent the same state of the system. In consequence, the partition function for a system of N non-interacting indistinguishable particles is:

$$Q = \frac{q^N}{N!} \tag{2.10}$$

Equation 2.10 is valid for most systems except at very small temperatures. This happens because usually the number of molecular states (particularly, translational states) available is exceedingly large, much larger than the number of molecules in the system. Therefore, the cases when two molecules occupy the same state are relatively rare and their contribution to the system's partition function is negligible. When Eq. 2.10 is applicable to our system we say that we work with **Boltzmann statistics**.

The use of Boltzmann statistics is valid at relatively high temperature but in the limit of $T \to 0$ we can no longer assume that all molecules occupy different states since most molecules will be in their ground state, and therefore Eq. 2.10 is no longer valid. In addition, when the temperature is very low, the quantum nature of the particles in the system imposes additional constraints on the state occupations. The nature of these constraints depends on whether the system is composed of fermions or bosons.

Fermions are particles with half-integer spin like, for instance, electrons, protons, neutrons, or ^{3}He atoms in their ground state. The wavefunction of a system composed of indistinguishable fermions must be antisymmetric with respect to the exchange of any two fermions. The fermionic nature of electrons has very important consequences in chemistry, such as the fact that two electrons cannot occupy the same electronic state (Pauli exclusion principle) and the subsequent bottom-up filling of atomic and molecular orbitals (the *auf bau* principle). In a system composed of non-interacting fermions, only one of the molecules can occupy the ground state in the same way that atomic and molecular spin-orbitals can be occupied by only one electron at a time.

Bosons are particles with integer spin. Examples of bosons include the deuterium atom, the ^{4}He atom, force-carrier particles such as photons and quasiparticles like phonons. The wavefunction of a system composed of indistinguishable bosons must be symmetric with respect to the exchange of any two particles. Unlike fermions, bosons place have no restrictions on the occupation of the different quantum states, and they are perfectly happy to share the ground state. (Note that, despite this, Eq. 2.10 is still not valid because bosons are still indistinguishable.)

Carrying out the summation in Eq. 2.3 in a system of indistinguishable fermions or bosons is possible, and yields expressions known as **Fermi-Dirac statistics** for fermions and **Bose-Einstein statistics** for bosons. The use of these statistics is essential in the description some systems like electrons in metals, liquid helium, and electromagnetic radiation. However, both statistics converge to the Boltzmann statistics with increasing temperature. For most systems of chemical interest at non-vanishing temperatures, Boltzmann statistics can be used. Note that at even higher temperatures, the three statistics converge to the classical limit, i.e., to the results obtained by using classical mechanics to describe the molecular motions.

2.2 The Molecular Partition Function

We have seen that the thermodynamic properties of a system can be derived from the canonical partition function. In a system of indistinguishable non-interacting particles, we write this partition function in terms of molecular partition functions. Like Q, the latter can be either written in terms of molecular states or molecular energy levels:

$$q = \sum_i^{\text{states}} e^{-\beta\epsilon_i} = \sum_i^{\text{levels}} g_i e^{-\beta\epsilon_i} \tag{2.11}$$

where ϵ_i are the molecular energy levels and g_i is the degeneracy of level i. Now we address how to calculate the molecular partition function.

The energy of a molecule can be approximated as the sum of several contributions from each of its degrees of freedom:

$$\epsilon_i = \epsilon_i^{\text{trans}} + \epsilon_i^{\text{rot}} + \epsilon_i^{\text{vib}} + \epsilon_i^{\text{elec}} \tag{2.12}$$

where $\epsilon_i^{\text{trans}}$ is the translational energy, ϵ_i^{rot} is the rotational energy, ϵ_i^{vib} is the vibrational energy, and ϵ_i^{elec} is the electronic energy. We can express the molecular energy in this way because the molecular Hamiltonian is approximately separable into those contributions. For instance, molecular vibrations affect only slightly the rotational levels of the molecule. Consequently, the corresponding Schrödinger equations can be solved independently of each other. This approximation is not necessarily good for the coupling between the electronic and vibrational energies but at the temperatures we will be considering only electronic ground-state will be significantly populated in most cases.

Since the molecular energy is a sum of independent contributions, the molecular partition function can be factorized into the corresponding product. First, the sum over molecular states can be separated into a sum over all states of all modes of motion of the molecule:

$$q = \sum_i e^{-\beta\epsilon_i} = \sum_{i_t}\sum_{i_r}\sum_{i_v}\sum_{i_e} e^{-\beta(\epsilon_{i_t}^{\text{trans}} + \epsilon_{i_r}^{\text{rot}} + \epsilon_{i_v}^{\text{vib}} + \epsilon_{i_e}^{\text{elec}})} \tag{2.13}$$

where i_t runs over all possible translational states, i_r runs over rotational states, i_v runs over vibrational states, and i_e runs over electronic states. In the same way as before, we factorize this quadruple sum into the product of four terms, one for each mode of motion:

$$\begin{aligned} q &= \sum_{i_t}\sum_{i_\mathrm{r}}\sum_{i_v}\sum_{i_e} e^{-\beta(\epsilon_{i_t}^{\mathrm{trans}}+\epsilon_{i_r}^{\mathrm{rot}}+\epsilon_{i_v}^{\mathrm{vib}}+\epsilon_{i_e}^{\mathrm{elec}})} \\ &= \left(\sum_{i_t} e^{-\beta\epsilon_{i_t}^{\mathrm{trans}}}\right)\left(\sum_{i_r} e^{-\beta\epsilon_{i_r}^{\mathrm{rot}}}\right)\left(\sum_{i_v} e^{-\beta\epsilon_{i_v}^{\mathrm{vib}}}\right)\left(\sum_{i_e} e^{-\beta\epsilon_{i_e}^{\mathrm{elec}}}\right) \\ &= q_{\mathrm{trans}} \times q_{\mathrm{rot}} \times q_{\mathrm{vib}} \times q_{\mathrm{elec}} \end{aligned} \tag{2.14}$$

Although exact expressions for these contributions cannot be found, we can use reasonable approximations to derive important results.

2.2.1 The Boltzmann Distribution for Molecules

In a system of non-interacting particles, we can write the energy as a sum over molecular states. If the state i of the system has $N_i(j)$ molecules in molecular state j, then its energy can be written as a sum over molecular states:

$$E_i = \sum_j^{\mathrm{mol}} N_i(j)\epsilon_j \tag{2.15}$$

where ϵ_j is the energy of molecular state j. The canonical partition function is:

$$Q = \sum_i^{\mathrm{sys}} \exp\left(-\beta \sum_j^{\mathrm{mol}} N_i(j)\epsilon_j\right) \tag{2.16}$$

where i runs over states of the system and j over states of the molecule (the superscript “mol” indicates a sum over molecular states and “sys” over system states). The average number of molecules in molecular state k is given by the corresponding ensemble average:

$$\langle N_k\rangle = \sum_i^{\mathrm{sys}} p_i N_i(k) = \frac{\sum_i^{\mathrm{sys}} N_i(k)e^{-\beta E_i}}{Q} = \frac{\sum_i^{\mathrm{sys}} N_i(k)\exp\left(-\beta\sum_j^{\mathrm{mol}} N_i(j)\epsilon_j\right)}{Q} \tag{2.17}$$

The derivative of the partition function with respect to the molecular energy levels (Eq. 2.16) is:

$$\frac{\partial Q}{\partial \epsilon_k} = -\beta \sum_i^{\mathrm{sys}} N_i(k)\exp\left(-\beta\sum_j^{\mathrm{mol}} N_i(j)\epsilon_j\right) = -\beta\langle N_k\rangle Q \tag{2.18}$$

Rearranging, we have:

$$\langle N_k\rangle = -\frac{1}{\beta Q}\frac{\partial Q}{\partial \epsilon_k} = -\frac{1}{\beta}\frac{\partial \ln Q}{\partial \epsilon_k} \tag{2.19}$$

From the expression for the canonical partition function in a system of non-interacting indistinguishable particles (Eq. 2.10), we have:

$$\ln Q = N\ln q - \ln N! \tag{2.20}$$

and substituting in the previous equation, we find:

$$\langle N_k\rangle = -\frac{N}{\beta}\frac{\partial \ln q}{\partial \epsilon_k} = -\frac{N}{\beta q}\frac{\partial q}{\partial \epsilon_k} \tag{2.21}$$

Using the definition of the molecular partition function ($q = \sum_i^{\mathrm{mol}} e^{-\beta\epsilon_i}$), we have:

$$\langle N_k\rangle = -\frac{N}{\beta q}\left(-\beta e^{-\beta\epsilon_k}\right) = \frac{Ne^{-\beta\epsilon_k}}{q} \tag{2.22}$$

The probability of finding a molecule in state k is given by the average number of molecules in state k divided by the total number of molecules:

$$\pi_k = \frac{\langle N_k \rangle}{N} = \frac{e^{-\beta\epsilon_k}}{q} \tag{2.23}$$

Note the parallelism between this probability and the equivalent expression for the whole system we derived earlier (Eq. 1.48). It is the same expression except the system's energies (E_i) and partition function (Q) are replaced by the equivalent molecular quantities (ϵ_i and q). This is **Boltzmann's distribution law**. The probability of a state is higher the smaller its energy and the higher the temperature. This can also be used to predict the relative populations of two molecular states:

$$\frac{\langle N_i \rangle}{\langle N_j \rangle} = \frac{\pi_i}{\pi_j} = \frac{\frac{e^{-\beta\epsilon_i}}{q}}{\frac{e^{-\beta\epsilon_j}}{q}} = e^{-\beta(\epsilon_i - \epsilon_j)} \tag{2.24}$$

The population of the two states diverges as the difference in energy between them increases and the temperature decreases. When comparing the relative population of two states, all molecules are in the state with lower energy of the two at zero temperature ($\beta = \infty$). Conversely, at a very high temperature, where $k_BT \gg \epsilon_i - \epsilon_j$, the exponential tends to one and the population of both states tends to the same value. In addition, the higher the energy difference between both states, the higher the temperature that is required to significantly populate the high-energy state. Note, however, that in the limit of infinite temperature the population of all states is equal, regardless of their energy. (A common error is to assume that very high temperature preferentially populates the high-energy states—this is not true.)

Sometimes we are interested not in a particular state but in the probability of a molecule being in a given energy level, which is simply given by the sum of the probabilities of all states associated with it:

$$\pi_l = \frac{g_l e^{-\beta\epsilon_l}}{q} \tag{2.25}$$

where l represents the energy level ϵ_l and g_l is its degeneracy. Likewise, the relative population of two energy levels is:

$$\frac{\langle N_k \rangle}{\langle N_l \rangle} = \frac{\pi_k}{\pi_l} = \frac{\frac{g_k e^{-\beta\epsilon_k}}{q}}{\frac{g_l e^{-\beta\epsilon_l}}{q}} = \frac{g_k}{g_l} e^{-\beta(\epsilon_k - \epsilon_l)} \tag{2.26}$$

The Boltzmann's distribution law can be applied to each molecular mode of motion (translational, rotational, etc.) individually. The average number of molecules in molecular state k (Eq. 2.22) can be written as:

$$\langle N_k \rangle = \frac{N e^{-\beta\epsilon_k}}{q} = \frac{N e^{-\beta(\epsilon_k^{\text{trans}} + \epsilon_k^{\text{rot}} + \epsilon_k^{\text{vib}} + \epsilon_k^{\text{elec}})}}{q_{\text{trans}} q_{\text{rot}} q_{\text{vib}} q_{\text{elec}}} \tag{2.27}$$

where the index k representing the molecular state can be considered a combination of four indices, each representing the state of the molecule in each mode of motion. The average number of molecules in, for instance, vibrational state n is given by summing all $\langle N_k \rangle$ that correspond to vibrational state n and any translational, rotational, and electronic states.

$$\langle N_n^{\text{vib}} \rangle = \frac{N e^{-\beta\epsilon_n^{\text{vib}}}}{q_{\text{trans}} q_{\text{rot}} q_{\text{vib}} q_{\text{elec}}} \left(\sum_{i_t} e^{-\beta\epsilon_{i_t}^{\text{trans}}} \right) \left(\sum_{i_r} e^{-\beta\epsilon_{i_r}^{\text{rot}}} \right) \left(\sum_{i_e} e^{-\beta\epsilon_{i_e}^{\text{elec}}} \right) = \frac{N e^{-\beta\epsilon_n^{\text{vib}}}}{q_{\text{vib}}} \tag{2.28}$$

Therefore, the probability that the system is in vibrational state n is:

$$\pi_n^{\text{vib}} = \frac{\langle N_n^{\text{vib}} \rangle}{N} = \frac{e^{-\beta\epsilon_n^{\text{vib}}}}{q_{\text{vib}}} \tag{2.29}$$

The equivalent result can be obtained for the other molecular modes of motion in a similar way.

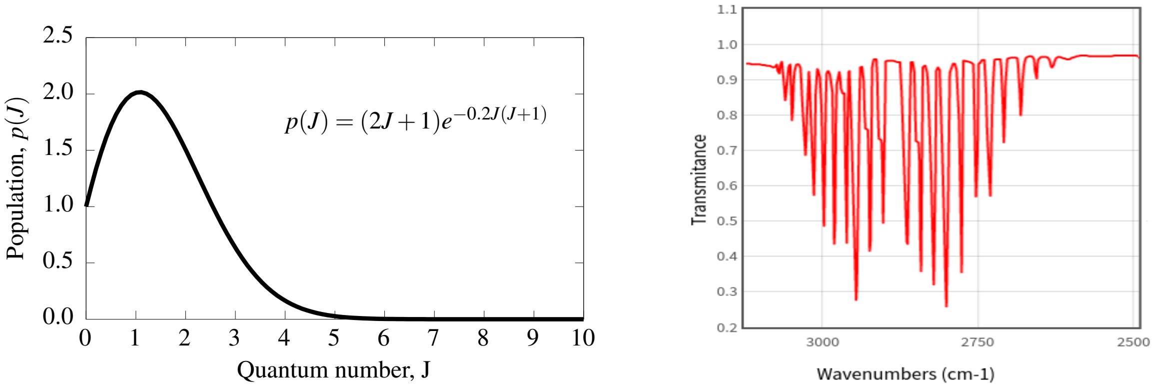


Figure 2.2: Left: Profile of the fraction of (linear) molecules in rotational level J as a function of J, for some arbitrary rotational constant. Right: Rotational-vibrational spectrum of HCl (from the NIST webbook, compiled by the Coblentz Society).

Question: Calculate the relative populations of the J=1 and J=0 rotational levels in HCl at 25 °C, assuming a closed system and ideal gas behavior. (For HCl, $\tilde{B} = 10.591\,\mathrm{cm}^{-1}$.)

If we assume the molecule is a rigid rotor, its energy levels are given by:

$$\epsilon_J^{\mathrm{rot}} = hc\tilde{B}J(J+1)$$

where h is Planck constant, c is the speed of light, and $\tilde{B}$ is the rotational constant characteristic of this molecule, typically expressed with units of cm^{-1}. The rotational energy levels are given by the quantum number $J = 0, 1, \dots$ with degeneracy equal to $g_J = 2J + 1$.

The energy separation between the $J = 1$ and $J = 0$ levels is:

$$\epsilon_1 - \epsilon_0 = 2hc\tilde{B}$$

and the degeneracies are $g_0 = 2\times 0+1 = 1$ and $g_1 = 2\times 1+1 = 3$. The ratio of the populations of the two energy levels is:

$$\frac{N_1}{N_0} = \frac{3e^{-\beta\epsilon_1}}{e^{-\beta\epsilon_0}} = 3\exp\left(-\frac{\epsilon_1 - \epsilon_0}{k_BT}\right) = 3\exp\left(-\frac{2hc\tilde{B}J}{k_BT}\right)$$

At room temperature, the ratio k_BT/hc is $207.22\,\mathrm{cm}^{-1}$. Substituting in the above equation, the ratio of populations in the two levels is:

$$\frac{N_1}{N_0} = 3\exp\left(-\frac{2\times 10.591\,\mathrm{cm}^{-1}}{207.22\,\mathrm{cm}^{-1}}\right) = 2.708$$

Note that the population of the excited level ($J = 1$) is higher than the ground-state level ($J = 0$). In the infinite-temperature limit, the population ratio tends to $g_1/g_0 = 3$.

We can generalize the discussion in this last question to explain some known spectroscopic results. The fraction of molecules in rotational energy level J is proportional to:

$$p_J \propto (2J+1)e^{-\beta hc\tilde{B}J(J+1)} \tag{2.30}$$

This function has the shape shown in Figure 2.2 (left). At low J the degeneracy pre-exponential factor $(2J + 1)$ dominates and the population increases with J. However, at some point, the exponential term overcomes the degeneracy and the function decreases exponentially as J increases. This very same profile can be seen in the experimental rovibrational (rotational-vibrational) spectrum of HCl, shown in Figure 2.2 (right). All transitions in this spectrum have $\Delta J = \pm 1$ because of the corresponding selection rules. Both branches on the right and on the left of the fundamental vibrational transition (the center of the band) show a series of narrow peaks, each corresponding to a transition between the rotational energy level J and either level $J+1$ (right part of the spectrum in Figure 2.2) or $J-1$ (left part of the spectrum). Therefore, the intensity (height) of each peak is proportional to the number of molecules in rotational level J. The intensity profile for this spectrum is in excellent agreement with Boltzmann's distribution.

Another example of the use of Boltzmann's distribution law is the choice of atomizer in atomic spectroscopy. Atomic spectroscopy is used for rapid elemental analysis of complex samples. It relies on the atomization of the sample followed by the detection of emission (atomic emission spectroscopy, AES) or absorption (atomic absorption spectroscopy, AAS) from the analyte atoms. The intensity of the signal in AES is directly proportional to the population of excited states whereas in AAS, the signal intensity is proportional to the number of ground state atoms. Therefore, an atomizer capable of producing a very high and stable temperature, such as a plasma, is preferred in AAS over lower temperature alternatives such as a flame or a graphite furnace (see Harris' *Quantitative Chemical Analysis*, section 21-3).

2.2.2 Translational Partition Function

The translational energy levels of a molecule with mass m moving freely in a one-dimensional box of length L are:

$$\epsilon_n^{\mathrm{1D}} = \frac{n^2h^2}{8mL^2} = n^2\epsilon \quad ; \quad n = 1, 2, \ldots \tag{2.31}$$

where $h = 6.626\,06 \times 10^{-34}\,\mathrm{J\,s}$ is Planck constant and we define:

$$\epsilon = \frac{h^2}{8mL^2} = \frac{h^2}{8mV^{2/3}} \tag{2.32}$$

We have identified the box length with the container volume ($V = L^3$) for simplicity. In these expressions, n is the quantum number for the translational motion. n can be any positive integer and all energy levels are non-degenerate (i.e. $g_n = 1$ for all n).

The translational energy for a molecule moving in a three dimensional container is separable into contributions from the translation movement in each dimension:

$$\epsilon^{\mathrm{trans}} = \epsilon^x + \epsilon^y + \epsilon^z = (n_x^2 + n_y^2 + n_z^2)\epsilon \tag{2.33}$$

where n_x, n_y, and n_z are the corresponding quantum numbers. Because the energy is separable into independent contributions, we can write the translational partition function as a product of three partition functions, one for each dimension:

$$\begin{aligned} q_{\mathrm{trans}} &= \sum_i e^{-\beta\epsilon_i^{\mathrm{trans}}} = \sum_{n_x}\sum_{n_y}\sum_{n_z} e^{-\beta(\epsilon_{n_x}^x + \epsilon_{n_y}^y + \epsilon_{n_z}^z)} \\ &= \left(\sum_{n_x} e^{-\beta\epsilon_{n_x}^x}\right)\left(\sum_{n_y} e^{-\beta\epsilon_{n_y}^y}\right)\left(\sum_{n_z} e^{-\beta\epsilon_{n_z}^z}\right) = q_{\mathrm{trans}}^x q_{\mathrm{trans}}^y q_{\mathrm{trans}}^z = (q_{\mathrm{trans}}^{\mathrm{1D}})^3 \end{aligned} \tag{2.34}$$

where we have used that the box length and the sum over available translational states is the same in all dimensions. The one-dimensional partition function for translation is:

$$q_{\mathrm{trans}}^{\mathrm{1D}} = \sum_{n=1}^{\infty} e^{-\beta n^2\epsilon} \tag{2.35}$$

This series cannot be summed directly. However, the translational energy levels are very close to each other for typical macroscopic volumes. For instance, the value of ϵ for a hydrogen atom moving in a $1\,\mathrm{m}^3$ box is:

$$\epsilon = \frac{h^2}{8mL^2} = \frac{(6.626\,069\,57\times 10^{-34}\,\mathrm{J\,s})^2}{8\left(1.0074\,\mathrm{g/mol}\times\frac{1\,\mathrm{mol}}{6.022\,141\,29\times 10^{23}}\times 1\,\mathrm{kg}/1000\,\mathrm{g}\right)\times(1\,\mathrm{m})^2} \tag{2.36}$$

$$= 3.280\,73\times 10^{-64}\,\mathrm{J} \tag{2.37}$$

and we define the corresponding **translational temperature** as:

$$\Theta_t = \frac{\epsilon}{k_B} = \frac{3.280\,73\times 10^{-64}\,\mathrm{J}}{1.380\,648\,8\times 10^{-23}\,\mathrm{J/K}} = 2.376\,23\times 10^{-41}\,\mathrm{K} \tag{2.38}$$

Therefore at almost any temperature above absolute zero, the translational contribution is in the high-temperature classical limit ($T \gg \Theta_t$). Contributions to the partition function extend to translational excited states with very high energy and the difference between energy levels is much smaller than the available energy. Therefore, the sum can be approximated with an integral:

$$q_{\text{trans}}^{\text{1D}} = \sum_{n=1}^{\infty} e^{-\beta n^2\epsilon} \approx \int_1^{\infty} e^{-\beta n^2\epsilon}dn \approx \int_0^{\infty} e^{-\beta n^2\epsilon}dn \tag{2.39}$$

Given the small value of ϵ compared to $1/\beta = k_BT$, there are very many terms in the series that are approximately equal to one, so very little error is introduced by starting the integral at zero instead of one. Using the change of variable:

$$x = n^2\beta\epsilon \quad ; \quad n = \sqrt{\frac{x}{\beta\epsilon}} \quad ; \quad dx = 2n\beta\epsilon dn \quad ; \quad dn = \frac{1}{2\sqrt{x\beta\epsilon}}dx \tag{2.40}$$

Then the integral becomes:

$$q_{\text{trans}}^{\text{1D}} = \int_0^{\infty} \frac{1}{2\sqrt{x\beta\epsilon}}e^{-x}dx = \frac{1}{2\sqrt{\beta\epsilon}}\underbrace{\int_0^{\infty} x^{-1/2}e^{-x}dx}_{\Gamma(1/2)=\sqrt{\pi}} = \frac{\sqrt{\pi}}{2\sqrt{\beta\epsilon}} \tag{2.41}$$

where $\Gamma(x)$ is the gamma function, whose definition is:

$$\Gamma(n) = \int_0^{\infty} x^{n-1}e^{-x}dx \tag{2.42}$$

The gamma function is an extension of the concept of factorial to real and complex numbers. For integers, $\Gamma(n) = (n-1)!$. In addition, $\Gamma(x) = (x-1)\Gamma(x-1)$ and $\Gamma(1/2) = \sqrt{\pi}$.

Going back to the translational partition function, we can now unpack $\epsilon = \frac{h^2}{8mL^2}$ to arrive at:

$$q_{\text{trans}}^{\text{1D}} = \frac{\sqrt{\pi}}{2\sqrt{\beta\left(\frac{h^2}{8mL^2}\right)}} = \left(\frac{2\pi m}{h^2\beta}\right)^{1/2} L = \frac{L}{\Lambda} \tag{2.43}$$

In the last identity we have defined the quantity Λ as:

$$\Lambda = \sqrt{\frac{h^2\beta}{2\pi m}} = \frac{h}{\sqrt{2\pi m k_B T}} \tag{2.44}$$

which is called the **thermal (de Broglie) wavelength**. Λ has units of length and it can be identified with the wavelength of the particle by noting that it is similar to h/p with $p = \sqrt{2mE} = \sqrt{2mk_BT}$ being the momentum of a molecule with k_BT energy.

Finally, the translational partition function in three dimensions is (Eq. 2.34):

$$q_{\text{trans}} = \frac{L_x}{\Lambda} \times \frac{L_y}{\Lambda} \times \frac{L_z}{\Lambda} = \frac{V}{\Lambda^3} = \left(\frac{2\pi m}{h^2\beta}\right)^{3/2} V = \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} V \tag{2.45}$$

where we have used that the volume of the box is the product of its length in each of the three dimensions ($V = L_x L_y L_z$).

The translational partition function depends both on temperature and volume (the translational contribution is the only one that depends on volume, and that will become relevant later). Values of the translational partition function at room temperature are usually very high. For instance, for an O_2 molecule in a vessel of $100\,\text{cm}^3$, $q_{\text{trans}} \approx 2 \times 10^{28}$. Therefore, at room temperature, many translational states are occupied, which confirms the validity of the approximations we made when calculating the partition function. Also, it is important to note that the translational partition function (Eq. 2.45) is the same regardless of the shape of the molecule (i.e. it is valid for a single atom, a diatomic molecule, or a more complex molecule).

2.2.3 Rotational Partition Function

The simplest way to model molecular rotation is the **rigid rotor** approximation. In this approximation, the underlying assumption in that the molecule behaves like a rigid body during rotation. This assumption allows decoupling the vibrational and rotational degrees of freedom and simplifies the problem, at the cost of some accuracy, depending on the molecule.

The expression for the energy in the rigid rotor approximation depends on the shape of the molecule. In general, we calculate the 3 × 3 inertia matrix I_{ij}, in which the diagonal elements are of the form:

$$I_{xx} = \sum_k m_k (y_k^2 + z_k^2) \tag{2.46}$$

and the non-diagonal elements are:

$$I_{xy} = -\sum_k m_k x_k y_k \tag{2.47}$$

where the sum runs over atoms in the molecule and m_k are the atomic masses. Diagonalization of the inertia matrix yields eigenvectors, called the **principal axes of inertia**, and eigenvalues, the **moments of inertia**, typically labeled I_A, I_B, and I_C. If the molecule is symmetric, the principal axes of inertia are usually related to symmetry operations in the molecule's point group. For instance, in a linear molecule, one axis of inertia must be aligned with the molecule.

The number of unique and non-zero moments of inertia depends on the symmetry of the molecule. If the molecule is linear, it has one vanishing and two identical moments of inertia ($I_A = I_B \neq 0$, $I_C = 0$). If the molecule is non-linear, all its moments of inertia are non-zero, and the molecule can be classified according to how many of them are different into: spherical top ($I_A = I_B = I_C$), symmetric top ($I_A \neq I_B = I_C$), or asymmetric top ($I_A \neq I_B \neq I_C$).

We start with the case of a linear molecule. In the rigid rotor approximation, its rotational energy levels are given by:

$$\epsilon_J^{\text{rot}} = hc\tilde{B}J(J+1) \quad ; \quad J = 0, 1, \ldots \tag{2.48}$$

with c the speed of light and $\tilde{B}$ the rotational constant for the linear molecule. $\tilde{B}$ is expressed as a wavenumber, typically with units of cm^{-1}, and is given by:

$$\tilde{B} = \frac{h}{8\pi^2 cI} \tag{2.49}$$

and $I = I_A = I_B$ is the only moment of inertia in the molecule. In the particular case of a diatomic molecule, $I = \mu R_e^2$ with R_e the interatomic distance and μ the reduced mass ($\mu = m_1 m_2/(m_1 + m_2)$). A common way of expressing a rotational constant is in terms of the **rotational temperature**, defined as:

$$\Theta_R = \frac{hc\tilde{B}}{k_B} \tag{2.50}$$

Together with J, there is a second quantum number M_J that does not enter the energy expression and can take $2J + 1$ values, from $-J$ to J. A rotational energy level given by quantum number J is $2J + 1$-degenerate. The rotational partition function for a linear molecule is:

$$q_{\text{rot}}^{\text{linear}} = \sum_{J=0}^{\infty} (2J+1) e^{-\beta hc\tilde{B}J(J+1)} = \sum_{J=0}^{\infty} (2J+1) e^{-J(J+1)\Theta_R/T} \tag{2.51}$$

As in the case of the translational partition function, this series cannot be evaluated directly. Although the rotational levels are not as closely spaced as the translational levels, many of the excited rotational levels are populated at room temperature, since for most molecules $T \gg \Theta_R$. Therefore, we can treat the energy levels as a continuum (the classical or high-temperature limit) and replace the series with an integral. Some rotational temperatures for small molecules are: $^1H^{35}Cl$ (15.2 K), $^{14}N_2$ (2.88 K), and $^{35}Cl_2$ (0.351 K). Larger molecules have even smaller rotational temperatures. There are only a few instances in which this is not the case, most notably $^1H_2$ (87.6 K). In those cases, the rotational partition must be summed term by term and the transformation to the integral cannot be carried out.

Assuming we are in the high-temperature limit, Eq. 2.51 becomes:

$$q_{\text{rot}}^{\text{linear}} \approx \int_0^{\infty} (2J+1) e^{-\beta hc\tilde{B}J(J+1)} dJ \tag{2.52}$$

and we note that the derivative of the exponent is:

$$\frac{d(-\beta hc\tilde{B}J(J+1))}{dJ} = -\beta hc\tilde{B}(2J+1) \tag{2.53}$$

Therefore, the integral is:

$$q_{\text{rot}}^{\text{linear}} = -\frac{1}{\beta hc\tilde{B}} \left[e^{-\beta hc\tilde{B}J(J+1)} \right]_0^{\infty} = \frac{1}{\beta hc\tilde{B}} = \frac{k_B T}{hc\tilde{B}} \tag{2.54}$$

which is the rotational partition function for a linear molecule in the high-temperature limit. In terms of the rotational temperature:

$$q_{\text{rot}}^{\text{linear}} = \frac{T}{\Theta_R} \tag{2.55}$$

which is valid only when $T \gg \Theta_R$.

The rotational partition function in Eq. 2.55 is not complete because there are symmetry restrictions placed on the wavefunction in symmetric molecules. The simplest illustration of this is the case of a homodiatomic molecule (i.e. a diatomic molecule where both atoms are the same species and isotope). In a homodiatomic molecule, a rotation of 180 degrees around an axes perpendicular to the molecule leaves the molecule unchanged because both atoms are indistinguishable, so the partition function in Eq. 2.55 represents approximately twice as many rotational terms as it should.

The molecular wavefunction is a product of electronic, vibrational, rotational, translational, and nuclear factors:

$$\psi_{\text{total}} = \psi_{\text{trans}} \times \psi_{\text{rot}} \times \psi_{\text{vib}} \times \psi_{\text{elec}} \times \psi_{\text{nuc}} \tag{2.56}$$

The total molecular wavefunction must be symmetric or antisymmetric with respect to the exchange of the two indistinguishable nuclei in a homodiatomic molecule, depending on whether these nuclei are fermions or bosons. From the nuclear spin of the two nuclei, one can construct a number of symmetric and antisymmetric nuclear wavefunctions (ψ_{nuc}), which can be subsequently combined with the wavefunctions for the other modes of motion in order to give an overall wavefunction (ψ_{total}) with the correct symmetry with respect to the exchange of the nuclei. Besides the nuclear wavefunction, the rotational wavefunction can be variously symmetric or antisymmetric with respect to a nuclei exchange, depending on the value of the J quantum number. (The symmetry of the electronic wavefunction depends on the electronic ground state but, for the cases we will consider, it is symmetric.) Odd values of J result in an antisymmetric rotational wavefunction and even values of J give a symmetric rotational wavefunction. Therefore, depending on the nuclear spin of both atoms, the molecule can access only the odd J or the even J rotational states and, in either case, the partition function in Eq. 2.51 contains only about half of the terms. If enough rotational levels are occupied (i.e. in the high-temperature limit), these two sums converge to half of our previous result:

$$q_{\text{rot}}^{\text{linear,sym}} = \frac{T}{2\Theta_R} \tag{2.57}$$

The additional 2 factor arises from the fact that only half of the rotational levels are accessible, and ultimately from atomic indistinguishability in the homodiatomic molecule. The wavefunction symmetry requirement is also responsible for the existence of two **spin isomers** in the hydrogen molecule: ortho-H_2 (with symmetric nuclear spin function and antisymmetric rotational wavefunction) and para-H_2 (antisymmetric nuclear spin function and symmetric rotational wavefunction). Because the rotational temperature of $^1H_2$ is relatively high (87.6 K), the two spin isomers have different thermodynamic properties at low temperature.

For a heterodiatomic molecule, there are no restrictions on the rotational wavefunction, so Eq. 2.55 is still valid. We can now generalize our result to any linear molecule. If the molecule is symmetric around its center of mass ($D_{\infty h}$ point group), then our arguments above apply and the factor of 2 in the denominator is present (Eq. 2.57). If the molecule is not symmetric around the center ($C_{\infty v}$ point group), then the factor is absent (Eq. 2.55). Both results can be combined by introducing the **symmetry number** (σ):

$$q_{\text{rot}}^{\text{linear}} = \frac{T}{\sigma\Theta_R} \tag{2.58}$$

where σ is 1 for a linear non-symmetric molecule and 2 for a linear symmetric molecule.

In the case of a non-linear polyatomic molecule, the expression for the rotational energy involves more quantum numbers than just J and the calculation of the rotational partition function is more convoluted, so we will just state the result in the high-temperature limit without derivation. For an asymmetric top (the most general case), the rotational partition function is:

$$\begin{aligned} q_{\text{rot}}^{\text{non-linear}} &= \frac{1}{\sigma(hc\beta)^{3/2}}\left(\frac{\pi}{\tilde{A}\tilde{B}\tilde{C}}\right)^{1/2} = \frac{1}{\sigma}\left(\frac{k_BT}{hc}\right)^{3/2}\left(\frac{\pi}{\tilde{A}\tilde{B}\tilde{C}}\right)^{1/2} \\ &= \frac{\sqrt{\pi}}{\sigma}\left(\frac{T}{\Theta_R^A}\right)^{1/2}\left(\frac{T}{\Theta_R^B}\right)^{1/2}\left(\frac{T}{\Theta_R^C}\right)^{1/2} \end{aligned} \tag{2.59}$$

where $\tilde{A}$, $\tilde{B}$, and $\tilde{C}$ are the rotational constants associated to each of the moments of inertia:

$$\tilde{A} = \frac{h}{8\pi^2 cI_A} \tag{2.60}$$

and the equivalent expressions apply to $\tilde{B}$ and I_B and to $\tilde{C}$ and I_C (compare to Eq. 2.49). We have also defined the rotational temperatures associated with each of these constants in the same way as above (Eq. 2.50):

$$\Theta_R^A = \frac{hc\tilde{A}}{k_B} \tag{2.61}$$

and with similar definitions for Θ_R^B and Θ_R^C. The symmetry number in this more general case is the number of unique rotations that bring the molecule into coincidence with itself. (In terms of group theory, σ is the number of pure rotation operations in the point group, including the identity.) Examples of symmetry numbers: H_2O (2, around the 2-fold axis), NH_3 (3, around the 3-fold axis), and CH_4 (12, around the four 3-fold axes), and benzene (12, from a combination of the 6-fold axis perpendicular to the molecule and the in-plane C_2 axes).

The rotational partition function for a symmetric top or a spherical top can be obtained from the general equation (Eq. 2.59), where $\tilde{B} = \tilde{C}$ and $\tilde{A} = \tilde{B} = \tilde{C}$, respectively.

2.2.4 Vibrational Partition Function

The simplest model for molecular vibrations is the **harmonic oscillator**, in which each vibrational degree of freedom in the molecule is represented by a particle moving in a parabolic potential well. The energy levels of the harmonic oscillator are:

$$\epsilon_n^{\text{vib}} = hc\tilde{\nu}(n + 1/2) \tag{2.62}$$

where $\tilde{\nu}$ is the vibrational constant for the harmonic oscillator (in wavenumbers, typically with units of cm^{-1}). The vibrational constant is related to the steepness of the potential well. In a diatomic molecule, the vibrational constant is related to the force constant k, i.e., the second derivative of the molecular energy as a function of internuclear separation:

$$\tilde{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}} \tag{2.63}$$

with $\mu = m_A m_B/(m_A + m_B)$ the reduced mass. Vibrational energy levels are determined by the quantum number $n = 0, 1, \ldots$ and all levels are non-degenerate ($g_n = 1$). Note that the energy of the vibrational ground state is not zero, since even at $n = 0$ there is a residual energy called the **zero-point energy**:

$$\epsilon_0^{\text{vib}} = \frac{hc\tilde{\nu}}{2} \tag{2.64}$$

The vibrational partition function in the case when we have a single harmonic oscillator (for instance, a diatomic molecule) can be calculated easily by extracting the factor corresponding to the zero-point energy:

$$q_{\text{vib}} = \sum_{n=0}^{\infty} e^{-\beta\epsilon_n^{\text{vib}}} = \sum_{n=0}^{\infty} e^{-\beta hc\tilde{\nu}(n+1/2)} = e^{-\beta hc\tilde{\nu}/2} \sum_{n=0}^{\infty} \left(e^{-\beta hc\tilde{\nu}}\right)^n = \frac{e^{-\beta hc\tilde{\nu}/2}}{1 - e^{-\beta hc\tilde{\nu}}} \tag{2.65}$$

where we have used the formula for the geometric series (with $0 \leq r < 1$):

$$\sum_{i=0}^{\infty} r^i = \frac{1}{1-r} \tag{2.66}$$

The fraction of molecules in vibrational energy level n is therefore:

$$\pi_n^{\text{vib}} = \frac{\langle N_n^{\text{vib}} \rangle}{N} = \frac{e^{-\beta\epsilon_n^{\text{vib}}}}{q_{\text{vib}}} = \frac{e^{-\beta hc\tilde{\nu}(n+1/2)}}{e^{-\beta hc\tilde{\nu}/2}\left(1 - e^{-\beta hc\tilde{\nu}}\right)^{-1}} = e^{-n\beta hc\tilde{\nu}}(1 - e^{-\beta hc\tilde{\nu}}) \tag{2.67}$$

where we canceled out the factor from the zero-point energy in the numerator and the denominator.

Question: Calculate the fraction of molecules in excited ($n > 0$) vibrational states in H_2 ($\tilde{\nu} = 4319.6\,\mathrm{cm}^{-1}$) and I_2 ($\tilde{\nu} = 215.5\,\mathrm{cm}^{-1}$) at room temperature and at 1000 K.

The fraction of molecules in excited vibrational levels (any $n > 0$) is:

$$p_{\mathrm{exc}} = \sum_{n=1}^{\infty} p_n = 1 - p_0$$

where p_0 is the fraction of molecules in the vibrational ground state. (We can do this because a molecule must occupy one and only one vibrational level.) Using Eq. 2.67, we find for the ground state:

$$p_0 = 1 - e^{-\beta hc\tilde{\nu}}$$

and therefore:

$$p_{\mathrm{exc}} = e^{-\beta hc\tilde{\nu}} = \exp\left(-\frac{hc\tilde{\nu}}{k_B T}\right)$$

Applying this equation to the two molecules, we find:

$$\begin{aligned}
p_{\mathrm{exc}}(\mathrm{H_2}, \mathrm{RT}) &= \exp\left(-\frac{6.626\times10^{-34}\,\mathrm{J\,s}\times 2.998\times10^{8}\,\mathrm{m/s}\times 4319.6\,\mathrm{cm}^{-1}\times \frac{100\,\mathrm{cm}}{m}}{1.381\times10^{-23}\,\mathrm{J/K}\times 300\,\mathrm{K}}\right)\\
&= 1.01\times10^{-9}\\
p_{\mathrm{exc}}(\mathrm{H_2}, 1000\,\mathrm{K}) &= \exp\left(-\frac{6.626\times10^{-34}\,\mathrm{J\,s}\times 2.998\times10^{8}\,\mathrm{m/s}\times 4319.6\,\mathrm{cm}^{-1}\times \frac{100\,\mathrm{cm}}{m}}{1.381\times10^{-23}\,\mathrm{J/K}\times 1000\,\mathrm{K}}\right)\\
&= 2.00\times10^{-3}\\
p_{\mathrm{exc}}(\mathrm{I_2}, \mathrm{RT}) &= \exp\left(-\frac{6.626\times10^{-34}\,\mathrm{J\,s}\times 2.998\times10^{8}\,\mathrm{m/s}\times 215.5\,\mathrm{cm}^{-1}\times \frac{100\,\mathrm{cm}}{m}}{1.381\times10^{-23}\,\mathrm{J/K}\times 300\,\mathrm{K}}\right)\\
&= 0.356\\
p_{\mathrm{exc}}(\mathrm{I_2}, 1000\,\mathrm{K}) &= \exp\left(-\frac{6.626\times10^{-34}\,\mathrm{J\,s}\times 2.998\times10^{8}\,\mathrm{m/s}\times 215.5\,\mathrm{cm}^{-1}\times \frac{100\,\mathrm{cm}}{m}}{1.381\times10^{-23}\,\mathrm{J/K}\times 1000\,\mathrm{K}}\right)\\
&= 0.733
\end{aligned}$$

In H_2, the vibrational constant is sufficiently high that, even at 1000 K, the population of molecules in excited vibrational states is relatively low. In contrast, this is not the case in I_2 with approximately 35% excited molecules at room temperature and 73% at 1000 K.

In the case of a polyatomic molecule (a molecule with more than two atoms), its vibration energy in the harmonic approximation can be described as the sum of the energies of $3m-6$ (or $3m-5$ if the molecule is linear) uncoupled harmonic oscillators, where m is the number of atoms in the molecule. The vibrational energy levels are:

$$\epsilon_{\mathrm{vib}} = \sum_{i=1}^{3m-6} \epsilon_{\mathrm{vib}}^{i} = \sum_{i=1}^{3m-6} hc\tilde{\nu}_i (n_i + 1/2) \tag{2.68}$$

where n_i are the vibrational quantum numbers associated to each of the $3m-6$ normal modes, and $\tilde{\nu}_i$ are their vibrational constants. (Or $3m-5$ if linear, we will use $3m-6$ for simplicity in the rest of this section, but remember that a linear molecule has one fewer normal mode.) Since the energy can be written as a sum over normal modes, the partition function can be factorized into contributions from each normal mode:

$$\begin{aligned}
q_{\mathrm{vib}} &= \sum_{n_1}\cdots\sum_{n_{3m-6}} e^{-\beta(\epsilon_{\mathrm{vib}}^{1}+\ldots+\epsilon_{\mathrm{vib}}^{3m-6})} = \left(\sum_{n_1} e^{-\beta\epsilon_{\mathrm{vib}}^{1}}\right)\cdots\left(\sum_{n_{3m-6}} e^{-\beta\epsilon_{\mathrm{vib}}^{3m-6}}\right)\\
&= \left(\frac{e^{-\beta hc\tilde{\nu}_1/2}}{1-e^{-\beta hc\tilde{\nu}_1}}\right)\cdots\left(\frac{e^{-\beta hc\tilde{\nu}_{3m-6}/2}}{1-e^{-\beta hc\tilde{\nu}_{3m-6}}}\right) = \prod_{i=1}^{3m-6} q_{\mathrm{vib}}^{i}
\end{aligned} \tag{2.69}$$

At room temperature, $k_BT/hc = 207.22\,\mathrm{cm}^{-1}$. Typical vibrational constants are in the range of hundreds to thousands of cm^{-1}, depending on the types of bonds in the molecule and the weight of the atomic species involved in the vibration. Examples: H_2 ($4319.6\,\mathrm{cm}^{-1}$), HCl ($2937.9\,\mathrm{cm}^{-1}$), N_2 ($2345.0\,\mathrm{cm}^{-1}$), CO ($2154.6\,\mathrm{cm}^{-1}$), Cl_2 ($563.0\,\mathrm{cm}^{-1}$), and I_2 ($215.5\,\mathrm{cm}^{-1}$). For normal modes that have a significantly higher vibrational constant than k_BT/hc at the experiment's temperature, the thermal energy available (represented by k_BT) is not enough to populate any level other than the vibrational ground state. For normal modes with vibrational constant comparable or lower than k_BT/hc, excited vibrational states are significantly populated.

We can also consider the uncommon situation in which the temperature is high enough that k_BT/hc is much greater than $\tilde{\nu}$ for a particular normal mode. This is not a very useful limit because the energy difference between vibrational energy levels in a molecule decreases for higher levels, which indicates that the harmonic approximation becomes less good for excited states of very high quantum number. At very high temperature, the molecule does not vibrate very quickly, it just dissociates. However, it is interesting to consider the limit nonetheless. In the high temperature limit, $\beta hc\tilde{\nu}$ is close to zero. We can rewrite the vibrational partition function as:

$$q_{\mathrm{vib}} = \frac{e^{-\beta hc\tilde{\nu}/2}}{1 - e^{-\beta hc\tilde{\nu}}} = \frac{1}{e^{\beta hc\tilde{\nu}/2} - e^{-\beta hc\tilde{\nu}/2}} = \frac{1}{2\sinh\left(\beta hc\tilde{\nu}/2\right)} \tag{2.70}$$

where $\sinh(x) = (e^x - e^{-x})/2$ is the hyperbolic sine function. The Taylor expansion around $x = 0$ for this function is:

$$\sinh(x) = x + \frac{x^3}{3!} + \frac{x^5}{5!} + \ldots \tag{2.71}$$

so in the limit $x \to 0$ the sinh function can be replaced by the leading term in the Taylor series (x):

$$q_{\mathrm{vib}} = \frac{1}{2\sinh\left(\beta hc\tilde{\nu}/2\right)} \approx \frac{1}{2\times\beta hc\tilde{\nu}/2} = \frac{k_BT}{hc\tilde{\nu}} \tag{2.72}$$

This is the high-temperature (classical) limit of the vibrational partition function.

Similarly to what we did for the rotational partition function, we define a **vibrational temperature** for each normal mode:

$$\Theta_V = \frac{hc\tilde{\nu}}{k_B} \tag{2.73}$$

The general expression for the vibrational partition function of a single harmonic oscillator (Eq. 2.65, valid at all temperatures) can be rewritten in terms of the vibrational temperature as:

$$q_{\mathrm{vib}} = \frac{e^{-\Theta_V/2T}}{1 - e^{-\Theta_V/T}} \tag{2.74}$$

and, for a polyatomic molecule (Eq. 2.69):

$$q_{\mathrm{vib}} = \prod_{i=1}^{3m-6} q_{\mathrm{vib}}^i = \prod_{i=1}^{3m-6}\left(\frac{e^{-\Theta_V^i/2T}}{1 - e^{-\Theta_V^i/T}}\right) \tag{2.75}$$

where Θ_V^i are the vibrational temperatures corresponding to each normal mode. The vibrational partition function for a single oscillator in the classical limit is:

$$q_{\mathrm{vib}} = \frac{T}{\Theta_V} \tag{2.76}$$

As in the rotational case, comparison of the system's temperature with the vibrational temperature provides a guideline for how far we are from the classical limit. Note, that, as mentioned before, the harmonic approximation fails at high temperature and a molecule only has a finite number of vibrational levels before it dissociates. Hence, the high-temperature expression for the vibrational partition function is seldom used in practice.

For complex molecules that have internal rotation (for instance, the rotation about the C-C bond in ethane), the harmonic approximation is not appropriate if the rotational energy barrier is not very high (in ethane, $2.9\,\mathrm{kcal/mol}$ to be compared to $k_BT = 0.6\,\mathrm{kcal/mol}$ at room temperature). This is because there is enough thermal energy to cause almost free rotation around that bond and therefore the assumption that this motion behaves like a harmonic oscillator is not appropriate. In this case, the vibrational normal modes associated to these rotations are treated separately using a **hindered rotor** approximation, in which the levels of a hindered rotor are calculated by solving the corresponding Schrödinger equation, and the corresponding partition function is calculated numerically.

2.2.5 Electronic Partition Function

The differences in energy between electronic excited states and the corresponding ground state are usually much higher than k_BT for the typical temperatures used in experiments. For instance, the energy of a hydrogen atom is:

$$E_n = -\frac{1}{2n^2} \tag{2.77}$$

in atomic units. In terms of cm^{-1} it is:

$$E_n = -\frac{109\,737\,\mathrm{cm}^{-1}}{n^2} \tag{2.78}$$

The separation between the ground state and the first excited state is:

$$\Delta E = E_2 - E_1 = \frac{3}{4} \times 109\,737\,\mathrm{cm}^{-1} = 82\,302\,\mathrm{cm}^{-1} \tag{2.79}$$

This value is much higher than the corresponding thermal energy at room temperature, which we have seen is $k_BT/hc = 207.22\,\mathrm{cm}^{-1}$.

In most cases, the electronic partition function contains only one term, corresponding to the ground state. We will use the convention that the zero of energy when dealing with molecular species is the separated neutral atoms in their ground state, i.e., the electronic ground state has energy $-D_e$, where D_e is the dissociation energy of the molecule, if the molecule is diatomic, or the atomization energy if it is not. The choice of energy zero is arbitrary but it must be consistent. As we have seen in the previous chapter and we shall see later, the impact of this choice is a constant shift in the thermodynamic energies (U, G,...) and no change in the entropy and the relative populations and probabilities of the different energy levels. The reason for the chosen convention will be apparent when we study equilibrium constants of chemical reactions.

The electronic partition function is:

$$q_{\text{elec}} = g_0 e^{D_e/k_BT} + \ldots \tag{2.80}$$

where g_0 is the degeneracy of the electronic ground state and the other terms are usually negligible. Usually, $g_0 = 1$ but an important exception is the cases where the electronic ground state is degenerate: radicals (doublets), molecular oxygen (triplet), open-shell atoms, etc. In most molecules, the multiplicity of the electronic ground state equals the spin multiplicity ($2S + 1$, where S is the total electronic spin), and it is equal to the number of unpaired electrons plus one.

In some (rare) cases, there are excited states that have relatively low energy compared to the thermal energy (k_BT) at room temperature. This is the case, for instance, in the NO molecule. If excited states with relatively low energy are present, then the partition function contains one (or more) terms besides the one corresponding to the ground state.

2.3 Calculation of Thermodynamic Properties

2.3.1 Internal Energy

The internal energy can be calculated as a derivative of the canonical partition function (Eq. 1.66):

$$U = -\frac{\partial \ln Q}{\partial \beta} \tag{2.81}$$

or, using the chain rule (Eq. 1.102):

$$U = k_BT^2\frac{\partial \ln Q}{\partial T} \tag{2.82}$$

For a system of indistinguishable non-interacting particles, the partition function is:

$$Q = \frac{q^N}{N!} \tag{2.83}$$

where q is the molecular partition function and N is the number of molecules in the system. Taking logarithms, we have:

$$\ln Q = N\ln q - \ln N! \tag{2.84}$$

and:

$$\frac{\partial \ln Q}{\partial T} = N\frac{\partial \ln q}{\partial T} \tag{2.85}$$

from which the internal energy is written as:

$$U = Nk_BT^2\frac{\partial \ln q}{\partial T} \tag{2.86}$$

We have seen in Section 2.2 that, due to the corresponding degrees of freedom being weakly coupled, the partition function of the molecule can be factorized into its translational, vibrational, rotational, and electronic contributions:

$$q = q_{\text{trans}} \times q_{\text{rot}} \times q_{\text{vib}} \times q_{\text{elec}} \tag{2.87}$$

Substituting this result in the internal energy expression, we have that the internal energy itself can be split into contributions from each of the molecular degrees of freedom:

$$\begin{aligned} U &= Nk_BT^2\frac{\partial \ln(q_{\text{trans}} \times q_{\text{rot}} \times q_{\text{vib}} \times q_{\text{elec}})}{\partial T} \\ &= Nk_BT^2\frac{\partial(\ln q_{\text{trans}} + \ln q_{\text{rot}} + \ln q_{\text{vib}} + \ln q_{\text{elec}})}{\partial T} \\ &= Nk_BT^2\frac{\partial \ln q_{\text{trans}}}{\partial T} + Nk_BT^2\frac{\partial \ln q_{\text{rot}}}{\partial T} + Nk_BT^2\frac{\partial \ln q_{\text{vib}}}{\partial T} + Nk_BT^2\frac{\partial \ln q_{\text{elec}}}{\partial T} \\ &= U_{\text{trans}} + U_{\text{rot}} + U_{\text{vib}} + U_{\text{elec}} \end{aligned} \tag{2.88}$$

Let us consider each of these contributions in turn using the expressions that we have for the corresponding partition functions.

Translational Contribution

The translational partition function is (Eq. 2.45):

$$q_{\text{trans}} = \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} V \tag{2.89}$$

and its logarithm is:

$$\ln q_{\text{trans}} = \ln\left(\frac{2\pi m k_B}{h^2}\right)^{3/2} V + \frac{3}{2}\ln T \tag{2.90}$$

Therefore, the translational contribution to the internal energy is:

$$U_{\text{trans}} = N k_B T^2 \frac{\partial \ln q_{\text{trans}}}{\partial T} = N k_B T^2 \times \frac{3}{2T} = \frac{3}{2} N k_B T = \frac{3}{2} nRT \tag{2.91}$$

where in the last transformation we used that the number of moles is related to the number of molecules by Avogadro's number ($N = N_A n$) and so is the gas constant and Boltzmann constant ($R = N_A k_B$). The translational motion of the molecules in an ideal gas contributes $\frac{3}{2}RT$ per mole of molecules to the internal energy.

Rotational Contribution

For a linear molecule, if the temperature is significantly higher than the rotational temperature Θ_R, the partition function is (Eq. 2.58):

$$q_{\text{rot}}^{\text{linear}} = \frac{T}{\sigma \Theta_R} \tag{2.92}$$

with σ the symmetry number and the rotational temperature is defined as:

$$\Theta_R = \frac{hc\tilde{B}}{k_B} \tag{2.93}$$

The logarithm of this partition function is:

$$\ln q_{\text{rot}}^{\text{linear}} = \ln T - \ln(\sigma \Theta_R) \tag{2.94}$$

From this expression, the rotational contribution to the internal energy is:

$$U_{\text{rot}}^{\text{linear}} = N k_B T^2 \frac{\partial \ln q_{\text{rot}}^{\text{linear}}}{\partial T} = N k_B T = nRT \tag{2.95}$$

So the rotational contribution to the internal energy for a linear molecule in the usual case where $T \gg \Theta_R$ is one RT per mole of molecules. If T is comparable or smaller than Θ_R then the series needs to be evaluated term by term and the expression for U_{rot} is more complicated.

In the case of a non-linear polyatomic molecule, we have:

$$q_{\text{rot}}^{\text{non-linear}} = \frac{1}{\sigma}\left(\frac{k_B T}{hc}\right)^{3/2}\left(\frac{\pi}{\tilde{A}\tilde{B}\tilde{C}}\right)^{1/2} \tag{2.96}$$

and:

$$\ln q_{\text{rot}}^{\text{non-linear}} = \frac{3}{2}\ln T + \ln\left[\frac{1}{\sigma}\left(\frac{k_B}{hc}\right)^{3/2}\left(\frac{\pi}{\tilde{A}\tilde{B}\tilde{C}}\right)^{1/2}\right] \tag{2.97}$$

so the contribution to the internal energy is:

$$U_{\text{rot}}^{\text{non-linear}} = N k_B T^2 \frac{\partial \ln q_{\text{rot}}^{\text{non-linear}}}{\partial T} = \frac{3}{2} N k_B T = \frac{3}{2} nRT \tag{2.98}$$

Thus, the rotational contribution to the internal energy in a non-linear molecule is $3/2RT$ per mole of gas in the high-temperature (classical) limit.

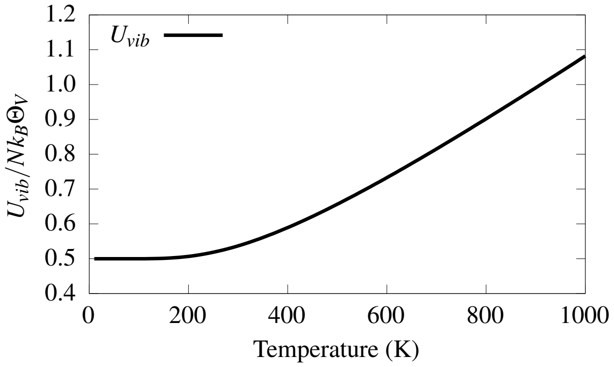


Figure 2.3: Vibrational contribution to the internal energy from a single normal mode as a function of temperature.

Vibrational Contribution

In the harmonic approximation, the vibrational partition function for a molecule with m atoms and $3m-6$ normal modes is:

$$q_{\text{vib}} = \prod_{i=1}^{3m-6} q_{\text{vib}}^i \tag{2.99}$$

with the contribution from each normal mode having the form:

$$q_{\text{vib}}^i = \frac{e^{-\Theta_V^i/2T}}{1-e^{-\Theta_V^i/T}} \tag{2.100}$$

Similarly to what we did with the molecular contributions themselves, since the vibrational partition function is written as a product of partition functions for each normal mode, we have that each normal mode contributes independently to the internal energy of the system:

$$\begin{aligned} U_{\text{vib}} = Nk_BT^2\frac{\partial \ln q_{\text{vib}}}{\partial T} &= Nk_BT^2\frac{\partial \ln\left(\prod_{i=1}^{3m-6} q_{\text{vib}}^i\right)}{\partial T} = Nk_BT^2\frac{\partial\left(\sum_{i=1}^{3m-6}\ln q_{\text{vib}}^i\right)}{\partial T} \\ &= \sum_{i=1}^{3m-6}\underbrace{Nk_BT^2\frac{\partial \ln q_{\text{vib}}^i}{\partial T}}_{U_{\text{vib}}^i} = \sum_{i=1}^{3m-6} U_{\text{vib}}^i \end{aligned} \tag{2.101}$$

and we can consider each normal mode contribution independently. The logarithm of the partition function for normal mode i is:

$$\ln q_{\text{vib}}^i = \ln(e^{-\Theta_V^i/2T}) - \ln(1-e^{-\Theta_V^i/T}) = -\frac{\Theta_V^i}{2T} - \ln(1-e^{-\Theta_V^i/T}) \tag{2.102}$$

And the corresponding contribution to the internal energy is:

$$U_{\text{vib}}^i = Nk_BT^2\frac{\partial \ln q_{\text{vib}}^i}{\partial T} = Nk_BT^2\times\left(\frac{\Theta_V^i}{2T^2} - \frac{e^{-\Theta_V^i/T}\times\left(-\frac{\Theta_V^i}{T^2}\right)}{1-e^{-\Theta_V^i/T}}\right) = Nk_B\Theta_V^i\left(\frac{1}{2}+\frac{1}{e^{\Theta_V^i/T}-1}\right) \tag{2.103}$$

where we have divided the numerator and denominator in the second term by $e^{-\Theta_V^i/T}$. The first term in this expression is the **zero-point contribution to the internal energy**, and it is independent of temperature and present even at absolute zero. The second term depends on temperature. A plot of U_{vib}^i as a function of temperature is shown in Figure 2.3.

At very low temperature, the denominator in the second term goes to infinity and the contribution from every normal mode (and therefore the vibrational contribution) goes to the corresponding zero-point energy. This is because at low temperature there is not sufficient thermal energy to excite any of the molecules appreciably. At high temperatures, at which $T \gg \Theta_V^i$ the exponent becomes very small and we can use the Taylor expansion of the exponential around zero ($e^x = 1 + x + \ldots$) to give:

$$\begin{aligned} U_{\text{vib}}^i &= Nk_B\Theta_V^i \left(\frac{1}{2} + \frac{1}{e^{\Theta_V^i/T} - 1}\right) \approx Nk_B\Theta_V^i \left(\frac{1}{2} + \frac{1}{1 + \Theta_V^i/T - 1}\right) \\ &= \frac{1}{2}Nk_B\Theta_V^i + Nk_BT \approx Nk_BT = nRT \end{aligned} \tag{2.104}$$

where we have neglected $\Theta_V^i/2$ with respect to T (because we are at the $T \gg \Theta_V^i$ limit and therefore $T/\Theta_V^i \gg 1$). Therefore, if the temperature is sufficiently high relative to the molecular vibration frequencies, then each normal mode in the molecule contributes one RT to the internal energy per mole of molecules (i.e. $U_{\text{vib}} = (3m - 6)RT$ per mole for a non-linear molecule, where m is the number of atoms). Note that Eq. 2.104 can also be obtained as the temperature derivative (Eq. 2.82) of the high-temperature expression for the vibrational partition function (Eq. 2.76). Reaching the vibrational high-temperature limit, in general, requires temperatures much higher than room temperature and at very high temperature the harmonic approximation is not appropriate, so this limit is seldom applied. Some examples of vibrational temperatures have been given in Section 2.2.4.

Electronic Contribution

For most molecules, the spacing between electronic levels is much higher than k_BT and therefore the electronic partition function contains only one term involving the degeneracy of the ground state, g_0 (usually, it is also the case that $g_0 = 1$):

$$q_{\text{elec}} \approx g_0 e^{D_e/k_BT} \tag{2.105}$$

where we have used as zero of energy the state in which all atoms in the molecule are infinitely separated from each other, neutral, and in their ground state (c.f. Section 2.2.5). The logarithm of this partition function is:

$$\ln q_{\text{elec}} = \ln g_0 + \frac{D_e}{k_BT} \tag{2.106}$$

Therefore, the contribution of the electronic motion to the internal energy is:

$$U_{\text{elec}} = Nk_BT^2\frac{\partial \ln q_{\text{elec}}}{\partial T} = Nk_BT^2\left(-\frac{D_e}{k_BT^2}\right) = -ND_e \tag{2.107}$$

Note that the (more or less arbitrary) choice in the zero of energy results in a constant contribution to the electronic internal energy, equal to the minus the sum of the atomization energies of all molecules in the system (i.e. the system being composed of molecules means it is ND_e more stable than the separated atoms). In cases when more than one state is thermally accessible, the sum must be computed by hand, which is usually straightforward because only a few terms are important.

Summary and the Equipartition Theorem

Combining the translational, rotational, vibrational, and electronic contributions, we find that the internal energy of an ideal gas made of non-linear molecules is, in general:

$$\begin{aligned} U^{\text{non-linear}} &= U_{\text{trans}} + U_{\text{rot}} + U_{\text{vib}} + U_{\text{elec}} \\ &= \frac{3}{2}Nk_BT + \frac{3}{2}Nk_BT + \sum_{i=1}^{3m-6} Nk_B\Theta_V^i\left(\frac{1}{2} + \frac{1}{e^{\Theta_V^i/T}-1}\right) - ND_e \\ &= 3Nk_BT + \sum_{i=1}^{3m-6}\frac{Nk_B\Theta_V^i}{e^{\Theta_V^i/T}-1} + N\underbrace{\left(-D_e + \sum_{i=1}^{3m-6}\frac{k_B\Theta_V^i}{2}\right)}_{-D_0} \end{aligned} \tag{2.108}$$

where we have assumed (as it happens in most cases) that the temperature is much higher than the rotational temperature and that there are no low-energy excited electronic states. The term on the right corresponds to the zero of energy, equal to the atomization energy of the molecule in its electronic and vibrational ground-state ($-D_0$) (see Figure 2.6 for the distinction between D_e and D_0).

In linear molecules, the rotational (second) term in the expression needs to be replaced with Nk_BT, so the expression becomes:

$$\begin{aligned} U^{\text{linear}} &= \frac{3}{2}Nk_BT + Nk_BT + \sum_{i=1}^{3m-5} Nk_B\Theta_V^i\left(\frac{1}{2} + \frac{1}{e^{\Theta_V^i/T}-1}\right) - ND_e \\ &= \frac{5}{2}Nk_BT + \sum_{i=1}^{3m-5}\frac{Nk_B\Theta_V^i}{e^{\Theta_V^i/T}-1} + N\underbrace{\left(-D_e + \sum_{i=1}^{3m-6}\frac{k_B\Theta_V^i}{2}\right)}_{-D_0} \end{aligned} \tag{2.109}$$

These equations show that the internal energy of an ideal gas is completely determined by its temperature. This is a direct result from the fact that molecules do not interact with each other.

In the particular case that the ideal gas is composed of atoms instead of molecules, the rotational, vibrational, and electronic contributions are absent (assuming no low-energy electronic excited states). Therefore:

$$U^{\text{monoatomic}} = \frac{3}{2}Nk_BT \tag{2.110}$$

In a diatomic molecule, it is often the case that $T \ll \Theta_V$ and we have:

$$U^{\text{diatomic}} - U(0) = \frac{5}{2}Nk_BT \tag{2.111}$$

where we denote the zero-point energy with $U(0)$. In the rare cases where we have $T \gg \Theta_V$:

$$U^{\text{diatomic}} - U(0) = \frac{7}{2}Nk_BT \tag{2.112}$$

The internal energy in cases where T is comparable to Θ_V in a diatomic molecule lies between the two.

At very high temperatures the available thermal energy is much higher than the spacings between the levels and the fact that the energy levels are quantized loses importance (the classical limit). In this limit, it is appropriate to use the classical version of statistical mechanics, which uses the position and momenta of the particles in the systems and the classical Hamiltonian rather than quantum energy levels. If the temperature is higher than the vibrational temperature for any of the normal modes, then the vibrational term becomes $(3m-6)nRT$ and the internal energy (disregarding the zero-point energy) is $U=(3m-7/2)nRT$ for linear molecules and $U=(3m-3)nRT$ for non-linear molecules. The classical version of statistical mechanics is outside the scope of this course, but it is worth mentioning one relevant result that explains these high-temperature limits of U: the **equipartition theorem**.

The equipartition theorem states any term in the classical Hamiltonian (the total energy of the system written in terms of position and momenta of the particles) that is quadratic in the momentum or position of the particles contributes $k_BT/2$ to the internal energy per particle ($RT/2$ per mole). The translational energy is quadratic ($p^2/2m$) in each dimension, therefore the contribution is $\frac{3}{2}k_BT$. The rotational energy is the sum of three terms of the form $\frac{1}{2}I\omega^2$ where I is the moment of inertia and ω is the angular velocity. The rotational internal energy contribution is $\frac{3}{2}k_BT$. In a linear molecule, one of the moments of inertia is zero, so the rotational contribution is only k_BT. Finally, the total energy of a classical harmonic oscillator is the sum of kinetic and potential energy, and both are quadratic: $p^2/2m+\frac{1}{2}kx^2$. Therefore, the contribution is $2\times\frac{1}{2}k_BT=k_BT$ per normal mode. Note that the equipartition theorem only works in the classical (high temperature) limit, which in general is not valid for the vibrational term.

2.3.2 Heat Capacity

The constant-volume heat capacity is defined as the rate of change of the internal energy with temperature:

$$C_V=\left(\frac{\partial U}{\partial T}\right)_V \tag{2.113}$$

or, in other words, the amount of heat required to increase the temperature by a certain amount. The heat capacity measures the ability of the system to absorb energy when subjected to an increase in temperature. From Eq. 1.77, we know that the heat transferred to a system is related to the change in the probabilities of the different energy levels:

$$\delta q_{\text{rev}}=\sum_i E_i dp_i \tag{2.114}$$

so the heat capacity is larger the higher the number of accessible energy levels that the system can occupy when the temperature is raised.

Since the internal energy can be partitioned into contributions from each molecular degree of freedom, so can the heat capacity:

$$C_V=\left(\frac{\partial U}{\partial T}\right)_V=\frac{\partial(U_{\text{trans}}+U_{\text{rot}}+U_{\text{vib}}+U_{\text{elec}})}{\partial T}=C_V^{\text{trans}}+C_V^{\text{rot}}+C_V^{\text{vib}}+C_V^{\text{elec}} \tag{2.115}$$

where each term is the temperature derivative of the corresponding term in the internal energy.

We have seen (Eq. 2.108) that the internal energy contributions from each molecular degree of

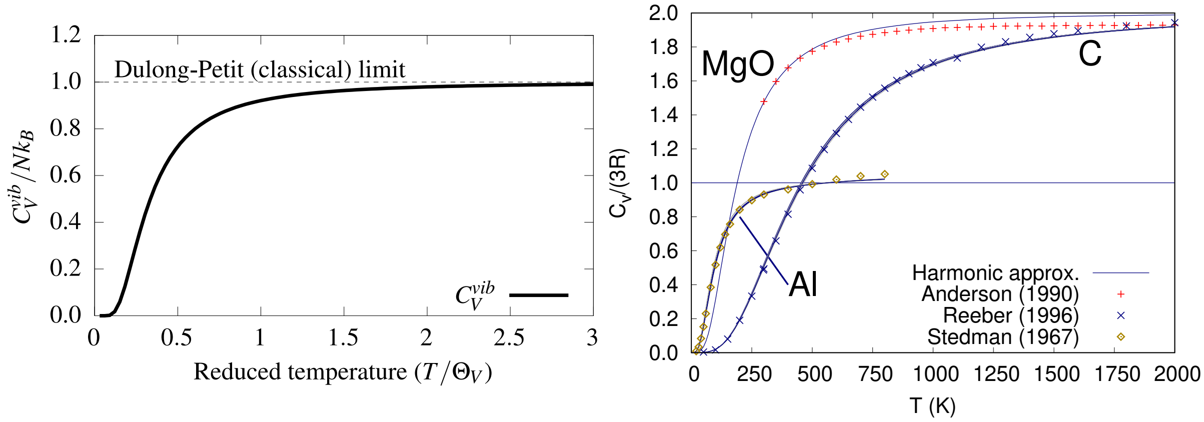


Figure 2.4: Left: typical C_V versus temperature curve in a system of non-interacting particles. Right: the points represent experimental observations of C_V as a function of temperature in three solids: MgO, diamond, and aluminium. (Modified, with permission, from Phys. Rev. B **84** (2011) 184103.)

freedom are:

$$U_{\text{trans}} = \frac{3}{2}Nk_BT \tag{2.116}$$

$$U_{\text{rot}} = \frac{3}{2}Nk_BT \text{ (or } Nk_BT \text{ if the molecule is linear)} \tag{2.117}$$

$$U_{\text{vib}} = \sum_i^{3m-6} Nk_B\Theta_V^i\left(\frac{1}{2}+\frac{1}{e^{\Theta_V^i/T}-1}\right) \tag{2.118}$$

$$U_{\text{elec}} = -ND_e \tag{2.119}$$

and the total internal energy is the sum of them. Taking derivatives, the translational and rotational contributions to the heat capacity are:

$$C_V^{\text{trans}} = \frac{3}{2}Nk_B = \frac{3}{2}nR \tag{2.120}$$

$$C_V^{\text{rot}} = \frac{3}{2}Nk_B = \frac{3}{2}nR \text{ (or } Nk_B = nR \text{ if the molecule is linear)} \tag{2.121}$$

$$C_V^{\text{elec}} = 0 \tag{2.122}$$

The translational and rotational contributions to C_V are simply a constant times R per mole of particles. As in the previous section, the rotational contribution assumes that we are in the high-temperature limit, where $T \gg \Theta_R$. If not, then the contribution is lower than $\frac{3}{2}Nk_B$, since the gap between rotational energy levels is significant compared to the thermal energy and an increase in temperature does not necessarily lead to the excited states being populated. As before, this only happens for a few small molecules and at very low temperature. Note that the electronic contribution is zero because there are no available energy levels to occupy (or, rather, they are too high in energy) so an increase in temperature does not change the population of the electronic energy levels.

The vibrational contribution to the heat capacity is slightly more complicated. The vibrational internal energy is the sum of the contributions from each normal mode and therefore so is the heat capacity.

$$C_V^{\text{vib}} = \frac{\partial U_{\text{vib}}}{\partial T} = \sum_{i=1}^{3m-6} C_V^{\text{vib},i} \tag{2.123}$$

Each of the normal mode contributions to C_V is obtained by taking the temperature derivative from the corresponding term in U:

$$C_V^{\text{vib},i} = \frac{\partial U_{\text{vib}}^i}{\partial T} = -\frac{Nk_B\Theta_V \times e^{\Theta_V/T} \times \left(-\frac{\Theta_V}{T^2}\right)}{\left(e^{\Theta_V/T}-1\right)^2} = Nk_B\left(\frac{\Theta_V}{T}\right)^2 \frac{e^{\Theta_V/T}}{(e^{\Theta_V/T}-1)^2} \tag{2.124}$$

Note that the zero-point energy term, just like the electronic contribution to the heat capacity, vanishes when taking the derivative. In the limit of low temperature ($T \to 0$), the squared exponential in the denominator dominates and $C_V \to 0$. In the high-temperature limit, the exponents are very small and we can expand $e^x = 1 + x + ...$, which gives:

$$C_V^{\text{vib},i} = Nk_B\left(\frac{\Theta_V}{T}\right)^2 \frac{e^{\Theta_V/T}}{(\Theta_V/T)^2} = Nk_B e^{\Theta_V/T} \approx Nk_B = nR \tag{2.125}$$

so the molar constant-volume heat capacity ($c_v = C_V/n$) is equal to R per normal mode. Note that this is exactly the temperature derivative of the high-temperature vibrational energy expression (Eq. 2.104). A typical profile for the vibrational contribution to C_V from a single normal mode is shown in Figure 2.4 (left).

The heat capacity given by Eq. 2.124 is useful for systems other than ideal gases, and it is of historical importance. One of the simplest models for the vibrations in a solid is the **Einstein model**. In the Einstein model, it is assumed that each atom in a solid vibrates in three dimensions around its equilibrium position with an associated vibrational temperature equal to θ_E (the Einstein temperature). In this model, a crystal is viewed as $3N$ harmonic oscillators where N is the number of atoms in the crystal and the 3 comes from the three dimensions for the oscillation. The $3N$ harmonic oscillators are independent and therefore the same equations we have derived can be used to describe them. In particular, the heat capacity of a solid given by the Einstein model is:

$$C_V^{\text{vib}} = 3Nk_B\left(\frac{\theta_E}{T}\right)^2 \frac{e^{\theta_E/T}}{(e^{\theta_E/T}-1)^2} = 3nR\left(\frac{\theta_E}{T}\right)^2 \frac{e^{\theta_E/T}}{(e^{\theta_E/T}-1)^2} \tag{2.126}$$

which is essentially the same as Eq. 2.124 but multiplied by a factor of 3 and with $\Theta_V = \theta_E$.

The Einstein model was the first successful model that explained the low-temperature behavior of $C_V(T)$ in solids. Before the Einstein model, statistical thermodynamic calculations using classical mechanics predicted that the C_V in a solid is a constant equal to $3Nk_B = 3nR$, with N is the number of atoms in the crystal. This result, called the **Dulong-Petit limit** is correct at high temperature (as shown in Figure 2.4) but it is completely wrong at low temperature. Einstein proposed this model in 1907, long before quantum theory was developed, and it demonstrated that, by assuming a quantization of the vibrational energy levels, the correct behavior of $C_V(T)$ is recovered. This is similar to how the Bohr atomic model was proposed in order to explain the discrete nature of the atomic absorption and emission spectra, and it ultimately paved the way for the development of quantum mechanics.

The Einstein model is not used very much today because it still gives somewhat incorrect results at low temperature due to the assumptions that there is only one vibrational temperature and that the harmonic oscillators are independent. However, similar models based on it, such as the Debye model, are in fact used. Figure 2.4 (right) shows the $C_V(T)$ for three simple solids: magnesium oxide, diamond, and elemental aluminium. It can be seen that the $C_V(T)$ curve calculated using a model similar to Einstein's is in excellent agreement with experimental data for three simple solids and that the Dulong-Petit limit is mostly correct at high temperature.

Going back to ideal gases, in the particular case of a monoatomic gas, the rotational and vibrational contributions to C_V are absent, so (compare to Eq. 2.110):

$$C_V^{\text{monoatomic}} = \frac{3}{2}Nk_B = \frac{3}{2}nR \tag{2.127}$$

In a diatomic gas, when $T \ll \Theta_V$, the contribution from the vibrational heat capacity vanishes and we have (c.f. Eq. 2.111):

$$C_V^{\text{diatomic}} = \frac{5}{2}Nk_B = \frac{5}{2}nR \tag{2.128}$$

and when $T \gg \Theta_V$ (c.f. Eq. 2.112),

$$C_V^{\text{diatomic}} = \frac{7}{2}Nk_B = \frac{7}{2}nR \tag{2.129}$$

with intermediate temperatures having C_V between these two limits.

2.3.3 Entropy

We have seen previously that the entropy is (Eq. 1.84):

$$S = \frac{U}{T} + k_B \ln Q \tag{2.130}$$

In a system of non-interacting particles, such as an ideal gas, we have: (Eq. 2.10):

$$Q = \frac{q^N}{N!} \tag{2.131}$$

and the entropy is:

$$\begin{aligned} S &= \frac{U}{T} + k_B(N \ln q - \ln N!) = \frac{U}{T} + Nk_B \ln q - k_B(N \ln N - N) \\ &= \frac{U}{T} + Nk_B \ln q - Nk_B \ln N + Nk_B \end{aligned} \tag{2.132}$$

where we have applied Stirling's approximation to $\ln N!$. By noting that $\ln e = 1$, we can combine the last three terms in a more convenient form:

$$S = \frac{U}{T} + Nk_B \ln\frac{q}{N} + Nk_B = \frac{U}{T} + Nk_B \ln\frac{qe}{N} \tag{2.133}$$

Contrary to what happens with the internal energy and the heat capacity, the entropy is not directly separable into contributions because of the terms coming from the $\ln N!$. These extra terms in the entropy come from the $N!$ denominator in the partition function (i.e. from the indistinguishability of particles) and are usually bundled in the translational component:

$$S = \frac{U}{T} + Nk_B \ln\frac{qe}{N} = S_{\text{trans}} + S_{\text{rot}} + S_{\text{vib}} + S_{\text{elec}} \tag{2.134}$$

where:

$$S_{\text{x}} = \frac{U_{\text{x}}}{T} + Nk_B \ln q_{\text{x}} \tag{2.135}$$

with "x" being the rotational, vibrational, and electronic contributions. The vibrational entropy can be split into contributions from normal modes, and expressions can be worked out for these quantities but we will forego the derivation. If necessary, they can be consulted in a statistical thermodynamics textbook. For the translational component, we have the extra e and N in the logarithm:

$$S_{\text{trans}} = \frac{U_{\text{trans}}}{T} + Nk_B \ln\frac{q_{\text{trans}}e}{N} \tag{2.136}$$

Substituting the translational internal energy (Eq. 2.91, $U = \frac{3}{2}Nk_BT$) and partition function (Eq. 2.45, $q_{\text{trans}} = \frac{V}{\Lambda^3}$), we find:

$$S_{\text{trans}} = \frac{3}{2}Nk_B + Nk_B \ln\frac{Ve}{N\Lambda^3} = Nk_B \ln\left(\frac{Ve^{5/2}}{N\Lambda^3}\right) = nR\ln\left(\frac{Ve^{5/2}}{N\Lambda^3}\right) \tag{2.137}$$

where Λ is the thermal wavelength defined in Eq. 2.44. This is the **Sackur–Tetrode** equation, developed independently by O. Sackur and H. M. Tetrode in 1912. It gives the entropy of a monoatomic ideal gas, since a single atom has no vibrational or rotational degrees of freedom, and the electronic contribution is usually zero if no low-energy excited states are available.

Question: Calculate the change in entropy for the isothermal expansion and isochoric heating of a monoatomic ideal gas.

Under isothermal expansion from (V_1, T) to (V_2, T), the change in entropy is:

$$\Delta S = nR\ln\left(\frac{V_2 e^{5/2}}{N\Lambda^3}\right) - nR\ln\left(\frac{V_1 e^{5/2}}{N\Lambda^3}\right) = nR\ln\left(\frac{V_2}{V_1}\right)$$

which matches the result obtained using classical thermodynamics (though note that can calculate the value of the entropies as well, not just the differences). Likewise, the isochoric heating from (V, T_1) to (V, T_2) gives:

$$\begin{aligned}\Delta S &= nR\ln\left(\frac{Ve^{5/2}}{N\Lambda_2^3}\right) - nR\ln\left(\frac{Ve^{5/2}}{N\Lambda_1^3}\right) = nR\ln\left(\frac{\Lambda_1^3}{\Lambda_2^3}\right) = \frac{3}{2}nR\ln\left(\frac{T_2}{T_1}\right)\\ &= nC_{V,m}\ln\left(\frac{T_2}{T_1}\right)\end{aligned}$$

where $C_{V,m} = C_V/n$ is the molar heat capacity, equal to $3/2R$ in the case of a monoatomic gas.

2.3.4 Equation of State of the Ideal Gas

Let us derive now the equation of state of an ideal gas. The pressure as a function of volume and temperature is:

$$p = -\left(\frac{\partial A}{\partial V}\right)_T = k_BT\left(\frac{\partial \ln Q}{\partial V}\right) \tag{2.138}$$

The canonical partition function is:

$$Q = \frac{q^N}{N!} = \frac{(q_{\text{trans}} \times q_{\text{rot}} \times q_{\text{vib}} \times q_{\text{elec}})^N}{N!} \tag{2.139}$$

Of all the factors in the molecular partition function only the translational contribution depends on the volume:

$$q_{\text{trans}} = \frac{V}{\Lambda^3} \tag{2.140}$$

The logarithm of the canonical partition function is:

$$\ln Q = N\ln q - \ln N! = N\ln q_{\text{trans}} + N\ln(q_{\text{rot}} \times q_{\text{vib}} \times q_{\text{elec}}) - \ln N! \tag{2.141}$$

where we separated out the only term that depends on volume. Substituting in the pressure:

$$p = k_BT\frac{\partial \ln Q}{\partial V} = Nk_BT\frac{\partial \ln q_{\text{trans}}}{\partial V} = \frac{Nk_BT}{q_{\text{trans}}}\frac{\partial q_{\text{trans}}}{\partial V} = Nk_BT\frac{\Lambda^3}{V}\frac{1}{\Lambda^3} = \frac{Nk_BT}{V} \tag{2.142}$$

Using $Nk_B = nR$, we have:

$$pV = nRT \tag{2.143}$$

which is the equation of state of the ideal gas. Note that this result has been derived only from the postulates of statistical mechanics and the assumption of non-interacting particles, and it is a proof of the relationship between the molar gas constant (R) and Boltzmann constant (k_B).

2.3.5 Chemical Equilibrium

We consider a reversible chemical reaction between ideal gases:

$$0 \longrightarrow \sum_i \nu_i \mathrm{A}_i \tag{2.144}$$

where ν_i are the stoichiometric coefficients (positive for products and negative for reactants). For example, this reaction:

$$\mathrm{aA} + \mathrm{bB} \longrightarrow \mathrm{cC} + \mathrm{dD} \tag{2.145}$$

has stoichiometric coefficients $\nu_1 = -a$, $\nu_2 = -b$, $\nu_3 = c$, and $\nu_4 = d$. Writing the reaction in this manner allows expressing reaction energies easily. For instance, the standard Gibbs free energy of the reaction is written in terms of the corresponding free energies as:

$$\Delta_r G^\circ(T) = \sum_i \nu_i G^\circ_{m,i}(T) = \sum_i \nu_i \Delta_f G^\circ_i(T) \tag{2.146}$$

where the sum runs over species in the reaction vessel (reactants and products), $G^\circ_{m,i}(T)$ is the standard molar Gibbs free energy for pure component i, and $\Delta_f G^\circ_i(T)$ is the standard Gibbs free energy of formation.

In a closed system with rigid walls (fixed V and T), we have:

$$dA = -SdT - pdV + \sum_i \mu_i dN_i \tag{2.147}$$

where the sum runs over all species in the mixture, N_i is the number of molecules of component i, and μ_i is the chemical potential:

$$\mu_i = \left(\frac{\partial A}{\partial N}\right)_{V,T} \tag{2.148}$$

When the chemical reaction occurs, the number of molecules of each species changes as:

$$N_i = N_i^0 + \nu_i \lambda \tag{2.149}$$

where N_i^0 is the initial number of molecules and λ is the extent of the reaction. Therefore:

$$dN_i = \nu_i d\lambda \tag{2.150}$$

and substituting in Eq. 2.147, we find:

$$dA = -SdT - pdV + \left(\sum_i \nu_i \mu_i\right) d\lambda \tag{2.151}$$

For a reaction at constant T and V, chemical equilibrium is reached when $dA = 0$, i.e.:

$$\sum_i \nu_i \mu_i = 0 \tag{2.152}$$

which is the condition for chemical equilibrium in classical thermodynamics.

The reaction occurs between ideal gases so, because the species are distinguishable from each other and non-interacting, the canonical partition function of the mixture can be written as the product of the partition functions for each individual species:

$$Q(\{N_i\}, V, T) = \prod_i Q_i(N_i, V, T) = \prod_i \frac{q_i(V,T)^{N_i}}{N_i!} \tag{2.153}$$

This is because, being an ideal gas mixture, the energy of the system can be written as a sum of the energies of each component, and the component molecules are distinguishable from each other (compare this with the derivation leading up to the partition function for distinguishable, non-interacting particles, Eq. 2.5). The logarithm of the partition function is:

$$\ln Q = \sum_i N_i \ln q_i(V,T) - \ln N_i! = \sum_i N_i \ln q_i(V,T) - (N_i \ln N_i - N_i) \tag{2.154}$$

where we applied the Stirling's approximation to each N_i term. The chemical potential of species i is (Eq. 1.114):

$$\begin{aligned}\mu_k = -k_B T \left(\frac{\partial \ln Q}{\partial N_k}\right)_{V,T,N_{j\neq k}} &= -k_B T \left[\ln q_k(V,T) - \left(\ln N_k + \cancel{N_k \frac{1}{N_k}} - \cancel{1}\right)\right] \\ &= -k_B T \ln\left(\frac{q_k}{N_k}\right) \end{aligned} \tag{2.155}$$

Substituting in the chemical equilibrium condition (Eq. 2.152), we find:

$$0 = \sum_k \nu_k \mu_k = -k_B T \sum_k \nu_k \ln\left(\frac{q_k}{N_k}\right) = -k_B T \ln\left[\prod_k \left(\frac{q_k}{N_k}\right)^{\nu_k}\right] \tag{2.156}$$

The $k_B T$ term cancels with the zero in the left hand side of the equation, and the argument of the logarithm must be equal to one:

$$\prod_k \left(\frac{q_k}{N_k}\right)^{\nu_k} = \frac{\prod_k q_k^{\nu_k}}{\prod_k N_k^{\nu_k}} = 1 \tag{2.157}$$

Rearranging:

$$\prod_k q_k^{\nu_k} = \prod_k N_k^{\nu_k} \tag{2.158}$$

This is the equilibrium condition in terms of partition functions. At chemical equilibrium, the product of the number of particles on the right hand side of this equation equals the product of the partition functions on the left hand side. The left-hand side of this equation does not depend on the number of particles. Note that this expression is similar to the familiar law of mass action. For instance, for the reaction:

$$2\,\mathrm{H}_{2(\mathrm{g})} + \mathrm{O}_{2(\mathrm{g})} \rightleftharpoons 2\,\mathrm{H_2O}_{(\mathrm{g})} \tag{2.159}$$

the equilibrium condition, assuming ideal gas behavior, is:

$$\frac{q_{\mathrm{H_2O}}^2}{q_{\mathrm{H_2}}^2 q_{\mathrm{O_2}}} = \frac{N_{\mathrm{H_2O}}^2}{N_{\mathrm{H_2}}^2 N_{\mathrm{O_2}}} \tag{2.160}$$

which looks very much like the equilibrium constant expression in classical thermodynamics.

It is also important to note that the equilibrum expression (Eq. 2.158) is equivalent to Boltzmann's distribution law between the states corresponding to the different species in the reaction. Consider a simple reaction:

$$\mathrm{A} \rightleftharpoons \mathrm{B} \tag{2.161}$$

The equilibrium condition is:

$$\frac{N_B}{N_A} = \frac{q_B}{q_A} \tag{2.162}$$

to be compared to Boltzmann's law (Eq. 2.26). A molecule in this system can exist as either A or B, and the two can interconvert. We represent the energies available to one of these molecules (referred to a common energy zero) in Figure 2.5. The probability that a molecule is A is proportional to the sum of the individual probabilities of all states belonging to molecule A (left column in Figure 2.5):

$$\sum_i^{\text{A states}} e^{-\beta\epsilon_i^A} = q_A \tag{2.163}$$

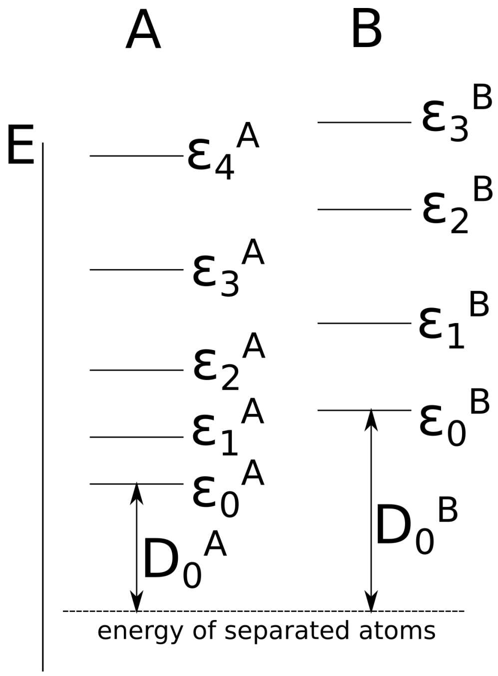


Figure 2.5: States available to a molecule that can interconvert between two species A and B. Provided the energies of each level are referred to a common energy zero (in this case, the separated atoms), the probability that the molecule is A or B is given by the Boltzmann distribution law.

which is just the partition function of A. Likewise, the probability that a molecule is B is:

$$\sum_{i}^{\text{B states}} e^{-\beta\epsilon_i^B} = q_B \tag{2.164}$$

The equilibrium condition in Eq. 2.158 is just a balance of probabilities between the energy levels on both sides of a chemical reaction, as given by the Boltzmann distribution law (Eq. 2.24).

We can divide both sides of Eq. 2.158 by the appropriate number of N_AV terms to give:

$$\prod_k \left(\frac{N_k}{N_AV}\right)^{\nu_k} = \prod_k \left(\frac{q_k}{N_AV}\right)^{\nu_k} \tag{2.165}$$

Using that the number of moles is $n_k = N_k/N_A$, and that the molar concentration is $c_k = n_k/V$, Eq. 2.165 is the expression for the **equilibrium constant in terms of concentration** (K_c) in terms of the molecular partition functions:

$$K_c(T) = \prod_k \left(\frac{n_k}{V}\right)^{\nu_k} = \prod_k c_k^{\nu_k} = \prod_k \left(\frac{q_k}{N_AV}\right)^{\nu_k} \tag{2.166}$$

The product of concentrations at equilibrium given by the law of mass action (left hand side of this equation) equals the product of molecular partition functions on the right hand side. For example, for the reaction in Eq. 2.145, we would have:

$$K_c(T) = \frac{c_C^{\nu_C} c_D^{\nu_D}}{c_A^{\nu_A} c_B^{\nu_B}} = \frac{\left(\frac{q_C}{N_AV}\right)^{\nu_C} \left(\frac{q_D}{N_AV}\right)^{\nu_D}}{\left(\frac{q_A}{N_AV}\right)^{\nu_A} \left(\frac{q_B}{N_AV}\right)^{\nu_B}} \tag{2.167}$$

The right hand side of this equation is a product of molecular partition functions and, therefore, can be calculated from microscopic information about the molecules. This expression is only valid for a system of non-interacting particles, i.e. in a reaction between ideal gases.

Note that K_c in Eq. 2.166 depends on temperature only. This is because the only term in the molecular partition functions $q_k(V,T)$ that depends on volume is q_k^{trans}:

$$q_k(V,T) = q_k^{\mathrm{trans}}(V,T)q_k^{\mathrm{rot}}(T)q_k^{\mathrm{vib}}(T)q_k^{\mathrm{elec}}(T) \tag{2.168}$$

and the translational component is (Eq. 2.45):

$$q_{\mathrm{trans}}(V,T) = \frac{V}{\Lambda^3} \tag{2.169}$$

where Λ depends only on temperature (Eq. 2.44). Therefore, the q_k/V factors that appear in Eq. 2.166 are a function of temperature only and, consequently, so is K_c. Using the equation of state of the ideal gas, it is easy to rewrite the **equilibrium constant in terms of pressure**:

$$K_p(T) = \prod_k p_k^{\nu_k} = (RT)^{\Delta\nu} \prod_k \left(\frac{q_k}{N_A V}\right)^{\nu_k} \tag{2.170}$$

where $\Delta\nu = \sum_k \nu_k$. We can also calculate the **adimensional equilibrium constant in terms of pressure** by inserting the standard pressure ($p^\circ = 1\,\mathrm{bar}$) on both sides of the last equation:

$$K_p^\circ(T) = \prod_k \left(\frac{p_k^{\nu_k}}{p^\circ}\right)^{\nu_k} = \left(\frac{RT}{p^\circ}\right)^{\Delta\nu} \prod_k \left(\frac{q_k}{N_A V}\right)^{\nu_k} = \prod_k \left(\frac{k_B T}{p^\circ} \times \frac{q_k}{V}\right)^{\nu_k} \tag{2.171}$$

And the adimensional $K_p^\circ(T)$ is related to the standard chemical potential and the standard reaction Gibbs free energy:

$$\ln K_p^\circ(T) = \sum_k \nu_k \ln\left(\frac{k_B T}{p^\circ} \times \frac{q_k}{V}\right) = -\sum_k \frac{\nu_k \mu_k^\circ}{k_B T} = -\frac{\Delta_r G^\circ(T)}{RT} \tag{2.172}$$

In this last equation, the standard chemical potential is the chemical potential (Eq. 2.155):

$$\mu_k = -k_B T \ln\left(\frac{q_k}{N_k}\right) = -k_B T \ln\left(\frac{q_k}{V}\frac{V}{N_k}\right) = -k_B T \ln\left(\frac{q_k}{V}\frac{k_B T}{p_k}\right) \tag{2.173}$$

evaluated at $p_k = p^\circ = 1\,\mathrm{bar}$. Note that q_k/V is a function of temperature only, so the standard chemical potential:

$$\mu_k^\circ(T) = -k_B T \ln\left(\frac{q_k}{V}\frac{k_B T}{p^\circ}\right) \tag{2.174}$$

is a function of temperature only. The standard chemical potential of many substances is tabulated in thermodynamic databases like the NIST-JANAF thermochemical tables (`https://janaf.nist.gov/`). (Note, however, that they typically use a different zero of energy than ours.)

2.3.6 An Alternative Form of the Equilibrium Constant

We now derive a version of the adimensional equilibrium constant (Eq. 2.171) that is easier to use by shifting the energy zeros of all molecules. The molecular partition function for any of the molecules in the system is:

$$q = q_{\mathrm{trans}} \times q_{\mathrm{rot}} \times q_{\mathrm{vib}} \times q_{\mathrm{elec}} \tag{2.175}$$

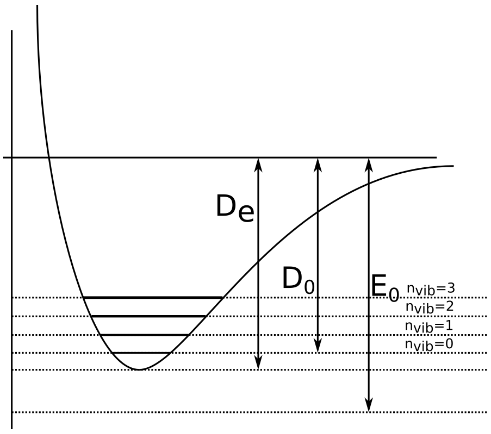


Figure 2.6: The dissociation energy of a diatomic molecule from the electronic ground state (D_e) from the vibrational ground state (D_0) and from some arbitrary reference energy (E_0). The first four vibrational energy levels are also shown.

and the vibrational and electronic contributions contain a factor that originates from the fact that the corresponding ground-state energies are not zero. For the vibrational partition function (Eq. 2.75):

$$q_{\text{vib}} = \prod_{k=1}^{3m-6} \left(\frac{e^{-hc\tilde{\nu}_k/2k_BT}}{1-e^{-hc\tilde{\nu}_k/k_BT}} \right) \tag{2.176}$$

we factor out the term coming from the zero-point energy and write the partition function as a product of a zero-point contribution and a vibrational partition function where the ground-state has zero energy (q^0_{vib}):

$$q_{\text{vib}} = \underbrace{\left[\prod_{k=1}^{3m-6} \left(\frac{1}{1-e^{-hc\tilde{\nu}_k/k_BT}} \right) \right]}_{q^0_{\text{vib}}} \times \underbrace{\left[\prod_{k=1}^{3m-6} e^{-hc\tilde{\nu}_k/2k_BT} \right]}_{\text{zero-point}} \tag{2.177}$$

For the electronic contribution, we can follow a similar procedure (Eq. 2.80):

$$q_{\text{elec}} = g_0 e^{D_e/k_BT} + \ldots = \underbrace{(g_0 + \ldots)}_{q^0_{\text{elec}}} \times \underbrace{e^{D_e/k_BT}}_{\text{zero-point}} \tag{2.178}$$

In the electronic case, the exponential term comes from our choice of zero point electronic energy as the separated neutral atoms. (Note that q_{trans} also has non-zero ground-state energy but the energy of the translational ground state is so small that it can be considered negligible.)

With these expressions, we can rewrite the molecular partition function as a product of a factor that has zero energy for the ground state of every molecular mode of motion (q^0) and an exponential factor containing our choice of energy reference:

$$\begin{aligned} q = q_{\text{trans}} q_{\text{rot}} q_{\text{vib}} q_{\text{elec}} &= \underbrace{q_{\text{trans}} q_{\text{rot}} q^0_{\text{vib}} q^0_{\text{elec}}}_{q^0} \times e^{D_e/k_BT} \times \prod_{k=1}^{3m-6} e^{-hc\tilde{\nu}_k/2k_BT} \\ &= q^0 \times e^{(D_e - 1/2\sum_k hc\tilde{\nu}_k)/k_BT} = q^0 \times e^{D_0/k_BT} \end{aligned} \tag{2.179}$$

where $D_0 = D_e - \frac{1}{2}\sum_k hc\tilde{\nu}_k$ is the atomization energy from the vibrational ground state, that is, the energy spent in going from the molecule in its electronic plus vibrational ground state to the separated neutral atoms (the difference between D_0 and D_e in a diatomic molecule is shown in Figure 2.6). This expression has this form because we chose $-D_0$ as the energy at the molecular ground state throughout this chapter.

Substituting Eq. 2.179 in the adimensional equilibrium constant in terms of pressure ($K_p^\circ(T)$, Eq. 2.171):

$$K_p^\circ(T) = \prod_k \left(\frac{k_B T}{p^\circ} \times \frac{q_k^0 \times e^{D_0^k/k_B T}}{V} \right)^{\nu_k} \tag{2.180}$$

where D_0^k is the atomization energy of species k. The volume of a mole of gas at standard pressure (p°) and temperature T is:

$$V^\circ = \frac{N_A k_B T}{p^\circ} \tag{2.181}$$

and, because the volume is a simple multiplicative factor in the translation partition function, the molecular partition function of species k evaluated at V^0 is:

$$q_k^0(V^\circ, T) = \frac{q_k^0(V,T)}{V} \times V^\circ = \frac{q_k^0(V,T)}{V} \times \frac{N_A k_B T}{p^\circ} \tag{2.182}$$

so we can rewrite Eq. 2.180 as:

$$K_p^\circ(T) = \prod_k \left(\frac{q_k^0(V^\circ, T)}{N_A} \times e^{D_0^k/k_B T} \right)^{\nu_k} = e^{-\Delta\epsilon_0/k_B T} \prod_k \left(\frac{q_k^0(V^\circ, T)}{N_A} \right)^{\nu_k} \tag{2.183}$$

where $\Delta\epsilon_0 = -\Delta D_0 = -\sum \nu_k D_0^k$ is the difference in atomization energy between the ground states of reactants and products (which also equals the energy difference between their ground states referred to any other arbitrary energy footing). The $q_k^0(V^\circ, T)$ is the molecular partition function of species k at the volume V° and temperature T calculated using zero as its ground state energy. This equation is much easier to use in practice when computing equilibrium constants for gas-phase reactions from quantum mechanical calculations or from spectroscopic data.

Chapter 3

Kinetic Theory of Gases

3.1 Assumptions in the Kinetic Theory of Gases

The **kinetic theory of gases** (also known as **kinetic-molecular theory**) is a theoretical model for the behavior of a perfect gas derived from the microscopic properties of its constituent particles, similar in spirit to statistical mechanics. The kinetic theory of gases assumes that the internal energy of a gas originates from the translational kinetic energy of its molecules and considers the molecules as structureless entities with no rotational, vibrational, or electronic degrees of freedom. We have seen in the previous chapters that the translational energy levels are so close to each other that translation can be treated classically. From a very small set of reasonable assumptions and a classical mechanics treatment, the equation of state of an ideal gas as well as important quantitative results regarding the distribution of molecular velocities, gas effusion, and collisions in a gas can be derived.

There are three basic assumptions in the kinetic theory of gases:

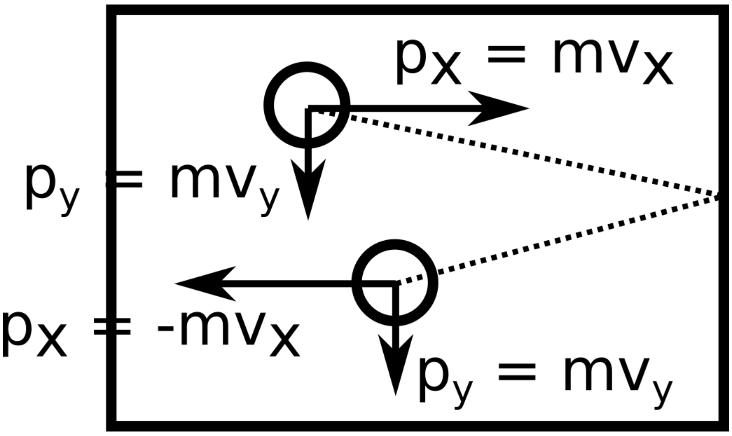
1. The gas consists of molecules of mass m moving randomly and obeying the laws of classical mechanics.
2. The molecules interact only via brief elastic collisions with each other and with the walls of the container.
3. The size of the molecules is negligible compared to the average distance traveled between collisions.

An **elastic collision** is one in which the total kinetic energy of the particles is the same before and after the collision. Although several potentials for the interaction between any two molecules can be used, we will focus on the simplest model possible, in which we treat the molecules as hard spheres. Under these assumptions, a molecular collision resembles a collision between two billiard balls, with no intermolecular interaction other than at the moment of contact.

3.2 The Pressure of an Ideal Gas

The collisions of particles with the walls of the container are responsible for pressure in a gas. Figure 3.1 shows a particle of mass m with velocity along the x coordinate equal to v_x collide elastically with the wall of the container. Since the collision is elastic, there is no loss of energy and the momentum of the particle before and after the collision is the same, with the sign of v_x reversed, and the sign of v_y unchanged. The total change in the x-component of momentum during the collision is $\Delta p_x = 2mv_x$.

Figure 3.1: Change in momentum of a molecule colliding elastically with the wall of the container.



Let us assume for now that we consider only molecules with velocity v_x along the x axis. A molecule with velocity v_x can travel $v_x\Delta t$ during the interval Δt, so all molecules within a distance $v_x\Delta t$ of the wall will strike it in that time interval, provided they are moving towards the wall. If the wall has area A, then all particles in the volume $A \times v_x\Delta t$ reach the wall if they are traveling towards it. The gas has a constant particle density (number of particles per volume) equal to nN_A/V, where n is the number of moles of gas, V is the volume of the container, and N_A is Avogadro's number. The number of particles that strike the wall in an interval Δt is therefore equal to:

$$\frac{1}{2}\left(\frac{nN_A}{V}\right) \times Av_x\Delta t \tag{3.1}$$

where we have added the 1/2 factor to account for the fact that at any point in time about half of the molecules are traveling towards the wall and half away from it. The total momentum change during the interval Δt is equal to the number of particles that strike the wall (Eq. 3.1) times the change in momentum for a single molecule ($2mv_x$):

$$\Delta P_x = \frac{nN_A Av_x\Delta t}{2V} \times 2mv_x = \frac{nMAv_x^2\Delta t}{V} \tag{3.2}$$

where we have used that the molar mass is $M = mN_A$.

The force exerted on the wall during interval Δt is equal to the rate of change of momentum, which for infinitesimal Δt is equal to the total change in momentum divided by Δt:

$$F_x = \frac{dP_x}{dt} \approx \frac{\Delta P_x}{\Delta t} = \frac{nMAv_x^2}{V} \tag{3.3}$$

and the pressure exerted on the wall is equal to the force divided by the area of the wall:

$$p = \frac{F}{A} = \frac{nMv_x^2}{V} \tag{3.4}$$

Molecules can travel with any velocity, not just v_x so the total pressure is calculated as an expectation value involving the probability density of finding a molecule with velocity v_x:

$$p = \int_0^\infty f(v_x)\frac{nMv_x^2}{V}dv_x = \frac{nM\langle v_x^2\rangle}{V} \tag{3.5}$$

where $\langle v_x^2\rangle$ is the expectation value of v_x^2 calculated using the as-yet unknown probability distribution of molecular velocities ($f(v_x)$). Finally, we note that there is nothing special about the x direction, so the three averages $\langle v_x^2 \rangle$, $\langle v_y^2 \rangle$, and $\langle v_z^2 \rangle$ must be equal. We define the root-mean-square (rms) of the molecular velocities as:

$$v_{\text{rms}}^2 = \langle v^2 \rangle = \langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle = 3\langle v_x^2 \rangle \tag{3.6}$$

where we have used that $\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle$ because the three directions are equivalent. With this, we arrive at:

$$\langle v_x^2 \rangle = \frac{1}{3} v_{\text{rms}}^2 \tag{3.7}$$

and, finally, the expression for the pressure is:

$$p = \frac{nMv_{\text{rms}}^2}{3V} \tag{3.8}$$

which is the pressure of an ideal gas given by the kinetic theory of gases. We will see later that v_{rms} depends on temperature only, so this equation already predicts Boyle's law ($pV = \text{constant}$ at constant temperature). We now try to calculate v_{rms}^2 by finding an expression for the probability distribution of molecular speeds.

3.3 The Maxwell-Boltzmann Distribution of Molecular Speeds

The translational energy associated with a particle moving with velocity $\boldsymbol{v}$ is:

$$\epsilon = \frac{1}{2}mv^2 = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2 \tag{3.9}$$

In the statistical thermodynamics chapter we showed that for a closed system with rigid walls in thermodynamic equilibrium, the probability that a molecule is in a state with energy ϵ is proportional to $e^{-\epsilon/k_B T}$. Therefore, the probability density associated with the molecule having velocity $\boldsymbol{v}$ is:

$$f(\boldsymbol{v}) = Ke^{-m(v_x^2+v_y^2+v_z^2)/2k_BT} = Ke^{-mv_x^2/2k_BT}e^{-mv_y^2/2k_BT}e^{-mv_z^2/2k_BT} \tag{3.10}$$

where K is some normalization constant. The movement of the particles in the three directions is assumed to be independent of each other, so the total probability density must factorize into a product of three densities, all with the same expression, and corresponding to each of the three dimensions:

$$f(\boldsymbol{v}) = f(v_x)f(v_y)f(v_z) \tag{3.11}$$

From the expression above, we define normalization constants for each dimension, and we have that:

$$K = K_x \times K_y \times K_z \tag{3.12}$$

with:

$$f(v_x) = K_x e^{-mv_x^2/2k_BT} \tag{3.13}$$

We now determine the normalization constant $K_x = K_y = K_z$ for the one-dimensional probability densities by integrating over the whole range of velocities:

$$\int_{-\infty}^{\infty} f(v_x)dv_x = 1 \tag{3.14}$$

Substitution of the expression for $f(v_x)$ gives:

$$1 = \int_{-\infty}^{\infty} f(v_x)dv_x = K_x \int_{-\infty}^{\infty} e^{-mv_x^2/2k_BT}dv_x = 2K_x \int_{0}^{\infty} e^{-mv_x^2/2k_BT}dv_x \tag{3.15}$$

where we have used that the integrand is an even function around $v_x = 0$. The last integral is solved using a change of variable:

$$u = \frac{mv_x^2}{2k_BT} \quad ; \quad v_x = \sqrt{\frac{2k_BTu}{m}} \quad ; \quad du = \frac{mv_x}{k_BT}dv_x$$
$$dv_x = \sqrt{\frac{2k_BT}{m}}\frac{1}{2\sqrt{u}}du = \sqrt{\frac{k_BT}{2mu}}du \tag{3.16}$$

and the integral becomes:

$$\int_0^\infty e^{-mv_x^2/2k_BT}dv_x = \int_0^\infty e^{-u}\sqrt{\frac{k_BT}{2mu}}du = \sqrt{\frac{k_BT}{2m}}\underbrace{\int_0^\infty u^{-1/2}e^{-u}du}_{\Gamma(1/2)} = \sqrt{\frac{\pi k_BT}{2m}} \tag{3.17}$$

Substituting in the normalization equation (Eq. 3.15),

$$1 = 2K_x \times \sqrt{\frac{\pi k_BT}{2m}} \tag{3.18}$$

The normalization constant is:

$$K_x = \sqrt{\frac{m}{2\pi k_BT}} \tag{3.19}$$

and the probability distribution of velocities in one dimension is:

$$f(v_x) = \sqrt{\frac{m}{2\pi k_BT}}e^{-\frac{mv_x^2}{2k_BT}} \tag{3.20}$$

This function is a probability density that gives the probability that a molecule has velocity between v_x and $v_x + dv_x$. If we want to find the probability that a molecule has velocity in the x direction between a and b,

$$P(a \leq v_x \leq b) = \int_a^b f(v_x)dv_x \tag{3.21}$$

The probability density for the other dimensions has exactly the same expression but for v_y and v_z. Combining the three, we find the probability density for the whole molecular velocity:

$$f(\boldsymbol{v}) = f(v_x)f(v_y)f(v_z) = \left(\frac{m}{2\pi k_BT}\right)^{3/2} e^{-\frac{m(v_x^2+v_y^2+v_z^2)}{2k_BT}} = \left(\frac{m}{2\pi k_BT}\right)^{3/2} e^{-\frac{mv^2}{2k_BT}} \tag{3.22}$$

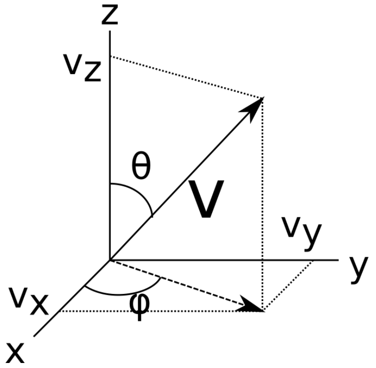
This is the **Maxwell-Boltzmann (MB) distribution of molecular velocities**. It is a probability density function. Integration of this function in a region ($v_x = v_a \leq v_b$, etc.) gives the probability of finding a molecule with velocity inside that region:

$$P(a_x \leq v_x \leq b_x, a_y \leq v_y \leq b_y, a_z \leq v_z \leq b_z) = \int_{a_x}^{b_x} dv_x \int_{a_y}^{b_y} dv_y \int_{a_z}^{b_z} dv_z f(\boldsymbol{v}) \tag{3.23}$$

The Maxwell-Boltzmann distribution is approximately valid for liquids and real gases, and it is exactly valid for an ideal gas.

Most often, we are not interested in the velocity vector but in its magnitude, the molecular speed ($v = \sqrt{v_x^2 + v_y^2 + v_z^2}$), so we want to find the probability density function of molecular

Figure 3.2: Transformation between Cartesian coordinates (v_x, v_y, v_z) and spherical coordinates (v,θ,ϕ).



speeds, $f(v)$. To do this, we first effect a change of variable on the molecular velocity distribution, from Cartesian to spherical coordinates:

$$v = \sqrt{v_x^2 + v_y^2 + v_z^2} \tag{3.24}$$

$$\cos\theta = \frac{v_z}{v} \tag{3.25}$$

$$\tan\phi = \frac{v_y}{v_x} \tag{3.26}$$

where v is the length of the vector (equivalent to r in the usual notation for spherical coordinates) θ is the polar angle and ϕ is the azimuthal angle (see Figure 3.2).

The determinant of the Jacobian matrix for this transformation is:

$$dv_x dv_y dv_z = (\det J) dv d\theta d\phi = (v^2 \sin\theta) dv d\theta d\phi \tag{3.27}$$

and the probability density in spherical coordinates is obtained from:

$$f(\boldsymbol{v}) dv_x dv_y dv_z = \underbrace{(v^2 \sin\theta)\left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-\frac{mv^2}{2k_B T}}}_{f(v,\theta,\phi)} dv d\theta d\phi \tag{3.28}$$

from where:

$$f(v,\theta,\phi) = (v^2 \sin\theta)\left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-\frac{mv^2}{2k_B T}} \tag{3.29}$$

Since we care only about the magnitude of v and not the angles, we find the distribution of speeds $f(v)$ by marginalization of the two angular variables:

$$\begin{aligned} f(v) = \int_0^{\pi} d\theta \int_0^{2\pi} d\phi f(v,\theta,\phi) &= v^2 \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-\frac{mv^2}{2k_B T}} \left(\int_0^{\pi} d\theta \int_0^{2\pi} d\phi \sin\theta\right) \\ &= 4\pi v^2 \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-\frac{mv^2}{2k_B T}} \end{aligned} \tag{3.30}$$

Finally, noting that the molar mass is $M = mN_A$ and $R = k_B N_A$, we have that $m/k_B = M/R$. With this change, we arrive at the expression for the **Maxwell-Boltzmann (MB) distribution of molecular speeds**:

$$f(v) = 4\pi \left(\frac{M}{2\pi RT}\right)^{3/2} v^2 e^{-\frac{Mv^2}{2RT}} \tag{3.31}$$

Figure 3.3: The Maxwell-Boltzmann distribution in O_2 at three different temperatures.

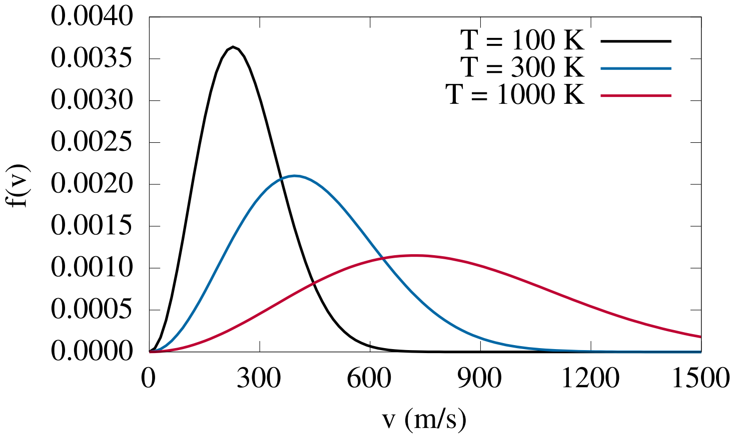


Figure 3.3 shows the main features of this distribution. Because of the Gaussian function, the distribution always decays exponentially at high velocities, where $\frac{1}{2}mv^2 \gg k_BT$. At low temperature or high molecular mass, most molecules have low velocities and the spread of the distribution is low, and centered around a very high peak. At higher temperatures or lower molecular masses, the distribution of speeds spreads out, the maximum moves to higher velocities and the peak becomes lower and broader. The factor v^2 in the distribution makes the probability of finding molecules go to zero as $v \to 0$. The Maxwell-Boltzmann distribution of speeds has been confirmed experimentally using thermalized low-pressure gases inside a container with a small puncture that leads to a molecular velocity selector (Miller and Kusch, *Phys. Rev.* **99** (1955) 1314). The agreement of the MB distribution with the experimental distribution is excellent.

3.3.1 Mean Values

We have seen before that $v_{\text{rms}} = \sqrt{\langle v^2 \rangle}$ enters the ideal gas equation of state in the kinetic theory of gases. There are a number of average values that are used to characterize a Maxwell-Boltzmann distribution. Before we calculate them, we need to know how to solve definite integrals involving Gaussian functions:

$$\int_0^\infty x^{2n} e^{-\alpha x^2} dx = \frac{(2n)!\sqrt{\pi}}{2^{2n+1} n! \alpha^{n+1/2}}$$

$$\int_0^\infty x^{2n+1} e^{-\alpha x^2} dx = \frac{n!}{2\alpha^{n+1}}$$

with $\alpha > 0$ and $n = 0, 1, \ldots$. These formulas are easy to prove by effecting the $u = \alpha x^2$ change of variable, then using the properties of the Gamma function.

The **mean speed**, v_{mean}, is just the average molecular speed calculated from the MB distribution:

$$\begin{aligned} v_{\text{mean}} &= \int_0^\infty v f(v) dv = \int_0^\infty 4\pi \left(\frac{M}{2\pi RT}\right)^{3/2} v^3 e^{-\frac{Mv^2}{2RT}} dv = 4\pi \left(\frac{M}{2\pi RT}\right)^{3/2} \int_0^\infty v^3 e^{-\frac{Mv^2}{2RT}} dv \\ &= 4\pi \left(\frac{M}{2\pi RT}\right)^{3/2} \frac{1!}{2\left(\frac{M}{2RT}\right)^2} = \frac{2}{\sqrt{\pi}} \sqrt{\frac{2RT}{M}} = \sqrt{\frac{8RT}{\pi M}} \end{aligned} \tag{3.32}$$

The mean speed is the average speed of a molecule in the gas. This expression is used in the formulas for effusion and the mean free path that we will see next.

The **root-mean-square** speed, v_{rms} is the square root of the second moment of the distribution:

$$v_{\mathrm{rms}} = \sqrt{\langle v^2 \rangle} \tag{3.33}$$

The second moment is:

$$\begin{aligned}\langle v^2 \rangle &= \int_0^\infty v^2 f(v) dv = \int_0^\infty 4\pi \left(\frac{M}{2\pi RT}\right)^{3/2} v^4 e^{-\frac{Mv^2}{2RT}} dv = 4\pi \left(\frac{M}{2\pi RT}\right)^{3/2} \int_0^\infty v^4 e^{-\frac{Mv^2}{2RT}} dv \\ &= 4\pi \left(\frac{M}{2\pi RT}\right)^{3/2} \frac{4! \times \sqrt{\pi}}{2^5 \times 2! \times \left(\frac{M}{2RT}\right)^{5/2}} = \frac{3}{2}\left(\frac{2RT}{M}\right) = \frac{3RT}{M}\end{aligned} \tag{3.34}$$

so the root-mean-square is:

$$v_{\mathrm{rms}} = \sqrt{\langle v^2 \rangle} = \sqrt{\frac{3RT}{M}} \tag{3.35}$$

With the calculated value of the v_{rms}, we arrive at the expression for the equation of state of an ideal gas in kinetic gas theory. We showed before (Eq. 3.8) that the pressure is:

$$p = \frac{nMv_{\mathrm{rms}}^2}{3V} \tag{3.36}$$

and using Eq. 3.35,

$$p = \frac{nM \times \frac{3RT}{M}}{3V} = \frac{nRT}{V} \tag{3.37}$$

which is the same as the experimental equation of state of an ideal gas.

The final characteristic value of the MB distribution is the **most probable speed**, which is the speed at which the probability density $f(v)$ is a maximum. The maximum is found by making the derivative of $f(v)$ equal to zero:

$$\begin{aligned}f'(v) &= 4\pi \left(\frac{M}{2\pi RT}\right)^{3/2} \frac{d}{dv}\left(v^2 e^{-\frac{Mv^2}{2RT}}\right) \\ &= 4\pi \left(\frac{M}{2\pi RT}\right)^{3/2} \left[2ve^{-\frac{Mv^2}{2RT}} + v^2 e^{-\frac{Mv^2}{2RT}}\left(-\frac{Mv}{RT}\right)\right] \\ &= 4\pi \left(\frac{M}{2\pi RT}\right)^{3/2} \left[2ve^{-\frac{Mv^2}{2RT}} - \frac{M}{RT}v^3 e^{-\frac{Mv^2}{2RT}}\right] = 0\end{aligned} \tag{3.38}$$

Rearranging,

$$2ve^{-\frac{Mv^2}{2RT}} = \frac{M}{RT}v^3 e^{-\frac{Mv^2}{2RT}} \tag{3.39}$$

and solving for v we find the most probable speed:

$$v_{\mathrm{mp}} = \sqrt{\frac{2RT}{M}} \tag{3.40}$$

The most probable speed is the speed of a molecule that has the same kinetic energy as the available thermal energy:

$$\frac{1}{2}mv_{\mathrm{mp}}^2 = k_B T \tag{3.41}$$

The most probable speed can also be used to rewrite the MB distribution of speeds (Eq. 3.31) in a simpler form, using v/v_{mp} as the variable:

$$f(v) = 4\pi \left(\frac{M}{2\pi RT}\right)^{3/2} v^2 e^{-\frac{Mv^2}{2RT}} = \frac{4}{\sqrt{\pi} v_{\mathrm{mp}}}\left(\frac{v}{v_{\mathrm{mp}}}\right)^2 e^{-(v/v_{\mathrm{mp}})^2} \tag{3.42}$$

Effecting the change of variable to the reduced speed $v_r = v/v_{\text{mp}}$, we have:

$$dv_r = \frac{dv}{v_{\text{mp}}} \tag{3.43}$$

and:

$$f(v)dv = \frac{4}{\sqrt{\pi}v_{\text{mp}}}\left(\frac{v}{v_{\text{mp}}}\right)^2 e^{-(v/v_{\text{mp}})^2} v_{\text{mp}}dv_r = \underbrace{\frac{4}{\sqrt{\pi}}v_r^2 e^{-v_r^2}}_{f(v_r)} dv_r \tag{3.44}$$

so the Maxwell-Boltzmann distribution can be written in terms of the reduced velocity such that the distribution independent of temperature and molecular mass:

$$f(v_r) = \frac{4}{\sqrt{\pi}}v_r^2 e^{-v_r^2} \tag{3.45}$$

Question: Calculate the root-mean-square, mean, and most probable velocities of N_2 at 25 °C. The molar mass is $M = 28.02\,\text{g/mol}$.

The characteristic velocities for the MB distribution in this gas are:

$$v_{\text{rms}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times 8.314\,\text{J/K/mol} \times 298.15\,\text{K}}{0.028\,02\,\text{kg/mol}}} = 515\,\text{m/s}$$

$$v_{\text{mean}} = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8 \times 8.314\,\text{J/K/mol} \times 298.15\,\text{K}}{\pi \times 0.028\,02\,\text{kg/mol}}} = 475\,\text{m/s}$$

$$v_{\text{mp}} = \sqrt{\frac{2RT}{M}} = \sqrt{\frac{2 \times 8.314\,\text{J/K/mol} \times 298.15\,\text{K}}{0.028\,02\,\text{kg/mol}}} = 420\,\text{m/s}$$

The magnitude of these average speeds is approximately the speed of sound in the gas.

3.4 Collisions

We now study molecular collisions in our kinetic model for a gas. Calculation of the collision rate between the particles is important because it establishes an upper bound for reaction rates in the gas phase (two molecules must collide before they can react).

In addition to the mean, rms, and most probable speeds, we can consider the mean relative speed, v_{rel}, which is the average relative speed between pairs of particles. The pair of particles can be either of the same type, in the case of a one-component homogeneous gas, or different types, in the case of mixtures. The mean relative speed is calculated as:

$$\langle v_{\text{rel}} \rangle = \int f(\boldsymbol{v}_B) f(\boldsymbol{v}_C) |\boldsymbol{v}_B - \boldsymbol{v}_C| d\boldsymbol{v}_B d\boldsymbol{v}_C \tag{3.46}$$

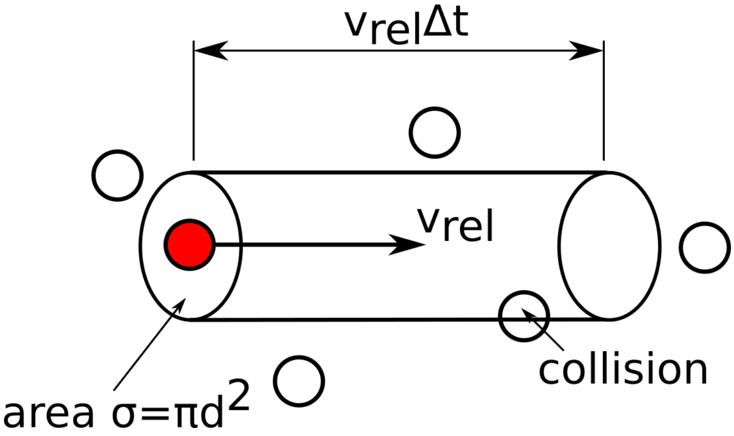
where the integral involves the velocity distributions of both particles. This integral is solved by transforming the $\boldsymbol{v}_B$ and $\boldsymbol{v}_C$ variables into the relative velocity $\boldsymbol{v}_{\text{rel}} = \boldsymbol{v}_B - \boldsymbol{v}_C$ and the center of mass velocity:

$$\boldsymbol{v}_{\text{cm}} = \frac{m_B \boldsymbol{v}_B + m_C \boldsymbol{v}_C}{m_B + m_C} \tag{3.47}$$

The calculation of this integral is rather lengthy, so we will skip it. It is possible to show that v_{rel} has the same expression as v_{mean} but with the molar mass replaced by the reduced mass:

$$v_{\text{rel}}^{\text{BC}} = \sqrt{\frac{8k_BT}{\pi\mu_{\text{BC}}}} \tag{3.48}$$

Figure 3.4: Collision tube for a particle moving in a gas.



where the $v_{\text{rel}}^{\text{BC}}$ is the mean relative speed between molecules of B and C type, and the reduced molecular mass is:

$$\mu_{\text{BC}} = \frac{m_B m_C}{m_B + m_C} \tag{3.49}$$

(Note that the denominator has $k_B T$ because m and μ are molecular masses, not molar masses. If we use M, then the denominator contains RT.)

Let us begin by considering collisions in a homogeneous gas first, i.e., all molecules are of the same species. In the case of a homogeneous gas the colliding particles are of the same type, and the reduced molecular mass is simply:

$$\mu = \mu_{\text{BB}} = \frac{m_B m_B}{m_B + m_B} = \frac{m_B}{2} \tag{3.50}$$

and the mean relative speed becomes:

$$v_{\text{rel}} = v_{\text{rel}}^{\text{BB}} = \sqrt{\frac{8k_B T}{\pi \mu_{\text{BB}}}} = \sqrt{\frac{16k_B T}{\pi m_B}} = \sqrt{\frac{16RT}{\pi M_B}} = \sqrt{2} v_{\text{mean}} \tag{3.51}$$

To evaluate the collision frequency (i.e. the number of molecular collisions per unit time) of a given molecule, we consider one molecule in the gas moving with the mean relative speed (v_{rel}) and the rest of the molecules frozen in place. (We can do this formally by using the change of variable into center-of-mass coordinates and relative coordinates.) As the molecule moves, it sweeps a "collision tube", as shown in Figure 3.4. The area of the base of the tube is given by the size of the molecule, as measured by its **cross-section**. The cross-section for a homogeneous gas is:

$$\sigma_{\text{BB}} = \sigma = \pi(r_{\text{B}} + r_{\text{B}})^2 = \pi d_{\text{BB}}^2 \tag{3.52}$$

where r_{B} is the radius of molecule B, and d_{BB} is the sum of the radii of the colliding particles. Since this is a homogeneous gas, both particles have the same radius and d_{BB} is also equal to the molecular diameter. Typical cross-section values for small molecules are in the nm^2 range: benzene ($0.88\,\text{nm}^2$), N_2 ($0.45\,\text{nm}^2$).

If we consider a time interval Δt, the length of the tube is equal to $v_{\text{rel}}\Delta t$. The volume of the collision tube is therefore $\sigma v_{\text{rel}}\Delta t$ and the particle density in the gas is given by nN_A/V, where n is the number of moles and V is the volume of the container. The number of collisions is approximated by the number of particles in the collision tube, which is:

$$\sigma v_{\text{rel}}\Delta t \times \frac{nN_A}{V} \tag{3.53}$$

The collision frequency is obtained by dividing the number of collisions by the time interval:

$$z = \left(\frac{nN_A}{V}\right)\sigma v_{\text{rel}} \tag{3.54}$$

and using the equation of state of the ideal gas, $V = nRT/p$, we have:

$$z = \frac{N_A \sigma v_{\text{rel}} p}{RT} = \frac{\sigma v_{\text{rel}} p}{k_B T} \tag{3.55}$$

The collision frequency gives the number of collisions per unit time for a single molecule in the gas. It has units of inverse time.

With the collision frequency for a given molecule it is easy to calculate its **mean free path** (λ). The mean free path is the average distance a molecule travels between successive collisions. If a molecule collides with frequency z, it spends a time equal to $1/z$ without collisions on average. If we assume the molecule travels with the mean speed v_{mean}, then the mean free path in a homogeneous gas is:

$$\lambda = \frac{v_{\text{mean}}}{z} = \frac{v_{\text{mean}}}{\frac{\sigma v_{\text{rel}} p}{k_B T}} = \frac{v_{\text{mean}}}{\frac{\sqrt{2}\sigma v_{\text{mean}} p}{k_B T}} = \frac{k_B T}{\sqrt{2}\sigma p} = \frac{RT}{\sqrt{2}\pi d^2 N_A p} \tag{3.56}$$

At constant volume, the mean free path is independent of the temperature because $p/RT = n/V$. In order to meet the hypotheses for the application of the kinetic theory of gases, the mean free path has to be much smaller than the size of the container and much higher than the molecular diameter.

Question: Calculate the collision frequency and the mean free path of an N_2 molecule in a pure gas of N_2 at 1 atm and 25 °C.

The mean relative speed for N_2 is:

$$v_{\text{rel}} = \sqrt{\frac{16RT}{\pi M}} = \sqrt{\frac{16 \times 8.314\,\text{J/K/mol} \times 298.15\,\text{K}}{\pi \times 0.028\,013\,4\,\text{kg/mol}}} = 671.33\,\text{m/s}$$

The cross-section of the N_2 molecule is:

$$\sigma = 0.45\,\text{nm}^2 = 4.5 \times 10^{-19}\,\text{m}^2$$

and therefore its collision frequency is:

$$z = \frac{\sigma v_{\text{rel}} p}{k_B T} = \frac{4.5 \times 10^{-19}\,\text{m}^2 \times 671.33\,\text{m/s} \times 101\,325\,\text{Pa}}{1.381 \times 10^{-23}\,\text{J/K} \times 298.15\,\text{K}} = 7.43 \times 10^{9}\,\text{s}^{-1}$$

The mean free path is:

$$\lambda = \frac{v_{\text{mean}}}{z} = \frac{v_{\text{rel}}}{z\sqrt{2}} = \frac{671.33\,\text{m/s}}{\sqrt{2} \times 7.7 \times 10^{9}\,\text{s}^{-1}} = 6.4 \times 10^{-8}\,\text{m}$$

The mean free path is 64 nm, which is about a thousand molecular diameters in the case of N_2. This result justifies *a posteriori* our assumption that the size of the molecules is negligible compared to the average distance traveled between collisions, at least in this specific system.

We now generalize these results to mixtures of gases. In a pure gas, the collision frequency of a molecule (the number of collisions that molecule suffers per unit time) is given by Eq. 3.54. If we denote $z_{\text{B}}(\text{C})$ the collision frequency between a molecule B and molecules of C in a gas that is a mixture of both molecules, then the collision frequency for like-molecules of the B species (Eq. 3.54) translates into:

$$z_{\text{B}}(\text{B}) = \left(\frac{n_{\text{B}} N_A}{V}\right)\sigma_{BB} v_{\text{rel}}^{BB} = \left(\frac{N_{\text{B}}}{V}\right)\sigma_{BB} v_{\text{rel}}^{BB} \tag{3.57}$$

where N_{B} is the number of molecules of B ($N_B = n_B N_A$) and v_{rel}^{BB} is the relative speed between B molecules (Eq. 3.48 with $\mu = m_B/2$). The cross-section is given by Eq. 3.52, which is:

$$\sigma_{\mathrm{BB}} = \pi d_{\mathrm{B}}^2 = \pi(r_{\mathrm{B}} + r_{\mathrm{B}})^2 \tag{3.58}$$

which is the same as in the case of the homogeneous gas (Eq. 3.52).

The collision frequency between B and C molecules is obtained using the same arguments as above, i.e., we assume that all C molecules are fixed and B moves around with speed equal to v_{rel}^{BC}, sweeping a collision tube with radius equal to the sum of the radii of B and C ($r_B + r_C$). From this, making the same argument as above, we find that the collision frequency of a B molecule with C molecules (number of collisions per unit time for a single B molecule) is:

$$z_{\mathrm{B}}(\mathrm{C}) = \left(\frac{N_{\mathrm{C}}}{V}\right) \sigma_{BC} v_{\mathrm{rel}}^{BC} \tag{3.59}$$

where in this case the relative velocity (Eq. 3.48) uses the reduced mass of B and C and the collision cross-section is:

$$\sigma_{\mathrm{BC}} = \pi(r_{\mathrm{B}} + r_{\mathrm{C}})^2 \tag{3.60}$$

with r_{B} and r_{C} the radius of each molecule. If the gas is composed solely of B and C, then the sum of $z_{\mathrm{B}}(\mathrm{B})$ and $z_{\mathrm{B}}(\mathrm{C})$ represent the number of collisions per second of a B molecule with any other molecule in the gas regardless of their type.

We now define Z_{BB}, Z_{CC}, and Z_{BC} as the total number of molecular collisions per unit time and per unit volume in the gas between the species in the subindices. In the case of unlike molecules, Z_{BC} is calculated simply as the number of collisions a molecule B suffers on average times the number of B molecules in that volume:

$$Z_{\mathrm{BC}} = \left(\frac{N_{\mathrm{B}}}{V}\right) z_{\mathrm{B}}(\mathrm{C}) = \left(\frac{N_{\mathrm{B}}}{V}\right)\left(\frac{N_{\mathrm{C}}}{V}\right) \sigma_{BC} v_{\mathrm{rel}}^{BC} \tag{3.61}$$

where σ_{BC} is given by Eq. 3.60 and v_{rel}^{BC} (Eq. 3.48) uses the reduced mass of B and C. In the case of Z_{BB}, we need to take into account that the number of collisions ($z_{\mathrm{B}}(\mathrm{B})$) times the number of molecules per volume (N_B/V) double-counts the number of B-B collisions and so we must add a factor of 1/2:

$$Z_{\mathrm{BB}} = \frac{1}{2}\left(\frac{N_{\mathrm{B}}}{V}\right) z_{\mathrm{B}}(\mathrm{B}) = \frac{1}{2}\left(\frac{N_{\mathrm{B}}}{V}\right)^2 \sigma_{BB} v_{\mathrm{rel}}^{BB} \tag{3.62}$$

where σ_{BB} is given by Eq. 3.58 and v_{rel}^{BB} is calculated using $\mu = m_{\mathrm{B}} m_{\mathrm{B}}/(m_{\mathrm{B}} + m_{\mathrm{B}}) = m_{\mathrm{B}}/2$. Sometimes the term collision frequency is applied to Z_{BB} and Z_{BC} instead of z_{BB} and z_{BC}. Note that, regardless of the term used to name them, the Z have SI units of $\mathrm{s}^{-1}\,\mathrm{m}^{-3}$ (collisions per time per volume) whereas the z have SI units of s^{-1} (collisions per time).

Finally, we generalize the concept of mean free path to a mixture of gases. In a mixture where there are several different molecules, the denominator in Eq. 3.56 is the sum of the collision frequencies with all the species present in the mixture and the molecular speed of B is the average speed. For instance, the mean-free path of a molecule of B in a mixture with B, C,... is:

$$\lambda = \frac{v_{\mathrm{mean}}}{z_{\mathrm{B}}(B) + z_{\mathrm{B}}(C) + \ldots} \tag{3.63}$$

where v_{mean} is the mean velocity of molecule B, given by Eq. 3.32.

3.5 Effusion

Effusion refers to the process in which a gas almost at equilibrium at a certain temperature escapes through a small puncture in the container. We assume that the size of the hole and the temperature are sufficiently low that the Maxwell-Boltzmann equilibrium distribution of velocities is still valid and no significant collisions happen between molecules traversing the aperture. (In the context of transport properties, this is called free-molecule or Knudsen flow.) Effusion phenomena are important in the generation of **molecular beams**, beams of particles that are used to study chemical reaction dynamics.

We know from the previous section that the number of particles with velocity v_x that strike a wall with area A in a time interval Δt is (Eq. 3.1):

$$\frac{1}{2}\left(\frac{nN_A}{V}\right) \times Av_x\Delta t \tag{3.64}$$

where n is the number of moles and V is the volume of the container. nN_A/V is the particle density, the number of particles per unit volume. The collision rate for molecules moving at velocity v_x is equal to this quantity divided by the time interval, in the limit of $\Delta t \to 0$:

$$\frac{1}{2}\left(\frac{nN_A}{V}\right) \times Av_x \tag{3.65}$$

Finally, we integrate over all possible velocities using the probability distribution to find the total collision rate with the wall:

$$\frac{dN_c}{dt} = \int_0^\infty \frac{nN_AAv_x}{V} f(v_x)dv_x = \left(\frac{nN_AA}{V}\right)\int_0^\infty v_xf(v_x)dv_x \tag{3.66}$$

where the 1/2 factor that we introduced in the first section to account for the fact that only half the molecules are moving towards the wall is removed because the integral runs only over the positive v_x, and thus the molecules moving in the opposite direction are not considered. The distribution of molecular velocities in the x-direction (Eq. 3.20) is:

$$f(v_x) = \sqrt{\frac{m}{2\pi k_BT}}e^{-\frac{mv_x^2}{2k_BT}} \tag{3.67}$$

and so the collision rate:

$$\frac{dN_c}{dt} = \left(\frac{nN_AA}{V}\right) \times \sqrt{\frac{m}{2\pi k_BT}}\int_0^\infty v_xe^{-\frac{mv_x^2}{2k_BT}}dv_x \tag{3.68}$$

The derivative of the exponent in this integral is $-\frac{mv_x}{k_BT}$, so:

$$\begin{aligned}\frac{dN_c}{dt} &= -\left(\frac{nN_AA}{V}\right) \times \sqrt{\frac{m}{2\pi k_BT}} \times \frac{k_BT}{m}\int_0^\infty \left(-\frac{mv_x}{k_BT}\right)e^{-\frac{mv_x^2}{2k_BT}}dv_x \\ &= -\left(\frac{nN_AA}{V}\right) \times \sqrt{\frac{k_BT}{2\pi m}}\left[e^{-\frac{mv_x^2}{2k_BT}}\right]_0^\infty \\ &= \left(\frac{nN_AA}{V}\right) \times \sqrt{\frac{RT}{2\pi M}} \end{aligned} \tag{3.69}$$

but the mean molecular speed is $v_{\text{mean}} = \sqrt{\frac{8RT}{\pi M}}$, so the second factor is $v_{\text{mean}}/4$ and:

$$\frac{dN_c}{dt} = \frac{nN_AAv_{\text{mean}}}{4V} \tag{3.70}$$

The **collisional flux** is defined as the number of collisions per unit time per unit area:

$$Z_c = \frac{dN_c/dt}{A} = \frac{nN_A v_{\text{mean}}}{4V} \tag{3.71}$$

and in an ideal gas the particle density is given by:

$$\frac{nN_A}{V} = \frac{p}{k_B T} \tag{3.72}$$

where p is the pressure, so the collisional flux is actually:

$$Z_c = \frac{p v_{\text{mean}}}{4k_B T} = \frac{p}{4k_B T} \times \sqrt{\frac{8k_B T}{\pi m}} = \frac{p}{\sqrt{2\pi m k_B T}} \tag{3.73}$$

Note that, if we solve for p in this equation:

$$p = Z_c \times \sqrt{2\pi m k_B T} \tag{3.74}$$

we find that the pressure is proportional to the collisional flux (the number of times molecules strike the wall per unit time and area) times the momentum ($h/\Lambda = \sqrt{2\pi m k_B T}$) with which each molecule strikes the wall, which increases with the mass of the molecule (m) and with their velocity (given by the temperature, T).

Question: The vapor pressure of silver at 2000 °C is 170 torr. A recipient contains molten silver in equilibrium with its vapor at that temperature. Calculate the amount of Ag that collides with the walls of the recipient in terms of collisions per unit time and per unit area ($\text{cm}^{-2}\,\text{s}^{-1}$) or of mass per unit time and per unit area ($\text{g}\,\text{cm}^{-2}\,\text{s}^{-1}$).

The number of collisions per unit time per unit area is given by the collisional flux, which is written as:

$$Z_c = \frac{p}{\sqrt{2\pi m k_B T}}$$

Using the problem data, we have:

$$\begin{aligned} Z_c &= \frac{170\,\text{torr} \times \frac{101\,325\,\text{Pa}}{760\,\text{torr}}}{\sqrt{2\pi \times 107.8682\,\text{g/mol} \times \frac{\text{kg}}{1000\,\text{g}} \times \frac{1}{6.022 \times 10^{23}\,\text{1/mol}} \times 1.381 \times 10^{-23}\,\text{J/K} \times 2273.15\,\text{K}}} \\ &= 1.205\,97 \times 10^{26}\,\text{m}^{-2}\,\text{s}^{-1} \times \frac{\text{m}^2}{1 \times 10^4\,\text{cm}^2} = 1.205\,97 \times 10^{22}\,\text{cm}^{-2}\,\text{s}^{-1} \end{aligned}$$

The amount of mass that collides with the wall of the container is equal to the mass of a single molecule times the collisional flux (the number of collisions per second per area):

$$\begin{aligned} Z_w &= Z_c m = 1.205\,97 \times 10^{22}\,\text{cm}^{-2}\,\text{s}^{-1} \times 107.8682\,\text{g/mol} \times \frac{1}{6.022 \times 10^{23}\,\text{1/mol}} \\ &= 2.160\,\text{g}\,\text{cm}^{-2}\,\text{s}^{-1} \end{aligned}$$

A container with a hole in it will lose pressure over time as the particles of the gas escape. Assuming the hole is small enough that the system is in quasi-equilibrium at all times, the decrease in pressure can be calculated with:

$$\frac{dp}{dt} = \frac{d}{dt}\left(\frac{Nk_B T}{V}\right) = \frac{k_B T}{V}\frac{dN}{dt} \tag{3.75}$$

If the particles of the gas do not return to the container (which is reasonable if the pressure outside the container is much smaller than inside and the walls are not very thick), we can calculate the rate at which the particles of the gas are lost as the number of collisions with the aperture or, equivalently, as the collisional flux times the area of the hole:

$$\frac{dN}{dt} = -Z_c A = -\frac{pA}{\sqrt{2\pi m k_B T}} \tag{3.76}$$

The decrease in pressure is therefore:

$$\frac{dp}{dt} = -\frac{k_BT}{V}\frac{pA}{\sqrt{2\pi m k_BT}} = -\frac{A}{V}\sqrt{\frac{k_BT}{2\pi m}}p = -\frac{A}{V}\sqrt{\frac{RT}{2\pi M}}p \tag{3.77}$$

Note that the rate at which molecules escape through a hole in the container is inversely proportional to the square root of their mass. This formula encapsulates **Graham's law of effusion**, which states that the rate of effusion is inversely proportional to the square root of the molecular mass. (The different effusion properties of UF_6 were used to to separate uranium isotopes for the construction of atomic bombs during World War II.)

To find the pressure as a function of time during effusion, we note that Eq. 3.77 is a separable differential equation:

$$\frac{dp}{p} = -\frac{A}{V}\sqrt{\frac{k_BT}{2\pi m}}dt \tag{3.78}$$

and integrating between time zero (initial pressure p_0) and time t,

$$\int_{p_0}^{p}\frac{dp}{p} = \ln\left(\frac{p}{p_0}\right) = -\frac{A}{V}\sqrt{\frac{k_BT}{2\pi m}}\int_0^t dt = -\frac{A}{V}\sqrt{\frac{k_BT}{2\pi m}}t \tag{3.79}$$

from where the pressure at any time t is given by:

$$p(t) = p_0\exp\left(-\frac{A}{V}\sqrt{\frac{k_BT}{2\pi m}}t\right) = p_0\exp\left(-\frac{A}{V}\sqrt{\frac{RT}{2\pi M}}t\right) \tag{3.80}$$

The effusion of a gas makes the pressure decrease exponentially with time.

Chapter 4

Chemical Kinetics

4.1 Reaction Rate and the Rate Law

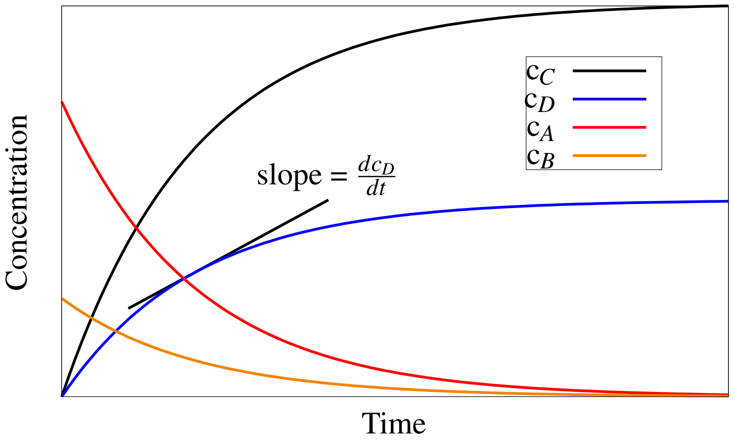
Chemical kinetics is the discipline that studies the rate of chemical reactions. The rate of a reaction is determined by the concentration of reactants and products and by other factors such as temperature, pressure, and the presence of catalysts. Chemical kinetics has two distinct but interconnected aspects: the description of a reaction rate by a set of differential equations (rate laws), and the discovery of the detailed sequence of microscopic steps that leads from reactants to products (the reaction mechanism). Knowledge of the mechanism determines the rate law and, consequently, allows us to predict the evolution of the concentration of each species with time. It also gives us a means to modify and control the outcome of a reaction and to predict its behavior when changes are made to the reactants.

Let us assume a homogeneous reaction (all species in the same phase) occurring in a system at constant volume and temperature:

$$\mathrm{aA} + \mathrm{bB} \longrightarrow \mathrm{cC} + \mathrm{dD} \tag{4.1}$$

where a, b, c, and d are the stoichiometric coefficients, A and B are the reactants, and C and D are the products. When the reactants are mixed there is an initial molar concentration $[\mathrm{A}]_0$, $[\mathrm{B}]_0$,... of all species in the reaction vessel. As the reaction progresses, the concentration of A and B decreases with time, and the concentration of C and D increases, as sketched in Figure 4.1. We define the **extent of the reaction** ($\xi(t)$) as the number of moles the reaction

Figure 4.1: Example of a possible time evolution of the reactant and product concentration in Reaction 6.60.



has progressed from reactants to products. The extent of the reaction is a function of time. We also define:

$$x(t) = \frac{\xi(t)}{V} \tag{4.2}$$

where $x(t)$ measures the concentration transferred from one side to the other of the reaction at time t. Assuming the concentration of intermediate species is negligible, the concentrations of reactants and products at time t are all related to x by the corresponding stoichiometric coefficients:

$$\begin{aligned} [\mathrm{A}](t) &= [\mathrm{A}]_0 - ax(t) \quad ; \quad [\mathrm{C}](t) = [\mathrm{C}]_0 + cx(t) \\ [\mathrm{B}](t) &= [\mathrm{B}]_0 - bx(t) \quad ; \quad [\mathrm{D}](t) = [\mathrm{D}]_0 + dx(t) \end{aligned} \tag{4.3}$$

Taking derivatives with respect to t we find that the **rate of generation** of products and the **rate of consumption** of reactants is:

$$\begin{aligned} \frac{d[\mathrm{A}]}{dt} &= -a\frac{dx}{dt} \quad ; \quad \frac{d[\mathrm{C}]}{dt} = +c\frac{dx}{dt} \\ \frac{d[\mathrm{B}]}{dt} &= -b\frac{dx}{dt} \quad ; \quad \frac{d[\mathrm{D}]}{dt} = +d\frac{dx}{dt} \end{aligned} \tag{4.4}$$

Therefore, we can define the **reaction rate** as:

$$r = \frac{dx}{dt} = -\frac{1}{a}\frac{d[\mathrm{A}]}{dt} = -\frac{1}{b}\frac{d[\mathrm{B}]}{dt} = +\frac{1}{c}\frac{d[\mathrm{C}]}{dt} = +\frac{1}{d}\frac{d[\mathrm{D}]}{dt} \tag{4.5}$$

In general, for a chemical reaction:

$$0 \rightarrow \textstyle\sum_i \nu_i\, \mathrm{X}_i \tag{4.6}$$

where ν_i is negative if i is a reactant and positive if i is a product. The reaction rate is therefore:

$$r = \frac{1}{\nu_i}\frac{d[\mathrm{X}_i]}{dt} \tag{4.7}$$

for any species i. The units of r are usually expressed in mol dm^{-3} s^{-1} or mol cm^{-3} s^{-1}. For homogeneous reactions in the gas phase, pressures can be used instead. The formalism is essentially the same so we will use concentrations for simplicity.

The reaction rate is an intensive quantity because it is expressed as a derivative of a molar concentration, which is also intensive. Therefore, the reaction rate depends on the concentration of all species in solution, temperature, and pressure (although the pressure dependence for reactions in solution is very slight, so we will not consider it in the following). The **(differential) rate law**, or **rate equation**, is the equation that relates the rate of a reaction with the concentrations of all species in the system and the temperature:

$$r = f(T, [\mathrm{A}], [\mathrm{B}], \ldots) \tag{4.8}$$

The differential rate law gives the reaction rate given the concentrations and temperature. Using Eq. 4.7 allows the prediction of the concentrations of all species as a function of time. For instance, we can rewrite Eq. 4.8 in the form:

$$-\frac{1}{a}\frac{d[\mathrm{A}]}{dt} = f(T, [\mathrm{A}], [\mathrm{B}], \ldots) \tag{4.9}$$

where all the concentrations other than [A] are functions of [A] using the stoichiometric relations (Eq. 4.3). This is a differential equation that can be solved, numerically or analytically, to yield the evolution of the concentration of A with time ([A](t)). The same procedure can be applied to find the time evolution of all the other concentrations.

It has been found experimentally that in many reactions the rate law has this expression:

$$r = k[\mathrm{A}]^{\alpha}[\mathrm{B}]^{\beta}\ldots[\mathrm{L}]^{\lambda} \tag{4.10}$$

where A,... can be either reactants, products, or some species that are involved in the reaction somehow but are neither consumed nor generated in appreciable quantities (catalysts, inhibitors, and the solvent, see below). The α,... exponents are the **partial reaction orders** of each species. In principle they can take any value and in general they are **not** equal to the stoichiometric coefficients, and have no relation with them. Usually, they tend to be integers or half-integers, but they can also be zero or negative. The reaction has **overall reaction order** equal to $n = \alpha + \beta + \ldots$. The k pre-factor in the rate law is the **rate constant** or **rate coefficient** and depends on temperature (and pressure) only. The units of the rate constant depend on the rate law. For the rate law above (Eq. 4.10), k has units of $(1/\mathrm{M})^{n-1}\ \mathrm{s}^{-1}$, where n is the overall reaction order.

While many reactions have rate laws that conform to Eq. 4.10, many do not, and apparently similar reactions can have very different rate laws. For instance, the hydrogenation of iodine:

$$\mathrm{H_2} + \mathrm{I_2} \longrightarrow 2\,\mathrm{HI} \tag{4.11}$$

has a simple rate law:

$$r = k[\mathrm{H_2}][\mathrm{I_2}] \tag{4.12}$$

whereas the hydrogenation of bromine:

$$\mathrm{H_2} + \mathrm{Br_2} \longrightarrow 2\,\mathrm{HBr} \tag{4.13}$$

has a much more complex rate law:

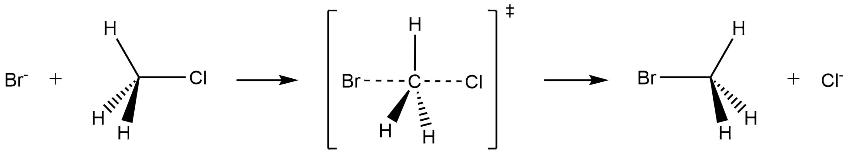
$$r = k\frac{[\mathrm{H_2}][\mathrm{Br_2}]^{3/2}}{[\mathrm{Br_2}] + k'[\mathrm{HBr}]} \tag{4.14}$$

This reaction is first order in $[\mathrm{H_2}]$ but the concept of partial reaction order is not applicable to $\mathrm{Br_2}$ or HBr. The product of the reaction (HBr) decreases the reaction rate, and therefore acts as an inhibitor. In general, **the stoichiometry of the reaction does not determine the rate law**.

4.2 Mechanism of a Reaction

The complex rate law of the seemingly simple bromine hydrogenation reaction arises from the fact that this is a **composite reaction** formed by a concatenation of simple (or elementary) molecular steps, which contribute individually to the overall rate law. A reaction is **elementary** if it is not composite, that is, if it cannot be broken down into several steps. Microscopically, an elementary reaction occurs during a single molecular encounter: two reactants approach each other, collide, bonds are broken and formed, and the products move away from each other. In terms of potential energy of the reacting molecules, an elementary reaction proceeds from reactants to products through a high-energy structure called a **transition state** (often also called the **activated complex**, although there are small differences between the two concepts, see below).

Let us take an example from organic chemistry: the S_N2 nucleophilic substitution reaction. An S_N2 substitution is an elementary reaction:



The nucleophile (Br^-) approaches the chloromethane from behind the C-Cl σ bond. In a single concerted step a bond between the nucleophile and the carbon is formed while, at the same time, the bond between the carbon and the leaving group is broken. The point of highest energy in this process, labeled with the ‡ symbol in the diagram, is the transition state.

An important fact when deriving rate laws from mechanisms is that **an elementary reaction has a simple rate law in which the partial orders of reaction coincide with the stoichiometric coefficients.** Therefore, an S_N2 reaction is first order in the nucleophile and in the substrate, and second order overall:

$$r = k[Br^-][CH_3Cl] \tag{4.15}$$

In contrast, the decomposition reaction of N_2O_5 is a composite reaction because it involves three different steps:

$$\begin{array}{lcr}
\text{Step 1:} & N_2O_5 \rightleftharpoons NO_2 + NO_3 & s = 2 \\
\text{Step 2:} & NO_2 + NO_3 \longrightarrow NO + O_2 + NO_2 & s = 1 \\
\text{Step 3:} & NO + NO_3 \longrightarrow 2\,NO_2 & s = 1 \\
\hline
\text{Overall:} & 2\,N_2O_5 \longrightarrow 4\,NO_2 + O_2 &
\end{array}$$

The detailed sequence of elementary steps for a given composite reaction is called the **reaction mechanism**. The three steps above are the mechanism of the N_2O_5 decomposition reaction. The **stoichiometric number** of a step (s) is the number of times that step occurs every overall step in the reaction. They are indicated on the right in the above diagram. The sum of all steps times their stoichiometric number gives the overall reaction. Other examples of composite reactions include the S_N1 nucleophilic substitution reaction and, for instance, any organic reaction that occurs via a tetrahedral intermediate. Most chemical reactions are composite.

We know that each elementary step has a simple rate law determined by the stoichiometric coefficients but the global reaction does not. However, from the knowledge of the mechanism, it is possible to predict the rate law of the overall reaction from the rate laws of the elementary reactions. For instance, let us take the case of a simple S_N1 reaction:

$$\begin{array}{lc}
\text{Step 1:} & {}^{t}Bu{-}Br \longrightarrow {}^{t}Bu^+ + Br^- \\
\text{Step 2:} & {}^{t}Bu^+ + H_2O \longrightarrow {}^{t}Bu{-}OH_2^+ \\
\text{Step 3:} & {}^{t}Bu{-}OH_2^+ + H_2O \longrightarrow {}^{t}Bu{-}OH + H_3O^+ \\
\hline
\text{Overall:} & {}^{t}Bu{-}Br + H_2O \longrightarrow {}^{t}Bu{-}OH + HBr
\end{array}$$

We know that the formation of the carbocation is much slower than the other two, and hence the rate law is equal to that of the first step to a very good approximation:

$$r = k[{}^{t}BuBr] \tag{4.16}$$

Note that $[H_2O]$ does not enter the rate law despite the fact that it is a reactant in the overall reaction. This is an example of the rate-determining step approximation, which we will see later in more detail.

Species that are generated in the course of a reaction but do not appear in the overall reaction or in the rate law are **reaction intermediates**. Reaction intermediates are stable but highly reactive and short-lived molecular species that are generated and almost immediately consumed. (However, the life time of intermediates depends on the particularities of the reaction—some of them are quite long lived.) The carbocation in the S_N1 reaction is an example of an intermediate. Note that intermediates are different from transition states, since the latter are not stable chemical species because they do not correspond to a minimum of the potential energy profile. Under certain conditions, intermediates may be observed or trapped by interfering reactions or detected using spectroscopic techniques. This is a common experimental method to investigate the mechanism of a chemical reaction.

There are only a few types of elementary reactions. The number of molecules involved in an elementary reaction is called the **molecularity**. Elementary reactions can be **unimolecular**:

$$\mathrm{A} \longrightarrow \cdots \tag{4.17}$$

with rate law $r = k[\mathrm{A}]$, **bimolecular**:

$$\mathrm{A} + \mathrm{B} \longrightarrow \cdots \tag{4.18}$$

with rate law $r = k[\mathrm{A}][\mathrm{B}]$, and **termolecular**:

$$\mathrm{A} + \mathrm{B} + \mathrm{M} \longrightarrow \cdots \tag{4.19}$$

with rate law $r = k[\mathrm{A}][\mathrm{B}][\mathrm{M}]$. Termolecular steps are rarer than the others because a three-molecule collision has relatively low probability of occurring, but they are nonetheless possible. Often, termolecular steps involve a species that does not change chemically in the reaction. For instance, if two atoms collide to form a diatomic molecule, a third molecule may assist by taking away part of the energy, so that the released energy does not immediately dissociate the newly formed diatomic molecule.

The very unlikely chance of four or more molecules colliding rules out any other possible elementary reactions. A corollary of this fact is that an overall reaction with a rate law or an stoichiometry other than the three mentioned above is necessarily a composite reaction. However, a simple rate law is no guarantee that a reaction is elementary. An example is the hydrogenation of iodine (Eq. 4.11), which is composite despite the rate law being the same as an elementary bimolecular reaction. (In fact, for a long time this reaction was thought to be elementary.)

If the mechanism for a reaction is known, then the differential rate law follows from the application of the above results to its elementary steps (we will see some examples later). From the differential rate law, the concentrations of all species as a function of time can be derived. Hence, the mechanism gives complete information about the concentration of all species involved in a given reaction as a function of time, as well as the response of the reaction rate to changes in the reaction conditions (e.g. temperature). When studying an unknown reaction, researchers need to follow the reverse process, from concentrations and rates as a function of time they need to propose a mechanism for the reaction. This is much harder and constitutes an important research area in chemistry. Also, strictly speaking, a mechanism for a reaction is never proven because it is always possible that new experimental evidence for the same reaction is not compatible with it.

Gathering experimental kinetic data about an unknown reaction is a complex task due to experimental uncertainties, the appearance of side-reactions and the difficulty in interpreting the experimental results. In the first step of an experimental kinetic study, information is gathered about the concentration of reactants and products over time in order to build a rate law. The measurements can be carried out via **chemical methods** (for instance, by stopping the reaction and analyzing the results chemically) or with **physical methods**. The latter include spectroscopic techniques, or measurements of changes in pressure, optical rotation, pH, conductivity, and other properties, depending on the nature of reactants and products. Likewise, the reaction may be carried out in a closed vessel (the **static method**) or in an open container where reactants come in and products flow out (the **flow method**). There are hybrids of both approaches, such as the **stopped-flow method**, which is used to study very fast reactions.

Regarding how the rate law is derived from the experimental concentration data, there are again several methods used to determine partial reaction orders. A common approach is the

isolation method. In this approach, all reactants except for one are used in large excess. For instance in the following rate law, we use an excess of B, which causes that $[\mathrm{B}] \approx [\mathrm{B}]_0$ throughout the experiment:

$$r = k[\mathrm{A}][\mathrm{B}]^2 \approx k'[\mathrm{A}] \tag{4.20}$$

$$k' = k[\mathrm{B}]_0^2 \tag{4.21}$$

Since the concentration of B is approximately constant, the rate law simplifies to a **pseudo-first order** reaction. In this expression, k' is called the **effective rate constant**.

Another approach is the **method of initial rates**, typically used in combination with the isolation method. In this case, we measure only the initial rate of a reaction and we vary the initial concentrations of each of the reactants. For instance, if the initial rate is:

$$r_0 = k'[\mathrm{A}]_0^\alpha \tag{4.22}$$

then the partial order of A can be obtained by plotting the logarithm of the measured initial reaction rates against the logarithm of the concentration:

$$\ln r_0 = \ln k' + \alpha \ln[\mathrm{A}]_0 \tag{4.23}$$

Naturally, more complex approaches need to be used if the reaction rate does not conform to Eq. 4.10. Also, the method of the initial rates will not detect a dependence of the rate on the presence of some product, as is the case in the hydrogenation of $\mathrm{Br_2}$ (Eq. 4.14)

Finally, the **half-life method** (or fractional-life method) is based on measuring the time it takes for the concentration of a reactant to reduce to half (or a fraction) of its initial value. As we shall see, this time interval (the **half-life**), can then be related to the rate law.

The rate law of a chemical reaction may involve species other than reactants and products. For instance, the oxidation of sulfur dioxide in the presence of NO:

$$2\,\mathrm{SO_2} + \mathrm{O_2} \xrightarrow{\mathrm{NO}} 2\,\mathrm{SO_3} \tag{4.24}$$

has a rate law:

$$r = k[\mathrm{O_2}][\mathrm{NO}] \tag{4.25}$$

Note that the NO species does not appear as reactant or product in the global reaction, but it appears in the rate law and it speeds up the reaction significantly. This is an example of a **catalyst**. A catalyst is a species that accelerates the rate of a reaction but that is neither consumed nor generated during the reaction. A catalyst works by providing an alternate mechanism that is faster than the mechanism the reaction would follow in its absence. A catalyst does not modify the thermodynamics of a reaction (i.e. its $\Delta_r G^\circ$, its equilibrium constant, or the equilibrium concentrations) but it does increase the rate at which equilibrium is reached. Note that, since a catalyst provides a new mechanism for the reaction, if that reaction is reversible, the catalyst also speeds up the reverse reaction. For instance, $\mathrm{H^+}$ catalyzes the esterification of a carboxylic acid but also the hydrolysis of the corresponding ester.

Another concept is that of an **inhibitor**, which is a species that decreases the reaction rate when present. An inhibitor can be a negative catalyst if it does not appear in the overall reaction. However, reaction products that decrease the reaction rate (e.g. HBr in the hydrogenation of bromine, Eq. 4.14) or species that sequester reactants or intermediates via side reactions are also considered inhibitors.

4.3 Integrated Rate Laws

The differential rate law (Eq. 4.8) gives the reaction rate in terms of the concentrations of all species in the system and temperature at any given time. In order to predict the evolution of the concentration of a given species with time, we need to first write the rate law as a differential equation involving the concentration of reactants and products. For instance, for reactant A we can write:

$$-\frac{1}{a}\frac{d[\mathrm{A}]}{dt} = f([\mathrm{A}],[\mathrm{B}],\ldots) \tag{4.26}$$

If we write the corresponding equation for all species involved in the reaction, we obtain a set of differential equations, which can be solved (usually employing numerical methods) to yield the concentration as a function of time ($[\mathrm{A}](t)$, $[\mathrm{B}](t)$,…) and of the initial conditions of the reaction ($[\mathrm{A}]_0$, $[\mathrm{B}]_0$,…). By doing this, we can predict the evolution of the concentrations of all species in the system with time. The set of concentrations as function of time and initial conditions is the **integrated rate law**, and it is instrumental in deriving a reaction mechanism from experimental observations.

Integrated rate laws for reactions with simple differential rate laws can be found analytically by solving the differential rate law directly. We examine several examples below. In more complex cases, we resort to approximations or numerical methods. In all cases, we will assume that temperature and volume are constant.

4.3.1 Zeroth-order Reactions

A zeroth-order reaction:

$$\mathrm{aA} + \cdots \longrightarrow \mathrm{cC} + \cdots \tag{4.27}$$

has a rate that is constant in time:

$$r = k \tag{4.28}$$

The differential rate law can be integrated directly for any reactant or product. For instance, for A:

$$-\frac{1}{a}\frac{d[\mathrm{A}]}{dt} = k \tag{4.29}$$

$$d[\mathrm{A}] = -akdt$$
$$\int_{[\mathrm{A}]_0}^{[\mathrm{A}]} d[\mathrm{A}] = -\int_0^t akdt$$
$$[\mathrm{A}] - [\mathrm{A}]_0 = -akt$$

from where the integrated rate law is:

$$[\mathrm{A}] = [\mathrm{A}]_0 - akt \tag{4.30}$$

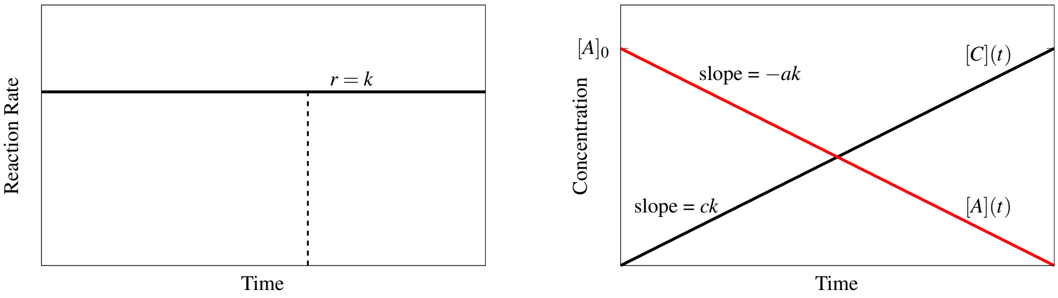
Therefore, the concentration of any reactant decreases linearly with time. Likewise, for any product C, the concentration increases linearly:

$$[\mathrm{C}] = [\mathrm{C}]_0 + ckt \tag{4.31}$$

Typical curves for $r(t)$ and concentration as a function of time are shown in Figure 4.2.

Zeroth order kinetics are typical of chemical reactions that are catalyzed by a compound present in small quantities compared to the substrate, and for which the reaction in absence of said catalyst does not occur. In a way, the amount of catalyst determines the number of “reaction sites” and, once all of these sites are saturated, the rate of the reaction becomes a

Figure 4.2: Rate (left) and concentrations as a function of time (right) in a zeroth order reaction.



constant given by the activity of the catalyst since there is a lot more reactant molecules than the reaction sites can process. Two typical examples of this are heterogeneous catalysis and enzymatic reactions.

In heterogeneous catalysis, a solid catalyst is added to the system, and the reaction occurs on its surface. This contrasts with homogeneous catalysis, in which the catalyst and the reactive species are all in the same phase. The application of heterogeneous catalysis is very common in the chemical industry. One of the most important industrial chemical reactions, the Haber-Bosch process for the synthesis of ammonia, is an example of heterogeneous catalysis:

$$3\,\mathrm{H_2} + \mathrm{N_2} \xrightarrow{\mathrm{FeO}_x} 2\,\mathrm{NH_3} \tag{4.32}$$

where the catalyst is iron oxide. This reaction is the main step in the manufacture of fertilizers, which usually employ ammonium nitrate or urea, both prepared from ammonia. The reverse Haber-Bosch process, catalyzed by elemental molybdenum, is a zeroth order reaction.

Another example of heterogeneous catalysis in industry is the oxidation of SO_2 to SO_3 in the presence of vanadium pentoxide:

$$\mathrm{SO_2} + \tfrac{1}{2}\,\mathrm{O_2} \xrightarrow{\mathrm{V_2O_5}} \mathrm{SO_3} \tag{4.33}$$

which is a key intermediate step in the manufacture of sulfuric acid, the most abundantly manufactured chemical worldwide.

Zeroth-order kinetics caused by limited reaction sites are also observed in many enzymatic reactions. Enzymes are extremely efficient biological catalysts. Enzymes are usually proteins, and are present in very small quantities. If the substrate concentration is high enough, then the enzymes become saturated and the enzymatic reaction reaches its maximum rate (see the Michaelis-Menten mechanism below). Under those conditions, the reaction is zeroth-order. A good example is the human alcohol dehydrogenase, which converts ethanol to acetaldehyde in the liver (and very quickly to other chemicals, since acetaldehyde is also very toxic). This reaction is zeroth order: an average liver processes a concentration of about 0.16 g/l of alcohol in blood per hour, regardless of the actual alcohol content in blood.

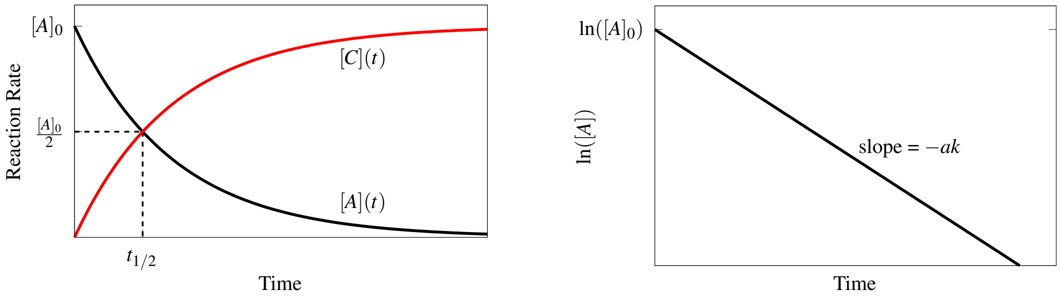
An important concept to characterize chemical reactions is the **half-life** ($t_{1/2}$). It is defined as the amount of time necessary for the reactant concentration to decrease to half its initial value:

$$[\mathrm{A}]_{t_{1/2}} = \frac{[\mathrm{A}]_0}{2} \tag{4.34}$$

In the case of a zeroth order reaction:

$$\frac{[\mathrm{A}]_0}{2} = [\mathrm{A}]_0 - akt_{1/2} \tag{4.35}$$

Figure 4.3: Concentration as a function of time in a first-order reaction.



from where:

$$t_{1/2} = \frac{[\mathrm{A}]_0}{2ak} \tag{4.36}$$

In this case, the half-life is proportional to the initial concentration. Half-lives are used in pharmacology to track the elimination of drugs and in characterizing the radioactive decay of unstable isotopes. The half-life is the time it takes for a drug/radioactive substance to decrease its (radio)activity by half. Half lives are also used in the half-life method, to determine partial orders of a chemical reaction.

4.3.2 First-order Reactions

A first-order reaction has a rate that is proportional to the concentration of one of the reactants:

$$r = -\frac{1}{a}\frac{d[\mathrm{A}]}{dt} = k[\mathrm{A}] \tag{4.37}$$

This differential equation is separable and can be solved straightforwardly:

$$\frac{d[\mathrm{A}]}{[\mathrm{A}]} = -akdt$$

$$\int_{[\mathrm{A}]_0}^{[\mathrm{A}]} \frac{d[\mathrm{A}]}{[\mathrm{A}]} = -\int_0^t akdt$$

$$\ln[\mathrm{A}]\Big|_{[\mathrm{A}]_0}^{[\mathrm{A}]} = \ln[\mathrm{A}] - \ln[\mathrm{A}]_0 = \ln\left(\frac{[\mathrm{A}]}{[\mathrm{A}]_0}\right) = -akt$$

Solving for the reactant concentration gives the first-order integrated rate law:

$$[\mathrm{A}] = [\mathrm{A}]_0 e^{-akt} \tag{4.38}$$

In a first order reaction, the concentration of A decreases exponentially and, likewise, the concentration of product increases exponentially, as shown in Figure 4.3. If a reaction has first-order kinetics, then a plot of ln[A] as a function of t gives a straight line, and the rate constant (k) can be extracted from the slope:

$$\ln[\mathrm{A}] = \ln[\mathrm{A}]_0 - akt \tag{4.39}$$

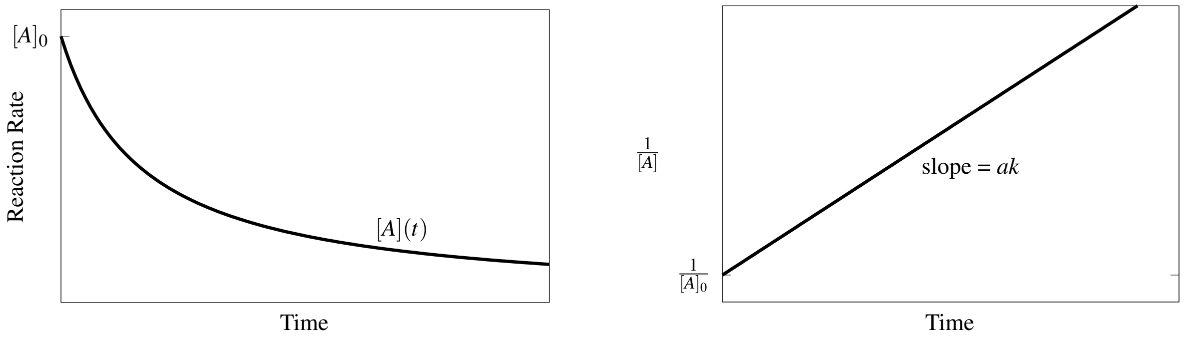
as shown in Figure 4.3 (right).

First-order reactions are typical in unimolecular decomposition reactions in which the slow step is the cleavage of a bond in the starting molecule. For example:

$$2\,\mathrm{N_2O}_{5(g)} \longrightarrow 4\,\mathrm{NO}_{2(g)} + \mathrm{O}_{2(g)} \tag{4.40}$$

Another example of first-order reaction is the S_N1 substitution reaction. In this case, the slow step is the formation of the carbocation, which is first-order in the substrate.

Figure 4.4: Concentration as a function of time in a second-order reaction.



To obtain the half-life, we substitute $[\mathrm{A}] = [\mathrm{A}]_0/2$ and $t = t_{1/2}$ in Eq. 4.38:

$$\frac{[\mathrm{A}]_0}{2} = [\mathrm{A}]_0 e^{-akt_{1/2}} \tag{4.41}$$

Solving for the half-life gives:

$$t_{1/2} = \frac{\ln 2}{ak} \tag{4.42}$$

Therefore, **in a first-order reaction, the half-life is constant**. It does not depend on the initial reactant concentration.

First-order reactions are also the kinetics of radioactive decay. The fact that the half-life does not depend on the initial concentration means that it carries the same information as the rate constant and it characterizes the rate of the reaction completely. This is why one usually talks about the half-life of radioactive elements instead of their rate constant, which has a much less intuitive interpretation.

A quantity related to the half-life that is also used in first-order reactions (particularly in the context of radioactive decay) is the mean lifetime (τ), which is similar but different from the half-life. The definition is:

$$\tau = \frac{1}{ak} \tag{4.43}$$

such that it is possible to write the concentration as:

$$[\mathrm{A}] = [\mathrm{A}]_0 e^{-t/\tau} \tag{4.44}$$

and therefore:

$$t_{1/2} = \tau \ln 2 \tag{4.45}$$

By examining the probability of decomposition of a given molecule as a function of time, it is possible to show that the mean lifetime is the average survival time of reactant molecule. As in the case of the half-life, the mean lifetime of a first-order reaction completely characterizes its kinetics.

4.3.3 Second-order Reactions

There are two possibilities for the rate law of a second-order reaction: $r = k[\mathrm{A}]^2$ and $r = k[\mathrm{A}][\mathrm{B}]$. Let us consider the former first:

$$r = -\frac{1}{a}\frac{d[\mathrm{A}]}{dt} = k[\mathrm{A}]^2 \tag{4.46}$$

This differential equation is separable and it is integrated as follows:

$$\int_{[\mathrm{A}]_0}^{[\mathrm{A}]} \frac{d[\mathrm{A}]}{[\mathrm{A}]^2} = -\int_0^t ak dt \tag{4.47}$$

$$\left[-\frac{1}{[\mathrm{A}]}\right]_{[\mathrm{A}]_0}^{[\mathrm{A}]} = -\left(\frac{1}{[\mathrm{A}]} - \frac{1}{[\mathrm{A}]_0}\right) = -akt \tag{4.48}$$

from where the integrated rate law is:

$$\frac{1}{[\mathrm{A}]} = \frac{1}{[\mathrm{A}]_0} + akt \tag{4.49}$$

$$[\mathrm{A}] = \frac{[\mathrm{A}]_0}{1 + [\mathrm{A}]_0 akt} \tag{4.50}$$

A representation of concentration against time is shown in Figure 4.4. If we have experimental data for a second-order reaction of this kind, then we can can derive the rate constant by plotting the inverse of the concentration as a function of time, which results in a straight line (Figure 4.4).

Second order reactions are typical of reactions with a bimolecular rate-determining step. Examples include the decomposition of NO_2:

$$2\,\mathrm{NO}_{2(g)} \longrightarrow 2\,\mathrm{NO}_{(g)} + \mathrm{O}_{2(g)} \tag{4.51}$$

and the S_N2 substitution reaction. The half-life of this reaction is:

$$t_{1/2} = \frac{1}{ak[\mathrm{A}]_0} \tag{4.52}$$

As in the case of the zeroth-order reaction, the half-life depends on the initial concentration, which greatly diminishes the usefulness of this measure.

Let us consider now the second-order reaction involving unlike reactants,

$$\mathrm{A} + \mathrm{B} \longrightarrow \cdots \tag{4.53}$$

where for simplicity we assumed that the stoichiometric coefficients are one. The rate in terms of [A] is:

$$r = -\frac{d[\mathrm{A}]}{dt} = k[\mathrm{A}][\mathrm{B}] \tag{4.54}$$

We define x as the concentration that measures the progress of the reaction:

$$[\mathrm{A}] = [\mathrm{A}]_0 - x \tag{4.55}$$

$$[\mathrm{B}] = [\mathrm{B}]_0 - x \tag{4.56}$$

Substituting in the rate law, we obtain:

$$-\frac{d[\mathrm{A}]}{dt} = \frac{dx}{dt} = k([\mathrm{A}]_0 - x)([\mathrm{B}]_0 - x) \tag{4.57}$$

Integrating between initial time and t, we have:

$$kt = \int_0^x \frac{dx}{([\mathrm{A}]_0 - x)([\mathrm{B}]_0 - x)} \tag{4.58}$$

The corresponding indefinite integral is solved by using the partial fractions method:

$$\frac{1}{(a-x)} - \frac{1}{(b-x)} = \frac{b - x - (a-x)}{(a-x)(b-x)} = \frac{b-a}{(a-x)(b-x)} \tag{4.59}$$

from where the integral we need is:

$$\begin{aligned}\int \frac{dx}{(a-x)(b-x)} &= \frac{1}{b-a}\left[\int \frac{dx}{a-x} - \int \frac{dx}{b-x}\right] \\ &= \frac{1}{b-a}\left[-\ln(a-x)+\ln(b-x)\right] = \frac{1}{b-a}\ln\left(\frac{b-x}{a-x}\right)\end{aligned} \tag{4.60}$$

The definite integral in Eq. 4.58 is therefore transformed into:

$$kt = \frac{1}{[\mathrm{B}]_0-[\mathrm{A}]_0}\ln\left(\frac{[\mathrm{B}]_0-x}{[\mathrm{A}]_0-x}\right)\Bigg|_0^x = \frac{1}{[\mathrm{B}]_0-[\mathrm{A}]_0}\left[\ln\left(\frac{[\mathrm{B}]_0-x}{[\mathrm{A}]_0-x}\right)-\ln\left(\frac{[\mathrm{B}]_0}{[\mathrm{A}]_0}\right)\right] \tag{4.61}$$

Using the relationship between the reactant concentrations and x (Eq. 4.55 and Eq. 4.56) yields:

$$kt = \frac{1}{[\mathrm{B}]_0-[\mathrm{A}]_0}\left[\ln\left(\frac{[\mathrm{B}]}{[\mathrm{A}]}\right)-\ln\left(\frac{[\mathrm{B}]_0}{[\mathrm{A}]_0}\right)\right] = \frac{1}{[\mathrm{B}]_0-[\mathrm{A}]_0}\ln\left(\frac{[\mathrm{B}]/[\mathrm{B}]_0}{[\mathrm{A}]/[\mathrm{A}]_0}\right) \tag{4.62}$$

$$kt([\mathrm{B}]_0-[\mathrm{A}]_0) = \ln\left(\frac{[\mathrm{B}]/[\mathrm{B}]_0}{[\mathrm{A}]/[\mathrm{A}]_0}\right) \tag{4.63}$$

which is the integrated rate law for this reaction. Representing the logarithm on the right hand side (the concentrations of B and A are related by Eq. 4.55 and Eq. 4.56) as a function of time gives a straight line, and from the slope we can extract the rate constant.

4.3.4 Reactions of Order n

We consider now the case of a general rate law of order n involving a single reactant:

$$r = -\frac{1}{a}\frac{d[\mathrm{A}]}{dt} = k[\mathrm{A}]^n \tag{4.64}$$

where $n \neq 1$ (the $n = 1$ case is a first-order reaction, which we already considered). This differential equation is separable and is integrated directly:

$$-akt = \int_{[\mathrm{A}]_0}^{[\mathrm{A}]} \frac{d[\mathrm{A}]}{[\mathrm{A}]^n} = \left[\frac{[\mathrm{A}]^{-n+1}}{-n+1}\right]_{[\mathrm{A}]_0}^{[\mathrm{A}]} \tag{4.65}$$

Solving for the concentration, we find:

$$\frac{1}{[\mathrm{A}]^{n-1}} = \frac{1}{[\mathrm{A}]_0^{n-1}} + akt(n-1) \tag{4.66}$$

The half-life is obtained by substituting $[\mathrm{A}] = [\mathrm{A}]_0/2$ and solving for $t_{1/2}$:

$$\frac{2^{n-1}-1}{[\mathrm{A}]_0^{n-1}} = akt_{1/2}(n-1) \tag{4.67}$$

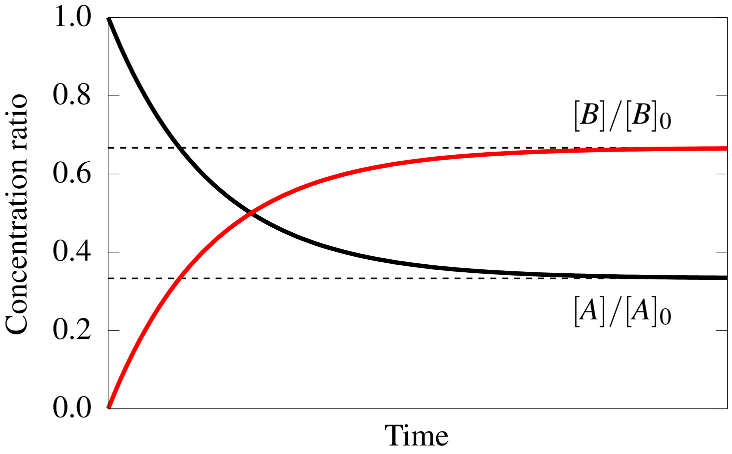
$$t_{1/2} = \frac{2^{n-1}-1}{ak(n-1)[\mathrm{A}]_0^{n-1}} \tag{4.68}$$

And taking logarithms we arrive at:

$$\ln(t_{1/2}) = \ln\left(\frac{2^{n-1}-1}{ak(n-1)}\right) - (n-1)\ln[\mathrm{A}]_0 \tag{4.69}$$

Therefore, a representation of $\ln(t_{1/2})$ with respect to $\ln[\mathrm{A}]_0$ gives a straight line whose slope gives the reaction order directly. Note that in the case of a first-order reaction ($n = 1$) we have

Figure 4.5: Concentration fractions of reactant and product in a reversible reaction.



seen that $t_{1/2}$ is constant and independent of the initial concentration. Hence, even though we derived Eq. 4.69 for cases other than $n = 1$, a linear least-squares fit of $\ln(t_{1/2})$ against $\ln[\mathrm{A}]_0$ gives the correct reaction order, even in the case of a first-order reaction. This equation is useful in determining the partial reaction rate of a reaction for a certain species, a procedure that is known as the **method of half-lives**. To do so, we measure the half-life of a given reactant at varying initial concentrations and with fixed (and possibly high) concentrations of the other reactants. Then, we plot $\ln(t_{1/2})$ versus $\ln[\mathrm{A}]_0$. If the resulting plot is a straight line, the slope gives the partial reaction order. If the plot is not a straight line, then the rate law is more complex and there is no partial order for that reactant. A more common variant of this technique is the fractional-life method, in which a fraction other than 1/2 (usually smaller) is employed.

4.3.5 Reversible Reactions

Now we will examine some model composite reactions. To find the rate law of a composite reaction, we combine the simple rate laws for each of the elementary steps in order to find the time evolution of reactants and products.

A **reversible reaction** consists of a direct and a reverse reaction between two species A and B:

$$\mathrm{A} \underset{k_i}{\overset{k_d}{\rightleftharpoons}} \mathrm{B} \tag{4.70}$$

The direct reaction has rate constant k_d and the reverse reaction has rate constant k_i, and both are elementary first-order reactions. Because both species convert into each other, given enough time the system will achieve a state of equilibrium, corresponding to concentrations equal to those predicted by the equilibrium constant equation.

At equilibrium, the rate of the direct reaction equals the rate of the reverse reaction, so:

$$k_d[\mathrm{A}]_{\mathrm{eq}} = k_i[\mathrm{B}]_{\mathrm{eq}} \tag{4.71}$$

$$K_{\mathrm{c}}^{\circ} = \frac{k_d}{k_i} = \frac{[\mathrm{B}]_{\mathrm{eq}}/c^{\circ}}{[\mathrm{A}]_{\mathrm{eq}}/c^{\circ}} = \frac{[\mathrm{B}]_{\mathrm{eq}}}{[\mathrm{A}]_{\mathrm{eq}}} \tag{4.72}$$

Focusing on reactant A, we see from the mechanism that it is generated by the reverse reaction, at a rate equal to $k_i[\mathrm{B}]$ and it is consumed by the direct reaction at a rate equal to $k_d[\mathrm{A}]$. Therefore, the overall change in the concentration of A is:

$$\frac{d[\mathrm{A}]}{dt} = k_i[\mathrm{B}] - k_d[\mathrm{A}] \tag{4.73}$$

and the rate of the reaction is minus this quantity.

As in the case of a bimolecular reaction, we define a concentration x that measures the progress of the reaction:

$$[\mathrm{A}] = [\mathrm{A}]_0 - x \tag{4.74}$$

$$[\mathrm{B}] = [\mathrm{B}]_0 + x \tag{4.75}$$

With these definitions, the rate law for this reaction becomes:

$$r = -\frac{d[\mathrm{A}]}{dt} = \frac{dx}{dt} = k_d([\mathrm{A}]_0 - x) - k_i([\mathrm{B}]_0 + x) = (k_d[\mathrm{A}]_0 - k_i[\mathrm{B}]_0) - (k_i + k_d)x \tag{4.76}$$

where we have defined the equilibrium quantities $[\mathrm{A}]_{\mathrm{eq}}$ and $[\mathrm{B}]_{\mathrm{eq}}$. The equilibrium value of x (x_{eq}) is defined by Eq. 4.74 and Eq. 4.75:

$$x_{\mathrm{eq}} = [\mathrm{A}]_0 - [\mathrm{A}]_{\mathrm{eq}} = [\mathrm{B}]_{\mathrm{eq}} - [\mathrm{B}]_0 \tag{4.77}$$

Substituting this value for x_{eq} in the equilibrium condition (Eq. 4.71) leads to:

$$k_d([\mathrm{A}]_0 - x_{\mathrm{eq}}) = k_i([\mathrm{B}]_0 + x_{\mathrm{eq}}) \tag{4.78}$$

$$k_d[\mathrm{A}]_0 - k_i[\mathrm{B}]_0 = (k_d + k_i)x_{\mathrm{eq}} \tag{4.79}$$

Substituting this result in Eq. 4.76, we arrive at:

$$\frac{dx}{dt} = (k_d + k_i)(x_{\mathrm{eq}} - x) \tag{4.80}$$

Integrating:

$$\begin{aligned}(k_d + k_i)t &= \int_0^x \frac{dx}{x_{\mathrm{eq}} - x} = \ln(x_{\mathrm{eq}}) - \ln(x_{\mathrm{eq}} - x) = \ln\left(\frac{x_{\mathrm{eq}}}{x_{\mathrm{eq}} - x}\right) \\ &= \ln\left(\frac{[\mathrm{A}]_0 - [\mathrm{A}]_{\mathrm{eq}}}{[\mathrm{A}]_0 - [\mathrm{A}]_{\mathrm{eq}} - ([\mathrm{A}]_0 - [\mathrm{A}])}\right) = \ln\left(\frac{[\mathrm{A}]_0 - [\mathrm{A}]_{\mathrm{eq}}}{[\mathrm{A}] - [\mathrm{A}]_{\mathrm{eq}}}\right)\end{aligned} \tag{4.81}$$

And the integrated rate law is:

$$[\mathrm{A}] = ([\mathrm{A}]_0 - [\mathrm{A}]_{\mathrm{eq}})e^{-(k_d+k_i)t} + [\mathrm{A}]_{\mathrm{eq}} \tag{4.82}$$

with the equilibrium concentrations given by:

$$x_{\mathrm{eq}} = \frac{k_d[\mathrm{A}]_0 - k_i[\mathrm{B}]_0}{k_d + k_i} \tag{4.83}$$

$$[\mathrm{A}]_{\mathrm{eq}} = [\mathrm{A}]_0 - x_{\mathrm{eq}} \tag{4.84}$$

$$[\mathrm{B}]_{\mathrm{eq}} = [\mathrm{B}]_0 + x_{\mathrm{eq}} \tag{4.85}$$

The concentration of B as a function of time can be derived by taking into account that the balance of mass in this reaction is:

$$[\mathrm{A}]_0 + [\mathrm{B}]_0 = [\mathrm{A}] + [\mathrm{B}] = [\mathrm{A}]_{\mathrm{eq}} + [\mathrm{B}]_{\mathrm{eq}} \tag{4.86}$$

from where:

$$[\mathrm{B}] = ([\mathrm{B}]_0 - [\mathrm{B}]_{\mathrm{eq}})e^{-(k_d+k_i)t} + [\mathrm{B}]_{\mathrm{eq}} \tag{4.87}$$

The rate law for a reversible reaction is similar to a first-order reaction in that it has an exponential factor (see Figure 4.5). However, in this case, the concentrations of reactants and products evolve from their initial values ($[\mathrm{A}]_0$ and $[\mathrm{B}]_0$) to their equilibrium values ($[\mathrm{A}]_{\mathrm{eq}}$ and $[\mathrm{B}]_{\mathrm{eq}}$). The ratio between the equilibrium concentrations is the same as the ratio between the rate coefficients (Eq. 4.71). If k_d is much higher than k_i, then the direct reaction will be much faster and the equilibrium concentration of A will be very small. In the limit of very high k_d/k_i, a normal first-order reaction is recovered, and the reaction becomes irreversible (the reverse reaction happens only negligibly).

4.3.6 Consecutive Reactions

A set of consecutive reactions occurs when two or more elementary unimolecular reactions happen one after the other. In the simplest case, there are only two consecutive reactions:

$$\mathrm{A} \xrightarrow{k_1} \mathrm{B} \xrightarrow{k_2} \mathrm{C} \tag{4.88}$$

The overall reaction is A $\longrightarrow$ C. The B compound is an intermediate in this reaction: it is generated and eventually consumed. How long- or short-lived this intermediate is will depend on the k_2/k_1 ratio of rate constants. If k_2 is much higher than k_1, B has a short life. If k_1 is lower than k_2 then B progressively accumulates until the fact that A is disappearing slows down the first reaction enough for the second reaction to catch up and clear the accumulated B.

The rate of the overall reaction is:

$$r = -\frac{d[\mathrm{A}]}{dt} = \frac{d[\mathrm{C}]}{dt} \tag{4.89}$$

From the mechanism, the rate of generation and consumption of each species is:

$$\frac{d[\mathrm{A}]}{dt} = -k_1[\mathrm{A}] \tag{4.90}$$

$$\frac{d[\mathrm{B}]}{dt} = k_1[\mathrm{A}] - k_2[\mathrm{B}] \tag{4.91}$$

$$\frac{d[\mathrm{C}]}{dt} = k_2[\mathrm{B}] \tag{4.92}$$

For simplicity, let us assume that at $t = 0$ there is only $[\mathrm{A}] = [\mathrm{A}]_0$ present. The first reaction is a simple first-order reaction. Therefore:

$$[\mathrm{A}] = [\mathrm{A}]_0 e^{-k_1 t} \tag{4.93}$$

Substituting this equation in the expression for the time dependence of B gives:

$$\frac{d[\mathrm{B}]}{dt} + k_2[\mathrm{B}] = k_1[\mathrm{A}]_0 e^{-k_1 t} \tag{4.94}$$

which is the differential equation we must solve to find the integrated rate law.

This is an example of a linear first-order differential equation. To solve one of these, you need to put it in the form:

$$\frac{dy}{dx} + P(x)y = Q(x) \tag{4.95}$$

and then multiply both sides by an "integrating factor" $\exp(\int P(x)dx)$. By doing this, we convert the equation into:

$$\frac{d[e^{\int P(x)dx} y]}{dx} = Q(x)e^{\int P(x)dx} \tag{4.96}$$

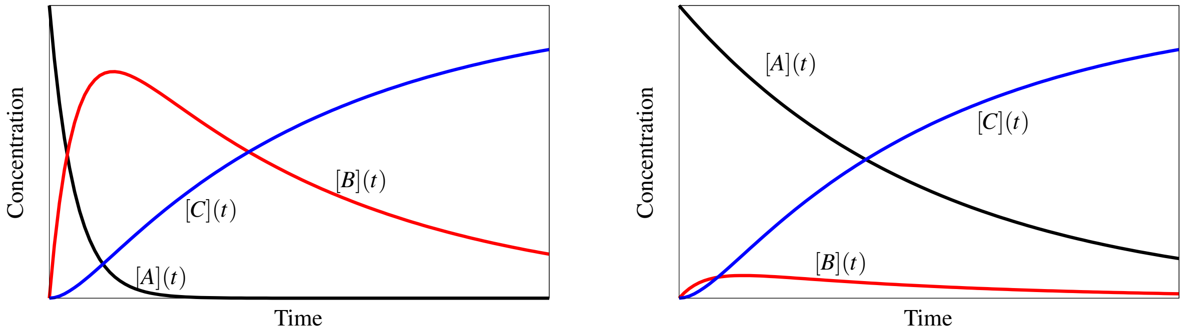
which is separable and can be readily solved. In our case (Eq. 4.94), $P(x) = k_2$ and the integrating factor is simply $e^{k_2 t}$, which gives:

$$\frac{d[[\mathrm{B}]e^{k_2 t}]}{dt} = k_1[\mathrm{A}]_0 e^{(k_2 - k_1)t} \tag{4.97}$$

and integrating (note that $[\mathrm{B}]_0 = 0$):

$$[\mathrm{B}]e^{k_2 t} = \left.\frac{k_1[\mathrm{A}]_0 e^{(k_2-k_1)t}}{k_2 - k_1}\right|_0^t = \frac{k_1[\mathrm{A}]_0 (e^{(k_2-k_1)t} - 1)}{k_2 - k_1} \tag{4.98}$$

Figure 4.6: Concentrations of the three species in a consecutive reaction. Left: when the second reaction is much slower than the first ($k_1 \gg k_2$). Right: when the first reaction is much slower than the second ($k_2 \gg k_1$).



Solving for the concentration of the intermediate:

$$[\mathrm{B}] = \frac{k_1[\mathrm{A}]_0(e^{-k_1 t} - e^{-k_2 t})}{k_2 - k_1} \tag{4.99}$$

To obtain the concentration of C, we apply the balance of mass during the reaction. That is, at any time all of the initial concentration of A ($[\mathrm{A}]_0$) must transform to either A, B, or C. Therefore:

$$\begin{aligned} [\mathrm{C}] = [\mathrm{A}]_0 - [\mathrm{B}] - [\mathrm{A}] &= [\mathrm{A}]_0 \left[1 - e^{-k_1 t} - \frac{k_1(e^{-k_1 t} - e^{-k_2 t})}{k_2 - k_1}\right] \\ &= [\mathrm{A}]_0 \left[1 - \frac{k_2}{k_2 - k_1} e^{-k_1 t} + \frac{k_1}{k_2 - k_1} e^{-k_2 t}\right] \end{aligned} \tag{4.100}$$

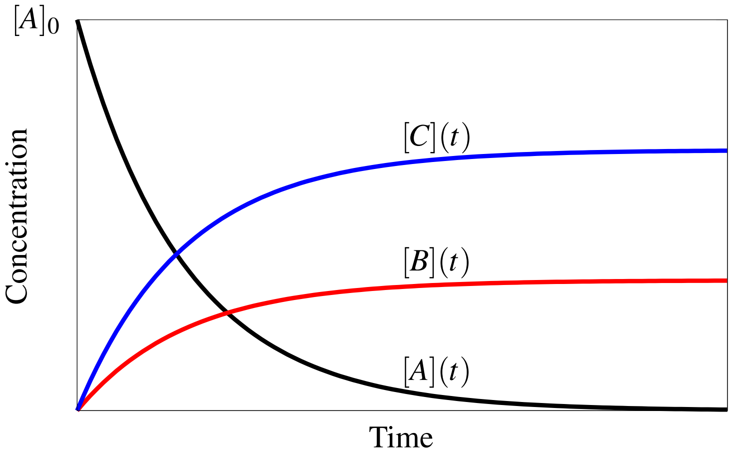
Figure 4.6 shows typical concentration profiles in a set of two consecutive reactions. In the case $k_1 \gg k_2$ (left), the intermediate accumulates and only after a certain time its concentration starts decreasing when the decrease in [A] compensates for the higher rate constant of the first reaction. At that point the intermediate concentration reaches a maximum and the rate of generation of product accelerates. This is an example of a chemical reaction with an **induction period**: an initial stage in which the reaction is slow, followed by an increase in rate. In the case $k_2 \gg k_1$ (right), the intermediate is very short lived because it is consumed almost as it is generated. In this case, note that the concentration of intermediate is almost constant in time after a small stabilization period. The fact that a short-lived intermediate behaves in this way is the basis for the steady-state approximation (see below), in which we assume that the concentration of short-lived intermediates is approximately constant.

Consecutive reactions are very common in the study of radioactive decay. Very unstable radioactive isotopes decay to other lighter isotopes that also radioactive. This results in **decay chains** (or series) throughout the periodic table. These decay chains relate isotopes with differences in their atomic mass of 4 (an alpha particle) but can also involve transformations between isotopes with the same atomic mass (beta decay, in which a proton transform into a neutron or *vice versa*). The four distinct decay chains end in the stable isotopes of lead ($A = 206$, 207, 208) and thallium ($A = 205$).

4.3.7 Competitive Reactions

In a set of competitive (or parallel) reactions, the reactions involved share the same reactant but lead to different products. This case is important in synthetic chemistry because there are many cases in which interfering side-reactions are present and we want to be able to control the reaction conditions in order to minimize the synthesis of undesired products.

Figure 4.7: Concentrations of the three species in a set of two competitive reactions with $k_2 = 2k_1$.



Let us consider the simple case of two competitive reactions:

$$\mathrm{A} \xrightarrow{k_1} \mathrm{B}$$
$$\mathrm{A} \xrightarrow{k_2} \mathrm{C}$$

The rate of consumption of A is given by:

$$\frac{d[\mathrm{A}]}{dt} = -k_1[\mathrm{A}] - k_2[\mathrm{A}] = -(k_1 + k_2)[\mathrm{A}] \tag{4.101}$$

This is a rate law that we have already seen: it is a first-order reaction with rate constant $k_1 + k_2$. Therefore, the integrated rate law is:

$$[\mathrm{A}] = [\mathrm{A}]_0 e^{-(k_1+k_2)t} \tag{4.102}$$

On the other hand, the rate of generation of the products is:

$$\frac{d[\mathrm{B}]}{dt} = k_1[\mathrm{A}] = k_1[\mathrm{A}]_0 e^{-(k_1+k_2)t} \tag{4.103}$$
$$\frac{d[\mathrm{C}]}{dt} = k_2[\mathrm{A}] = k_2[\mathrm{A}]_0 e^{-(k_1+k_2)t} \tag{4.104}$$

These differential equations are separable and are readily integrated to give (we assume $[\mathrm{B}]_0 = [\mathrm{C}]_0 = 0$ for simplicity):

$$[\mathrm{B}] = \frac{k_1[\mathrm{A}]_0}{k_1 + k_2}\left(1 - e^{-(k_1+k_2)t}\right) \tag{4.105}$$
$$[\mathrm{C}] = \frac{k_2[\mathrm{A}]_0}{k_1 + k_2}\left(1 - e^{-(k_1+k_2)t}\right) \tag{4.106}$$

The profiles for the concentrations as a function of time are shown in Figure 4.7. The concentration of A decays exponentially as in a normal first order reaction. However, part of the A that is consumed goes to B and part goes to C. The fraction between the amount of B and C generated can be found by noting that their concentrations have a constant ratio equal to the ratio of the corresponding rate constants:

$$\frac{[\mathrm{B}]}{[\mathrm{C}]} = \frac{k_1}{k_2} \tag{4.107}$$

This result is very useful to predict the selectivity of a set of competitive reactions in organic chemistry and to minimize the loss of yield due to side reactions. If the competitive reactions are irreversible:

$$\mathrm{C} \longleftarrow \mathrm{A} \longrightarrow \mathrm{B}$$

or the reaction is carried out at low temperature or during a short time, then the ratio of the product concentrations is the same as the ratio of the rate constants, as in the equation above. When this happens, we say the reaction is under **kinetic control**. If the reactions are reversible:

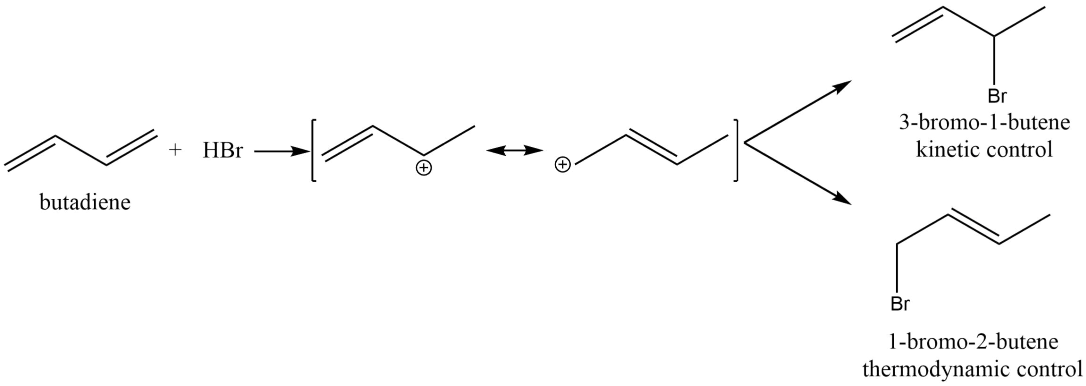
$$\mathrm{C} \rightleftharpoons \mathrm{A} \rightleftharpoons \mathrm{B}$$

which is favored by high temperatures and long reaction times, then the system evolves to the (thermodynamic) equilibrium state, which is determined by the equilibrium constant calculated from the $\Delta_r G^\circ = G^\circ_{\mathrm{B}} - G^\circ_{\mathrm{C}}$ of the two products:

$$\frac{[\mathrm{B}]_{\mathrm{eq}}}{[\mathrm{C}]_{\mathrm{eq}}} = K_{\mathrm{eq}} = e^{-\Delta_r G^\circ/RT} \tag{4.108}$$

In that case, we say the system is under **thermodynamic control**.

An example of kinetic *vs.* thermodynamic control is the electrophilic addition of HBr to 1,3-butadiene:



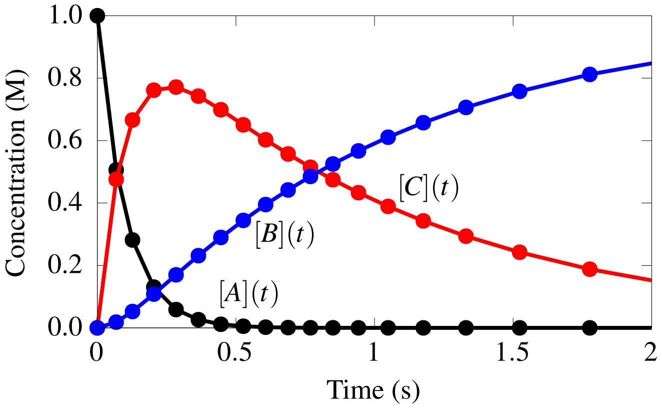
There are two possible products in this reaction: one with the Br attached to the primary carbon, and one with the Br bonded to the secondary carbon. The reaction starts by forming the more stable carbocation by adding a proton to the reactant following Markovnikov's rule (i.e. the H goes to the least-substituted carbon). This intermediate is resonant and the Br^- anion can attach itself to either the primary (1-bromo-2-butene) or the secondary (3-bromo-1-butene) carbon, since both carbon atoms bear some positive partial charge. The secondary carbon is more positively charged because it is the most stable resonant form due to favorable induction and hyperconjugation effects. Hence the rate constant for the generation of 3-bromo-1-butene is lower than that for 1-bromo-2-butene, and therefore 3-bromo-1-butene is the kinetic control product. However, 1-bromo-2-butene is more stable because the bromine atom is in a less sterically crowded position and the double bond is not terminal, so 1-bromo-2-butene is the thermodynamic control product.

4.4 Rate Laws of Complex Composite Reactions

Finding the rate law of a composite reaction comprising multiple elementary steps leads to a set of coupled differential equations and finding the concentration of all species as a function of time quickly becomes an intractable mathematical problem. Consider, for instance, what happens in the case of more than three consecutive reactions. The nth reaction would use the intermediate concentration resulting from the $(n-1)$th reaction, and the differential equations

Figure 4.8: Left: Example of an octave script to integrate the differential equations for three consecutive first-order reactions. Right: a plot of the resulting concentration *vs.* time curves that result from running the script. Compare to Figure 4.6.

```
function y1 = func(t,y0)
  k1 = 10;
  k2 = 1;
  y1 = zeros(3,1);
  y1(1) = -k1*y0(1);
  y1(2) = k1*y0(1) - k2*y0(2);
  y1(3) = k2*y0(2);
endfunction
y0 = [1 0 0];
[t,y] = ode45(@func,[0 5],y0);
```



get increasingly complicated with each additional step. Likewise, it is often not possible to solve for the concentration of a single species because all differential equations are coupled and all of them have to be solved at the same time.

For these complex cases, there are two possible solutions: numerical methods and simplifying approximations. The former consists of finding the integrated rate law numerically by using approximate integration methods based on discretization. In the numerical approach, we write the differential rate law as:

$$\frac{d\boldsymbol{y}}{dt} = f(\boldsymbol{y}) \tag{4.109}$$

where $\boldsymbol{y}$ is a vector composed of the concentrations of all species in the reaction. The $f(\boldsymbol{y})$ function gives the vector of the derivatives with respect to time, and can be easily obtained by using the rate laws for the elementary steps, as we have seen in the previous examples. If we know the initial concentrations ($\boldsymbol{y}_0$ at $t_0 = 0$), then we can approximate the concentrations after a short time Δt has passed by using the Taylor expansion of $\boldsymbol{y}(t)$:

$$\boldsymbol{y}(t_1) = \boldsymbol{y}_1 \approx \boldsymbol{y}_0 + \left.\frac{d\boldsymbol{y}}{dt}\right|_0 \Delta t = \boldsymbol{y}_0 + f(\boldsymbol{y}_0)\Delta t \tag{4.110}$$

Applying the same procedure, we can calculate the concentration at time $2\Delta t$ from $\boldsymbol{y}_1$:

$$\boldsymbol{y}_2 \approx \boldsymbol{y}_1 + f(\boldsymbol{y}_1)\Delta t \tag{4.111}$$

and, repeating this calculation, we obtain all concentrations as a function of time on a uniform grid of times, up to the completion of the reaction. The points in this uniform grid are separated by a constant Δt step. The concentration *vs.* time data obtained in this manner is somewhat in error because the formulas we used are only approximate but as we make Δt smaller, the curves converge to the correct solution (barring the presence of round-off errors that are a consequence of the finite precision with which numbers are represented on a computer). This is an example of the numerical integration of a set of coupled first-order differential equations using **Euler's method**.

More sophisticated methods for the numerical integration of coupled differential equations are available in open-source and commercial software packages. For instance, Figure 4.8 shows the `octave` script to integrate the set of differential equations that results from the set of consecutive reactions:

$$\mathrm{A} \xrightarrow{k_1} \mathrm{B} \xrightarrow{k_2} \mathrm{C} \tag{4.112}$$

namely:

$$\frac{d[\text{A}]}{dt} = -k_1[\text{A}] \tag{4.113}$$

$$\frac{d[\text{B}]}{dt} = k_1[\text{A}] - k_2[\text{B}] \tag{4.114}$$

$$\frac{d[\text{C}]}{dt} = k_2[\text{B}] \tag{4.115}$$

where, in this case, $\boldsymbol{y} = \{[\text{A}], [\text{B}], [\text{C}]\}$ and the three components in $f(\boldsymbol{y})$ are the right-hand side of these equations. The concentration *vs.* time curves resulting from the numerical integration are shown in the Figure 4.8 (right). Compare these to the analytical solutions in Figure 4.6.

Despite the widespread use of numerical integration software, it is often easier to find the rate law of a composite reaction by using simplifying approximations derived from knowledge about the mechanism. We will see two of these approaches: the rate-determining step and the steady-state approximations.

4.4.1 Rate-Determining Step Approximation

In a reaction mechanism there are steps that are slower (strictly, have lower rate constants) than others. In some mechanisms, we can consider that there is a **rate-determining step** (RDS) that controls the overall rate of the reaction. The RDS must fulfill two conditions: i) have a rate that is significantly lower than the other steps (typically but not necessarily by having a lower rate constant), and ii) play a crucial role in the overall outcome of the reaction, i.e., it acts as a bottleneck and cannot be sidestepped by alternative reaction pathways. The S_N1 reaction is an excellent example of a rate-determining step. Because the formation of the carbocation is so slow compared to the other steps, we can assume that the overall reaction rate is a simple first-order rate law in the concentration of the substrate. The RDS approximation, even in cases more complex than this one, usually leads to major simplifications in the overall rate law of a composite reaction.

Let us consider the diazotization reaction of aniline in nitrous acid to form the phenyldiazonium cation:

$$\text{H}^+ + \text{HNO}_2 + \text{C}_6\text{H}_5\text{NH}_2 \xrightarrow{\text{Br-}} \text{C}_6\text{H}_5\text{N}_2^+ + 2\,\text{H}_2\text{O}$$

The observed rate law for this reaction is:

$$r = k[\text{H}^+][\text{HNO}_2][\text{Br}^-] \tag{4.116}$$

where the bromide ion acts as a catalyst. The proposed mechanism for the reaction is as follows:

$$\text{H}^+ + \text{HNO}_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{H}_2\text{NO}_2^+ \qquad \text{(fast)}$$

$$\text{H}_2\text{NO}_2^+ + \text{Br}^- \xrightarrow{k_2} \text{BrNO} + \text{H}_2\text{O} \qquad \text{(slow)}$$

$$\text{BrNO} + \text{C}_6\text{H}_5\text{NH}_2 \xrightarrow{k_3} \text{C}_6\text{H}_5\text{N}_2^+ + \text{H}_2\text{O} + \text{Br}^- \qquad \text{(fast)}$$

In this reaction, the rate constant for the second step k_2 is much lower than the other three (k_1, k_{-1}, and k_3). Moreover, the second step is the only way to generate the BrNO (nitrosyl bromide) intermediate, which leads directly to product formation in the last step. Hence, the slow step is also a bottleneck. Therefore, both conditions for applying the RDS approximation are met, and we can identify the rate of the reaction with the rate of the slow step:

$$r = k_2[\text{H}_2\text{NO}_2^+][\text{Br}^-] \tag{4.117}$$

Now, we need to find the concentration of the $H_2NO_2^+$ intermediate. Since k_1 and k_{-1} are much higher than k_2, we can assume that the first reaction is in a state of **pre-equilibrium**:

$$k_1[H^+][HNO_2] = k_{-1}[H_2NO_2^+] \tag{4.118}$$

Substituting the concentration of the $H_2NO_2^+$ intermediate in the overall rate of the reaction, we get:

$$r = k_2\left(\frac{k_1}{k_{-1}}[H^+][HNO_2]\right)[Br^-] = k[H^+][HNO_2][Br^-] \tag{4.119}$$

where k is a combination of rate constants for the first three elementary steps:

$$k = \frac{k_2 k_1}{k_{-1}} \tag{4.120}$$

Note that the last rate constant (k_3) does not affect the overall rate of the reaction as long as it is much faster than the reaction rate of the slow step.

4.4.2 Steady-State Approximation

The steady-state approximation (SSA) is applied in cases when the mechanism of the reaction involves very short-lived intermediates. Because they are generated and quickly consumed, the concentration of these intermediates is always very low and, after a brief period, their concentration stabilizes and remains practically constant throughout the reaction. We have seen an example of this effect in the two consecutive reactions (Figure 4.6) when the second reaction (k_2) is much faster than the first (k_1).

In mathematical terms, if I is the short-lived intermediate then the SSA equates to assuming that:

$$\frac{d[I]}{dt} = 0 \tag{4.121}$$

at all t. The steady-state approximation is approximately correct after a brief induction period in which the concentration of the intermediate goes from zero to its steady state.

Note that the SSA is equivalent to assuming that the rate of generation of I equals its rate of consumption. This is consistent with the assumption that I is very short-lived—since the intermediate is consumed as soon as it is generated, the rate of generation and the rate of consumption are practically equal. To illustrate this, we use the consecutive reactions example:

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C \tag{4.122}$$

If we assume that the reaction rate for the second reaction (k_2) is very high, then the rate of generation of C is almost equal to the rate of consumption of A, since any A converted to B immediately reacts to form C. Effectively, it is as if the second reaction had disappeared and A went straight to C. Since:

$$\frac{d[C]}{dt} = -\frac{d[A]}{dt} = k_1[A] \tag{4.123}$$

then the rate of generation of the intermediate is:

$$\frac{d[B]}{dt} = -\frac{d[A]}{dt} + \frac{d[C]}{dt} = 0 \tag{4.124}$$

which justifies the use of the SSA for short-lived intermediates.

The application of SSA to all short-lived intermediates in a reaction leads to simplifications in the overall rate law. Let us consider the aniline diazotization example in the previous section:

$$H^+ + HNO_2 + C_6H_5NH_2 \xrightarrow{Br-} C_6H_5N_2^+ + 2\,H_2O$$

with mechanism:

$$H^+ + HNO_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H_2NO_2^+ \qquad \text{(fast)}$$

$$H_2NO_2^+ + Br^- \xrightarrow{k_2} BrNO + H_2O \qquad \text{(slow)}$$

$$BrNO + C_6H_5NH_2 \xrightarrow{k_3} C_6H_5N_2^+ + H_2O + Br^- \qquad \text{(fast)}$$

The two intermediates in this reaction, BrNO and $H_2NO_2^+$, are short-lived because some steps in the mechanism that lead to their consumption have relatively high rate constants (k_{-1} and k_3). The overall rate of the reaction is given by:

$$r = \frac{d[C_6H_5N_2^+]}{dt} = k_3[BrNO][C_6H_5NH_2] \tag{4.125}$$

Now we apply the steady state approximation to BrNO:

$$0 = \frac{d[BrNO]}{dt} = k_2[H_2NO_2^+][Br^-] - k_3[BrNO][C_6H_5NH_2] \tag{4.126}$$

Solving for the concentration of BrNO gives:

$$[BrNO] = \frac{k_2[H_2NO_2^+][Br^-]}{k_3[C_6H_5NH_2]} \tag{4.127}$$

and substituting in Eq. 4.125, we get:

$$r = k_2[H_2NO_2^+][Br^-] \tag{4.128}$$

Next we apply the SSA to the second intermediate ($H_2NO_2^+$) to find its concentration:

$$0 = \frac{d[H_2NO_2^+]}{dt} = k_1[H^+][HNO_2] - k_{-1}[H_2NO_2^+] - k_2[H_2NO_2^+][Br^-] \tag{4.129}$$

Solving for $[H_2NO_2^+]$ gives:

$$[H_2NO_2^+] = \frac{k_1[H^+][HNO_2]}{k_{-1} + k_2[Br^-]} \tag{4.130}$$

and substituting in Eq. 4.128 leads to the rate law for the overall reaction in terms of the concentration of all species involved:

$$r = \frac{k_1k_2[H^+][HNO_2][Br^-]}{k_{-1} + k_2[Br^-]} \tag{4.131}$$

In the assumption that $k_{-1} \gg k_2[Br^-]$, this expression reduces to the experimentally observed rate law (Eq.4.116) and to the equation we obtained using the rate-determining step approximation (Eq. 4.119).

4.5 Effect of Temperature on Reaction Rates

The rate of a chemical reaction changes very noticeably with temperature. In the majority of cases, an increase in temperature leads to an increase in the reaction rate. Experimentally, it is known that, in general, the rate constant depends on temperature but the reaction orders do not, and that this dependence is approximately exponential. Commonly, the rate of a reaction increases by a factor of 2–3 every 10 °C at room temperature.

The temperature dependence of the rate law is often given mathematically by the empirical **Arrhenius equation**:

$$k = Ae^{-E_a/RT} \tag{4.132}$$

Figure 4.9: Left: dependence of the rate constant with temperature. Right: linearized Arrhenius plot.

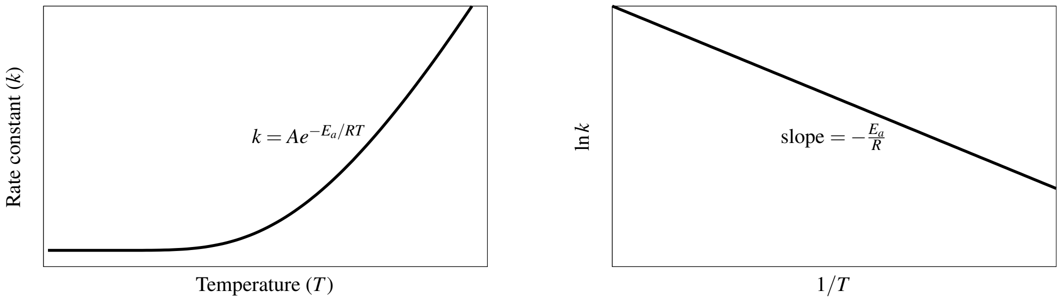
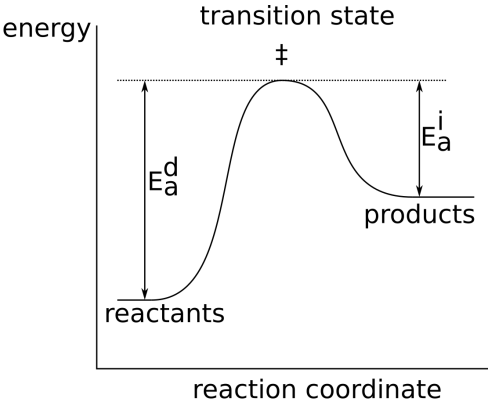


Figure 4.10: Example of a reaction coordinate illustrating the potential energy profile, direct and inverse activation energies, and transition state.



In this equation, A is the **frequency factor** (also called the **pre-exponential factor**) and E_a is the **activation energy**. Together, A and E_a are the **Arrhenius parameters** of the reaction. The units of A are the same as k (hence its units depend on the rate law) and the units of E_a are energy per mole, typically kcal/mol or kJ/mol. The Arrhenius parameters of a reaction are determined experimentally by measurements of the rate constant as a function of temperature.

The Arrhenius equation can be linearized:

$$\ln k = \ln A - \frac{E_a}{RT} \tag{4.133}$$

so a linear representation of $\ln k$ against $1/T$ (called the **Arrhenius plot**) gives a straight line and allows the calculation of the Arrhenius parameters from the slope and the intercept. The $k(T)$ and Arrhenius plots are shown in Figure 4.9.

The Arrhenius equation was developed empirically, and it is still used to describe the experimental dependence of reaction rates with temperature. Strictly, the Arrhenius equation is correct only for elementary reactions, and also A has a mild (non-exponential) dependence on temperature. However, many composite reactions are controlled by one or a few slow elementary steps and so the Arrhenius equation is applicable to many composite reactions as well.

The activation energy E_a has a simple interpretation, illustrated in Figure 4.10. The E_a is the minimum kinetic energy necessary for a reaction to take place when two molecules collide. The particular expression for the exponential term in the Arrhenius equation originates from the Boltzmann distribution of molecular energy levels: it is the population of molecules with energy higher than $\epsilon = E_a/N_A$ (Section 4.7). The higher the E_a, the slower the reaction at a given temperature.

Experimentally, activation energies tend to be between 0 and 80 kcal/mol for unimolecular and bimolecular elementary reactions, with typical values usually far lower than 80 kcal/mol. Activation energies of unimolecular elementary reactions also tend to be lower than those for bimolecular reactions. In elementary unimolecular reactions, A tends to be in the range 10^{12}–10^{15} s^{-1} whereas bimolecular reactions are in the 10^{8}–10^{13} $\text{dm}^3\text{mol}^{-1}\text{s}^{-1}$ range. Some reactions, such as the recombination of two radicals to form a stable molecule, have zero activation energy, and in those cases the reaction rate is essentially independent of temperature. Negative activation energies are rare but they do exist. For instance, consider Eq. 4.120 for the rate constant of a reaction under pre-equilibrium conditions. In this case, the combination of the three rate constants may result in a negative activation energy in the Arrhenius plot, and therefore in a decrease in reaction rate with increasing temperature. Finally, the activation energy can be reduced by introducing a catalyst that provides a more efficient reaction pathway from reactants to products.

While the activation energy is the fraction of molecules with enough energy to overcome the reaction barrier and progress to products, the frequency factor A in the Arrhenius equation is interpreted as the probability of a successful collision between reactants in an elementary step, as we shall see when we study collision theory. It has a mild dependence on temperature.

A reaction that does not give a straight line in the Arrhenius plot is a **non-Arrhenius reaction**. For these reactions, the activation energy and frequency factor can still be defined, although they are themselves a function of temperature. We do this by noting that:

$$\frac{d\ln k}{dT} = \frac{E_a}{RT^2} \tag{4.134}$$

Hence, we obtain the following definitions for the Arrhenius parameters in the general case:

$$E_a = RT^2\frac{d\ln k}{dT} \tag{4.135}$$

$$A = ke^{E_a/RT} \tag{4.136}$$

These definitions are consistent with the Arrhenius equation but they are general, and can be applied to any reaction. In a non-Arrhenius equation, the resulting E_a and A are not constants and depend on temperature. Typical non-Arrhenius behavior includes reactions involving enzyme denaturation, where the catalytic activity of the enzyme decreases as a consequence of a change in its structure. Another example is electron tunneling, where the experimentally observed rate constant at low temperature is higher than predicted by the Arrhenius equation. These formulas are also useful to calculate the activation energy and frequency factor from theoretical models derived using collision theory and transition-state theory.

4.6 Kinetics of Relevant Reactions

4.6.1 Unimolecular Reactions

Unimolecular reactions occur when a single molecule experiences a chemical transformation on its own after absorbing energy from the environment. The chemical transformation can be a decomposition (producing several molecules) but it can also be a rearrangement. Unimolecular reactions are common in the gas phase. A simple example of an elementary unimolecular reaction is the thermal isomerization of cyclopropane to propene.

In general, a unimolecular reaction needs not be an elementary unimolecular reaction, so the rate law does not need to be first order. In fact, unimolecular reactions present a contradiction:

because a unimolecular reaction occurs when the molecule undergoing the reaction is promoted to an excited state by a molecular collision, then one would expect the rate law to be second-order, since the excitation of the molecule, which is presumably the rate-limiting step, is bimolecular. Contradictions regarding unimolecular reactions, such as this one, were abundant in the early days of chemical kinetics. After much experimental work, it was found that a unimolecular reaction is first-order at high reactant concentration (pressure) and second-order at low reactant concentration (pressure).

These experimental observations and the rates of unimolecular reactions in general are explained using the model for unimolecular reactions known as the **Lindemann(-Hinshelwood) mechanism**, in which the energy for promoting molecules to their excited states comes from molecular collisions in the reaction environment:

$$\mathrm{A} + \mathrm{A} \xrightarrow{k_e} \mathrm{A}^* + \mathrm{A} \quad \text{(excitation)}$$

$$\mathrm{A} + \mathrm{A}^* \xrightarrow{k_r} \mathrm{A} + \mathrm{A} \quad \text{(relaxation)}$$

$$\mathrm{A}^* \xrightarrow{k_d} \mathrm{P} \quad \text{(decay)}$$

In the first step, the collision between two molecules results in a molecular excitation. Then, the excited molecule (also called the **energized** molecule, A*) can follow two routes: either it collides with another molecule and relaxes to a non-reactive state (relaxation) or it goes on to generate the products (decay).

We can calculate the rate law for this mechanism by applying the steady-state approximation to the short-lived intermediate A*:

$$\frac{d[\mathrm{A}^*]}{dt} = k_e[\mathrm{A}]^2 - k_r[\mathrm{A}^*][\mathrm{A}] - k_d[\mathrm{A}^*] = 0 \tag{4.137}$$

Solving for the concentration of the intermediate gives:

$$[\mathrm{A}^*] = \frac{k_e[\mathrm{A}]^2}{k_d + k_r[\mathrm{A}]} \tag{4.138}$$

The rate law is therefore:

$$r = \frac{d[\mathrm{P}]}{dt} = k_d[\mathrm{A}^*] = \frac{k_d k_e[\mathrm{A}]^2}{k_d + k_r[\mathrm{A}]} \tag{4.139}$$

There are two important limits for the Lindemann-Hinshelwood rate law. If the relaxation is much faster than the decay, then $k_r[\mathrm{A}] \gg k_d$ and the rate is first order in the concentration:

$$r \approx \frac{k_d k_l}{k_r}[\mathrm{A}] \tag{4.140}$$

This happens at high concentration (or pressure) of A. The bottleneck of the reaction is the the step in which the energized molecule decomposes, which is first order. In contrast, if the concentration A is low (for instance, if we decrease the pressure in the reaction chamber), then $k_r[\mathrm{A}] \ll k_d$ and the reaction becomes second order:

$$r \approx k_e[\mathrm{A}]^2 \tag{4.141}$$

In this case, the bottleneck is the excitation step, and therefore the reaction becomes bimolecular in the concentration of A. The fact that the Lindemann mechanism predicts that a unimolecular reaction is second-order at low pressure and first-order at high pressure agrees with the available experimental evidence for these reactions.

4.6.2 Enzymatic Reactions

Enzymes are biological molecules that function as homogeneous catalysts of biological reactions in living organisms. Enzymes are extremely efficient catalysts, much more so than the small-molecule organic and inorganic catalysts employed in chemistry. Due to their size, their concentrations are normally much smaller than those of the substrate. Typically, enzymes are proteins but it is known that fragments of RNA (called ribozymes) can also act as catalysts.

An enzymatic reaction occurs by first binding the substrate to the enzyme's **active site**. The active site of the enzyme is configured by the sequence of amino-acids (the primary structure) and by the way the amino-acid sequence folds onto itself to give rise to a three-dimensional shape (the secondary and tertiary structure). Sometimes, an enzyme requires one or more **co-factors** to function. These are organic or inorganic compounds that modify the active site and increase its binding affinity to the substrate molecule, such that the enzyme can only effect its catalytic activity if the co-factor is present.

The active site of a protein binds the substrate through weak non-covalent interactions. These are usually a mixture of electrostatic, van der Waals, and hydrogen bonding interactions. The "docking" of the substrate to the active site follows a **lock-and-key mechanism** in which the shape of the active site fits exactly that of the substrate, conferring enzymes great specificity regarding the substrate they bind and the reactions they catalyze.

A simple model of enzymatic catalysis is the **Michaelis-Menten mechanism**:

$$\mathrm{E} + \mathrm{S} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{ES}$$

$$\mathrm{ES} \xrightarrow{k_2} \mathrm{E} + \mathrm{P}$$

where E is the free enzyme, S is the substrate, P is the product, and ES is the enzyme-substrate complex. The Michaelis-Menten mechanism is the simplest model for enzymatic catalysis and does not take into account the existence of more than one substrate, co-factors, etc. The rate of the overall reaction in the Michaelis-Menten model is given by the last step:

$$r = \frac{d[\mathrm{P}]}{dt} = k_2[\mathrm{ES}] \tag{4.142}$$

We apply the steady-state approximation to the intermediate:

$$\frac{d[\mathrm{ES}]}{dt} = k_1[\mathrm{E}][\mathrm{S}] - k_{-1}[\mathrm{ES}] - k_2[\mathrm{ES}] = 0 \tag{4.143}$$

Solving for the concentration of the intermediate, we find:

$$[\mathrm{ES}] = \frac{k_1}{k_{-1} + k_2}[\mathrm{E}][\mathrm{S}] = \frac{[\mathrm{E}][\mathrm{S}]}{K_M} = \frac{([\mathrm{E}]_0 - [\mathrm{ES}])[\mathrm{S}]}{K_M} \tag{4.144}$$

where we defined the **Michaelis-Menten constant** (K_M) as:

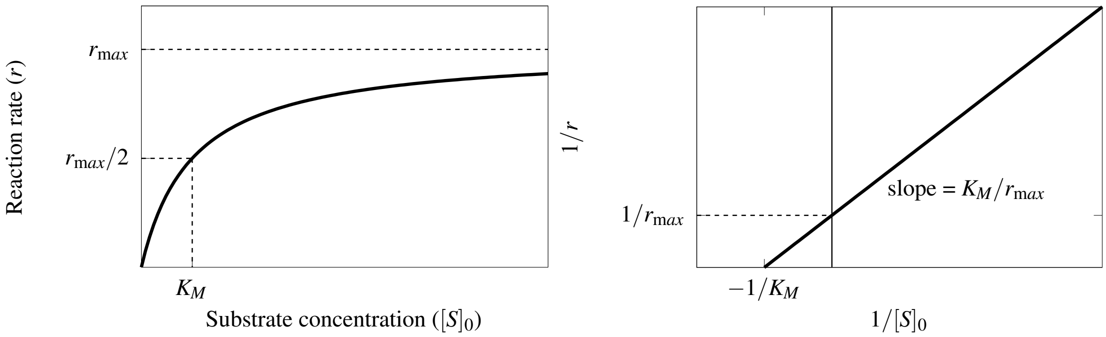
$$K_M = \frac{k_{-1} + k_2}{k_1} \tag{4.145}$$

Note that K_M has units of concentration. In addition, we used the material balance relation for the concentration of the enzyme: at any point the initial amount of enzyme ($[\mathrm{E}]_0$) can be in either its free or its complexated state:

$$[\mathrm{E}]_0 = [\mathrm{E}] + [\mathrm{ES}] \tag{4.146}$$

Finally, we assume that the enzyme concentration is much smaller than the substrate concentration and, therefore, we can assume that [S] is approximately the total substrate

Figure 4.11: Left: rate of a Michaelis-Menten mechanism as a function of substrate concentration. Right: Lineweaver-Burk plot.



concentration and [ES] is negligible in comparison. With this, we can solve for the concentration of ES in Eq. 4.144:

$$[\mathrm{ES}]K_M = [\mathrm{E}]_0[\mathrm{S}] - [\mathrm{ES}][\mathrm{S}] \tag{4.147}$$

$$[\mathrm{ES}] = \frac{[\mathrm{E}]_0[\mathrm{S}]}{K_M + [\mathrm{S}]} \tag{4.148}$$

from where the reaction rate is:

$$r = \frac{k_2[\mathrm{E}]_0[\mathrm{S}]}{K_M + [\mathrm{S}]} \tag{4.149}$$

which is the **Michaelis-Menten equation**.

There are several important points about the Michaelis-Menten equation. If the initial substrate concentration is much smaller than K_M, then the rate is pseudo-first order in the substrate:

$$r \approx \frac{k_2}{K_M}[\mathrm{S}][\mathrm{E}]_0 \propto [\mathrm{S}] \tag{4.150}$$

On the other hand, if the substrate concentration is much higher than K_M, then the reaction is pseudo-zeroth order:

$$r \approx k_2[\mathrm{E}]_0 = k_{\mathrm{cat}}[\mathrm{E}]_0 = r_{\mathrm{max}} \tag{4.151}$$

and independent of the substrate concentration (see Section 4.3.1).

Two constants appear in the Michaelis-Menten equation that are typically used to characterize an enzymatic reaction. The first is the **maximum rate** of the enzymatic reaction (r_{max}), which is the maximum rate at which the reaction can function and is approached by the actual reaction rate when the substrate is very abundant. The maximum rate is determined by the initial concentration of the enzyme and the k_2 rate constant, called its **catalytic activity** ($k_2 = k_{\mathrm{cat}}$), **catalytic constant** or **turnover frequency**. The k_{cat} constant measures the number of catalytic cycles of the enzyme per active site per time.

With these parameters, we can rewrite Eq. 4.149 as:

$$r = \frac{r_{\mathrm{max}}}{1 + K_M/[\mathrm{S}]} = \frac{k_{\mathrm{cat}}[\mathrm{E}]_0}{1 + K_M/[\mathrm{S}]} \tag{4.152}$$

where we can see that the maximum rate is only achieved in the limit of very large substrate concentration ([S] $\to \infty$) and, in general, $r < r_{\mathrm{max}}$. The rate as a function of substrate concentration is shown in Figure 4.11 (left). At a concentration equal to K_M, the rate of the enzymatic reaction is half its maximum rate.

A useful approach to determine the Michaelis-Menten parameters (K_M and $r_{\max}$) experimentally is to linearize Equation 4.152 as:

$$\frac{1}{r} = \frac{1}{r_{\max}} + \left(\frac{K_M}{r_{\max}}\right)\frac{1}{[\mathrm{S}]} \tag{4.153}$$

A representation of $1/r$ against $1/[\mathrm{S}]$ is used in the determination of the reaction parameters and is called a **Lineweaver-Burk plot**. From a linear least-squares fit to experimental data, we can derive the maximum rate from the intercept with the y-axis at $x = 0$ and the K_M from the intercept with the x-axis at $y = 0$. The slope is the ratio of the two.

Another important parameter besides K_M and k_{cat} is the ratio between these two quantities, called the **catalytic efficiency** (η):

$$\eta = \frac{k_{\mathrm{cat}}}{K_M} = \frac{k_2 k_1}{k_{-1} + k_2} \tag{4.154}$$

From Eq. 4.150, we see that the catalytic efficiency of an enzyme is the rate constant at low substrate concentration, when the rate is much lower than the maximum rate $r_{\max}$. The maximum efficiency is achieved when $k_2 \gg k_{-1}$ and $\eta = k_1$. In cases when the formation of the ES complex is very fast, k_1 is determined by the rate of diffusion of E and S in solution, and has maximum catalytic efficiencies of approximately 10^8–10^9 $\mathrm{M^{-1}\,s^{-1}}$ in water. Typical values of η are in the range 10^5–10^6 $\mathrm{M^{-1}\,s^{-1}}$ but some enzymes do approach the maximum diffusion-controlled catalytic efficiency.

Another important aspect of enzymatic reactions is the effect of **inhibitors**. Inhibitors can be irreversible, if they permanently prevent the enzyme from acting as catalyst, or reversible, if they merely interfere with the enzymatic mechanism. Reversible inhibitors can interfere with the enzymatic reaction by binding to the free enzyme, the enzyme-substrate complex, or both, thus sequestering the active sites and reducing the overall rate of the reaction:

$$\mathrm{EI} \xrightleftharpoons{K_I} \mathrm{E} + \mathrm{I}$$

$$\mathrm{ESI} \xrightleftharpoons{K_I'} \mathrm{ES} + \mathrm{I}$$

where the equations controlling both equilibria are:

$$K_I = \frac{[\mathrm{E}][\mathrm{I}]}{[\mathrm{EI}]} \tag{4.155}$$

$$K_I' = \frac{[\mathrm{ES}][\mathrm{I}]}{[\mathrm{ESI}]} \tag{4.156}$$

The lower the value of the equilibrium constants K_I and K_I', the more efficient the inhibition. To examine the effect of inhibition on the reaction site, we write the new material balance equation for the enzymatic reaction:

$$[\mathrm{E}]_0 = [\mathrm{E}] + [\mathrm{EI}] + [\mathrm{ES}] + [\mathrm{ESI}] = [\mathrm{E}]\left(1 + \frac{[\mathrm{I}]}{K_I}\right) + [\mathrm{ES}]\left(1 + \frac{[\mathrm{I}]}{K_I'}\right) \tag{4.157}$$

$$= [\mathrm{E}]\alpha + [\mathrm{ES}]\alpha' \tag{4.158}$$

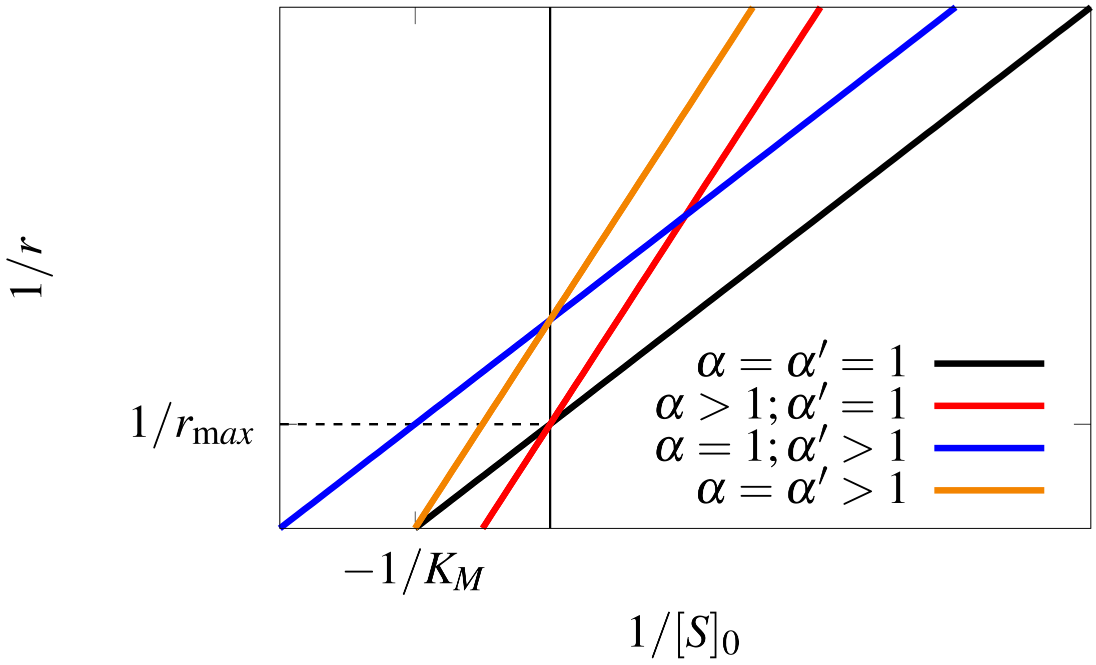
where we defined:

$$\alpha = 1 + \frac{[\mathrm{I}]}{K_I} \quad ; \quad \alpha' = 1 + \frac{[\mathrm{I}]}{K_I'} \tag{4.159}$$

In the zero-inhibition limit, $\alpha = \alpha' = 1$. Using Eq. 4.144 for the concentration of free enzyme, we have:

$$[\mathrm{E}]_0 = \frac{K_M[\mathrm{ES}]}{[\mathrm{S}]}\alpha + [\mathrm{ES}]\alpha' = [\mathrm{ES}]\left(\frac{K_M}{[\mathrm{S}]}\alpha + \alpha'\right) \tag{4.160}$$

Figure 4.12: The Lineweaver-Burk plots for the three types of enzymatic inhibition.



and the rate of the enzymatic reaction is:

$$r = k_2[\mathrm{ES}] = \frac{k_2[\mathrm{E}]_0}{\alpha' + \alpha K_M/[\mathrm{S}]} = \frac{r_{\max}}{\alpha' + \alpha K_M/[\mathrm{S}]} \tag{4.161}$$

The rate of the uninhibited enzymatic reaction (Eq. 4.152) is recovered by doing $\alpha = \alpha' = 1$. For values of either variable higher than 1, the rate decreases relative to the original reaction rate. Inverting this last equation yields the Lineweaver-Burk plot for the inhibited reaction:

$$\frac{1}{r} = \frac{\alpha'}{r_{\max}} + \left(\frac{\alpha K_M}{r_{\max}}\right)\frac{1}{[\mathrm{S}]} \tag{4.162}$$

Depending on the values of α and α', we classify enzymatic inhibition in three types. Their effects on the Lineweaver-Burk plot are shown in Figure 4.12.

- **Competitive inhibition**: the inhibitor binds only to the active site of the free enzyme and prevents the substrate from using it. This corresponds to the reaction in Eq. 4.155 and to $\alpha > 1$ and $\alpha' = 1$. The slope of the Lineweaver-Burk plot increases but the intercept stays the same.

- **Uncompetitive inhibition**: the inhibitor binds to the enzyme-substrate complex and sequesters it by forming the ESI species, thus preventing the formation of products. Corresponds to Eq. 4.156 and to $\alpha = 1$ and $\alpha' > 1$. The y-intercept of the Lineweaver-Burk plot moves up but the slope stays the same.

- **Non-competitive inhibition** (also **mixed inhibition**): the inhibitor binds to the enzyme in either its free (E) or associated state (ES) and sequesters it. It is a combination of the previous two, so $\alpha > 1$ and $\alpha' > 1$. In the particular case when $\alpha = \alpha' > 1$, shown in Figure 4.12, both the y-intercept and the slope of the plot increase and the x-intercept stays the same.

Enzymatic inhibition is a common mechanism by which drugs affect living organisms. For instance, HIV/AIDS antiretroviral medication works by inhibiting enzymes that are crucial to the life-cycle of the HIV retrovirus, thus impeding its ability to replicate inside the host's body.

4.7 Collision Theory

Collision theory is a simple theoretical model based on the kinetic theory of gases that attempts to explain the temperature dependence of the rate constant (Arrhenius equation) in elementary bimolecular reactions:

$$\mathrm{B} + \mathrm{C} \longrightarrow \mathrm{P} \tag{4.163}$$

In collision theory, same as in the kinetic theory of gases, molecules are considered rigid spheres of fixed diameter. A reaction between B and C can only occur if they collide, and not all collisions are reactive: The reaction only happens if the relative kinetic energy along the line that connects the centers of the molecules is higher than a certain threshold energy ϵ_0. At all times, the distribution of molecular velocities is assumed to be given by the Maxwell-Boltzmann distribution.

We have seen that in the kinetic theory of gases the mean relative speed of B and C molecules is (Eq. 3.48):

$$v_{\mathrm{rel}}^{\mathrm{BC}} = \sqrt{\frac{8k_BT}{\pi\mu_{\mathrm{BC}}}} \tag{4.164}$$

where the reduced mass is:

$$\mu_{\mathrm{BC}} = \frac{m_Bm_C}{m_B+m_C} \tag{4.165}$$

and m_B and m_C are the molecular masses for those two molecules. Also from the kinetic theory of gases, we know that the collision frequency per volume (i.e. the number of collisions per unit time per unit volume) between species B and C is (Eq. 3.61):

$$Z_{\mathrm{BC}} = \left(\frac{N_{\mathrm{B}}}{V}\right)\left(\frac{N_{\mathrm{C}}}{V}\right)\sigma_{\mathrm{BC}}v_{\mathrm{rel}}^{\mathrm{BC}} \tag{4.166}$$

with N_B and N_C the number of molecules of each species, and σ_{BC} the collision cross-section for the B and C molecules (Eq. 3.60):

$$\sigma_{\mathrm{BC}} = \pi(r_{\mathrm{B}}+r_{\mathrm{C}})^2 = \pi d^2 \tag{4.167}$$

with $d = r_{\mathrm{B}} + r_{\mathrm{C}}$ and r_{B} and r_{C} are the molecular radii.

If all collisions were reactive, then the number of product molecules generated per unit time per unit volume would equal the collision frequency per unit time per unit volume:

$$\frac{1}{V}\frac{dN_P}{dt} = Z_{\mathrm{BC}} = \left(\frac{N_{\mathrm{B}}}{V}\right)\left(\frac{N_{\mathrm{C}}}{V}\right)\sigma_{\mathrm{BC}}v_{\mathrm{rel}}^{\mathrm{BC}} \tag{4.168}$$

Dividing both sides by Avogadro's number, and taking into account that $n_X = N_X/N_A$, we find:

$$\frac{1}{V}\frac{dn_P}{dt} = N_A\left(\frac{n_{\mathrm{B}}}{V}\right)\left(\frac{n_{\mathrm{C}}}{V}\right)\sigma_{\mathrm{BC}}v_{\mathrm{rel}}^{\mathrm{BC}} = N_A\left(\frac{n_{\mathrm{B}}}{V}\right)\left(\frac{n_{\mathrm{C}}}{V}\right)\sigma_{\mathrm{BC}}v_{\mathrm{rel}}^{\mathrm{BC}} \tag{4.169}$$

And, using $[\mathrm{X}] = n_X/V$, we can write the rate of the reaction in terms of concentrations:

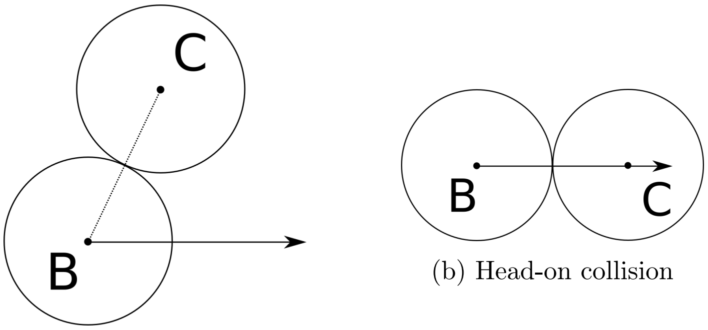
$$r = \frac{d[\mathrm{P}]}{dt} = \sigma_{\mathrm{BC}}v_{\mathrm{rel}}^{\mathrm{BC}}N_A[\mathrm{B}][\mathrm{C}] \tag{4.170}$$

From this expression, we can identify the rate constant as:

$$k = \sigma_{\mathrm{BC}}v_{\mathrm{rel}}^{\mathrm{BC}}N_A = \sigma_{\mathrm{BC}}N_A\left(\frac{8k_BT}{\pi\mu_{\mathrm{BC}}}\right)^{1/2} \tag{4.171}$$

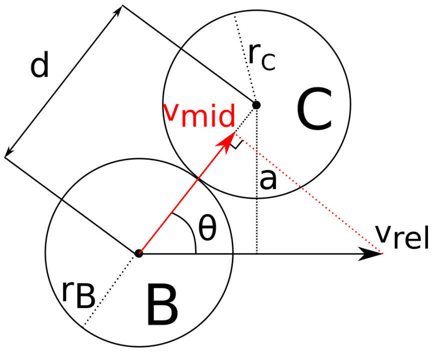
Therefore, using the assumption that all collisions are reactive we can already explain the partial orders in the rate law of an elementary bimolecular reaction. However, the

Figure 4.13: Diagrams illustrating possible orientations in the collision between two molecules B and C.



(b) Head-on collision

(a) Glancing collision



(c) A collision with glancing angle θ

temperature-dependence of the rate constant is wrong. Eq. 4.171 overestimates rate constants compared to experiment, and this is because not all collisions are reactive.

To introduce the exponential dependence, we need to take into account that only collisions with relative kinetic energy higher than a certain threshold may result in the formation of products. Let ϵ_0 be the energy threshold for the reaction, that is, the collision will be reactive if, at the time of the collision, the kinetic energy along the line connecting the centers of both molecules is higher than ϵ_0. The total kinetic energy of a collision is given by:

$$\epsilon = \frac{1}{2}\mu_{\mathrm{BC}}(v_{\mathrm{rel}}^{\mathrm{BC}})^2 \tag{4.172}$$

A collision that has $\epsilon < \epsilon_0$ is never reactive. For $\epsilon \geq \epsilon_0$, whether the collision results in a reaction or not depends on the orientation of B and C.

Figure 4.13 shows several possible collision orientations between B and C. If the collision is head-on (Fig. 4.13a), then any $\epsilon \geq \epsilon_0$ will overcome the energy barrier and result in a reaction. On the other hand, a glancing collision (Fig. 4.13b) requires an ϵ much higher than ϵ_0 to be reactive because only a little of the kinetic energy is transferred along the line connecting the molecular centers. This dependence on the orientation can be quantified by **reactive cross-section**, $\sigma(\epsilon)$, that measures the area around the center of the C molecule inside which a collision with energy ϵ results in a reaction. The reactive cross-section depends on the kinetic energy of the collision because, the higher the energy, the larger the reactive cross-section. In the limit $\epsilon \to \infty$, the reactive cross-section approaches the collision cross-section σ_{BC}. We can calculate this area by considering the diagram in Figure 4.13c.

If the relative velocity for the collision is $v_{\mathrm{rel}}^{\mathrm{BC}}$, the relative velocity along the molecular centers is:

$$v_{\mathrm{rel}}^{\mathrm{mid}} = v_{\mathrm{rel}}^{\mathrm{BC}} \cos\theta = v_{\mathrm{rel}}^{\mathrm{BC}} \frac{\sqrt{d^2 - a^2}}{d} \tag{4.173}$$

The kinetic energy along the BC center line is:

$$\epsilon_{\text{mid}} = \frac{1}{2}\mu_{\text{BC}}(v_{\text{rel}}^{\text{mid}})^2 = \frac{1}{2}\mu_{\text{BC}}(v_{\text{rel}}^{\text{BC}})^2\left(\frac{d^2-a^2}{d^2}\right) = \epsilon\left(\frac{d^2-a^2}{d^2}\right) \tag{4.174}$$

And it is the kinetic energy along the molecular centers that needs to be higher than the threshold energy (ϵ_0) for the collision to be reactive. This condition is:

$$\epsilon_{\text{mid}} = \epsilon\left(\frac{d^2-a^2}{d^2}\right) \geq \epsilon_0 \tag{4.175}$$

Solving for a, we find that:

$$a^2 \leq \left(1 - \frac{\epsilon_0}{\epsilon}\right) d^2 \tag{4.176}$$

Any a lower than the maximum a given by the expression on the right-hand side of this inequality gives a reactive collision. Therefore, the maximum a for a reactive collision is:

$$a_{\text{max}} = \begin{cases} d\sqrt{1-\frac{\epsilon_0}{\epsilon}} & \text{if } \epsilon > \epsilon_0 \\ 0 & \text{if } \epsilon \leq \epsilon_0 \end{cases} \tag{4.177}$$

where in the case in which $\epsilon \leq \epsilon_0$, $a_{\text{max}} = 0$ because the collision is not reactive regardless of the orientation.

With this, we can define the reactive cross-section, i.e., the area around the center of the C molecule where a collision results in a reaction. It is:

$$\sigma(\epsilon) = \pi a_{\text{max}}^2 = \begin{cases} \left(1-\frac{\epsilon_0}{\epsilon}\right)\pi d^2 = \left(1-\frac{\epsilon_0}{\epsilon}\right)\sigma_{\text{BC}} & \text{if } \epsilon > \epsilon_0 \\ 0 & \text{if } \epsilon \leq \epsilon_0 \end{cases} \tag{4.178}$$

Note that, because $a_{\text{max}} \leq d$, $\sigma(\epsilon) \leq \sigma_{\text{BC}}$ and the area molecule B needs to hit in order for C to be reactive increases with the collision kinetic energy (ϵ). At $\epsilon = \epsilon_0$, only a full head-on collision results in a reaction and so $\sigma(\epsilon_0) = 0$. The reactive cross-section approaches the value of the collision cross-section σ_{BC} in the limit of $\epsilon \to \infty$, where even a glancing collision has enough energy to result in a reaction.

Since the reactive cross section depends on the collision energies, the rate constant is found by integration over the distribution of all possible relative collision energies (compare to Eq. 4.171). It is possible to show that the distribution of relative velocities is given by the Maxwell-Boltzmann (Eq. 3.31) distribution where we replace the molecular mass with the reduced mass:

$$f(v_{\text{rel}}) = 4\pi\left(\frac{\mu}{2\pi k_BT}\right)^{3/2} v_{\text{rel}}^2 e^{-\frac{\mu v_{\text{rel}}^2}{2k_BT}} \tag{4.179}$$

We now transform this probability density by effecting a change of variable in order to have the distribution in terms of relative kinetic energies:

$$\epsilon = \frac{1}{2}\mu v_{\text{rel}}^2 \quad ; \quad v_{\text{rel}} = \sqrt{\frac{2\epsilon}{\mu}} \quad ; \quad d\epsilon = \mu v_{\text{rel}} dv_{\text{rel}} \quad ; \quad dv_{\text{rel}} = \frac{1}{\sqrt{2\mu\epsilon}} d\epsilon \tag{4.180}$$

As before, to carry out a change of variable in a probability density, we need to take into account its effect on the differential, since the probabilities in equivalent intervals of both random variables need to be the same:

$$f(v_{\text{rel}})dv_{\text{rel}} = \underbrace{f\left(\sqrt{\frac{2\epsilon}{\mu}}\right)\frac{1}{\sqrt{2\mu\epsilon}}}_{f(\epsilon)} d\epsilon \tag{4.181}$$

And we find:

$$f(\epsilon) = 4\pi \left(\frac{\mu}{2\pi k_B T}\right)^{3/2} \frac{2\epsilon}{\mu} e^{-\epsilon/k_B T} \times \frac{1}{\sqrt{2\mu\epsilon}} = 2\pi \left(\frac{1}{\pi k_B T}\right)^{3/2} \epsilon^{1/2} e^{-\epsilon/k_B T} \tag{4.182}$$

The rate constant given by Eq. 4.171 ($k = \sigma_{\mathrm{BC}} v_{\mathrm{rel}}^{\mathrm{BC}} N_A$) needs to be modified to take into account that not all collisions are reactive. Specifically, the reactive cross section now depends on the collision energy, so we need to replace this expression by an integral over all possible collision energies coupled with the probability distribution we just derived:

$$k = N_A \int_0^\infty v_{\mathrm{rel}}^{\mathrm{BC}}(\epsilon)\sigma(\epsilon) f(\epsilon) d\epsilon = N_A \int_0^\infty \sqrt{\frac{2\epsilon}{\mu}} \sigma(\epsilon) f(\epsilon) d\epsilon \tag{4.183}$$

The $\sigma(\epsilon)$ in the integrand is only non-zero when $\epsilon > \epsilon_0$ so this restricts the limits of the integration to $[\epsilon_0, \infty]$ because for $\epsilon < \epsilon_0$ the integrand vanishes. Unpacking the variables in the integrand gives:

$$\begin{aligned} k &= N_A \int_0^\infty \sqrt{\frac{2\epsilon}{\mu}} \sigma(\epsilon) f(\epsilon) d\epsilon \\ &= N_A \int_{\epsilon_0}^\infty \sqrt{\frac{2\epsilon}{\mu}} \times \left(1 - \frac{\epsilon_0}{\epsilon}\right) \sigma_{\mathrm{BC}} \times 2\pi \left(\frac{1}{\pi k_B T}\right)^{3/2} \epsilon^{1/2} e^{-\epsilon/k_B T} d\epsilon \\ &= N_A \sigma_{\mathrm{BC}} \sqrt{\frac{8}{\pi \mu k_B T}} \int_{\epsilon_0}^\infty \frac{\epsilon - \epsilon_0}{k_B T} e^{-\epsilon/k_B T} d\epsilon \end{aligned} \tag{4.184}$$

The integral on the right-hand side can be solved by parts:

$$u = \epsilon - \epsilon_0 \quad ; \quad du = d\epsilon$$
$$dv = \frac{1}{k_B T} e^{-\epsilon/k_B T} d\epsilon \quad ; \quad v = -e^{-\epsilon/k_B T}$$

which leads to:

$$\begin{aligned} \int_{\epsilon_0}^\infty \frac{\epsilon - \epsilon_0}{k_B T} e^{-\epsilon/k_B T} d\epsilon &= \cancel{(\epsilon_0 - \epsilon) e^{-\epsilon/k_B T} \Big|_{\epsilon_0}^\infty} + \int_{\epsilon_0}^\infty e^{-\epsilon/k_B T} d\epsilon \\ &= -(k_B T) e^{-\epsilon/k_B T} \Big|_{\epsilon_0}^\infty = k_B T e^{-\epsilon_0/k_B T} \end{aligned} \tag{4.185}$$

Substituting this result in the rate constant equation (Eq.4.184), we obtain:

$$k = N_A \sigma_{\mathrm{BC}} \left(\frac{8 k_B T}{\pi \mu}\right)^{1/2} e^{-\epsilon_0/k_B T} = N_A \sigma_{\mathrm{BC}} v_{\mathrm{rel}}^{\mathrm{BC}} e^{-\epsilon_0/k_B T} \tag{4.186}$$

Comparing to the rate constant assuming all collisions are reactive (Eq. 4.186), we see that imposing the energy threshold condition results in an additional factor that is a simple exponential ($e^{-\epsilon_0/k_B T}$).

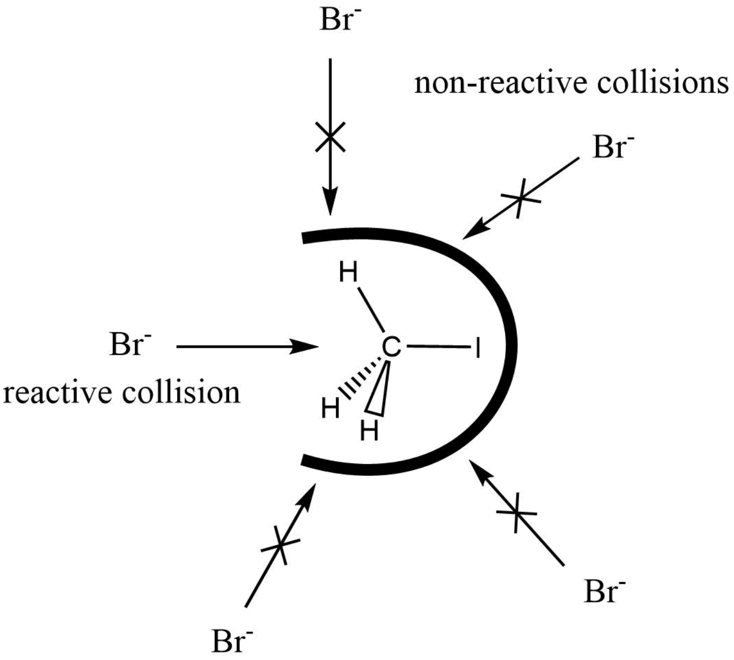
The activation energy and the frequency factor can now be calculated from the collision-theory rate constant we have just derived (Eq. 4.186) by using the corresponding definition for these quantities we obtained when we discussed non-Arrhenius equations. For the activation energy (Eq. 4.135), we have:

$$E_a = R T^2 \frac{d \ln k}{dT} \tag{4.187}$$

The logarithm of the rate constant is:

$$\ln k = \ln \left(N_A \sigma_{\mathrm{BC}} \sqrt{\frac{8 k_B}{\pi \mu}} \right) + \frac{1}{2} \ln T - \frac{\epsilon_0}{k_B T} \tag{4.188}$$

Figure 4.14: Diagram of steric effects on the success rate of collisions in collision theory. Only the approach between Br^- and CH_3I with the correct orientation results in a reactive collision.



where we separated the terms that depend on T from those that do not.

$$E_a = RT^2 \frac{d \ln k}{dT} = RT^2 \left(\frac{1}{2T} + \frac{\epsilon_0}{k_B T^2} \right) = \frac{1}{2} RT + E_0 \tag{4.189}$$

where $E_0 = N_A \epsilon_0$ is the threshold energy per mole of molecules. The term $\frac{1}{2}RT$ is approximately 0.3 kcal/mol at room temperature, which is relatively small compared to typical activation energies. Therefore, the collision energy threshold is essentially the same as the activation energy for the reaction. The exponential dependence of the rate constant of an elementary bimolecular reaction on temperature is explained in collision theory by appealing to the fact that only a few collisions between molecules B and C have enough energy to be reactive, and the fraction of reactive collisions is given by a Boltzmann-like factor $e^{-\epsilon_0/k_B T}$.

Regarding the frequency factor, we calculate it as (Eq. 4.136):

$$A = ke^{E_a/RT} = N_A \sigma_{\rm BC} v_{\rm rel}^{\rm BC} e^{-\epsilon_0/k_B T} \times \exp\left(\frac{\frac{1}{2}RT + E_0}{RT} \right) = N_A \sigma_{\rm BC} v_{\rm rel}^{\rm BC} \cancel{e^{-\epsilon_0/k_B T}} e^{1/2} \times \cancel{e^{\epsilon_0/k_B T}}$$

$$= \sigma_{\rm BC} N_A v_{\rm rel}^{\rm BC} e^{1/2} = \sigma_{\rm BC} N_A \sqrt{\frac{8 k_B T}{\pi \mu}} e^{1/2} \tag{4.190}$$

The frequency factor depends only slightly on temperature, so the exponential term with the activation energy dominates the overall temperature dependence. The frequency factor comes from considering the collision rate of the molecules, which increases with their size ($\sigma_{\rm BC}$) and their relative velocity.

In most cases, experimentally observed frequency factors are smaller than those predicted by collision theory, based on reasonable molecular diameters. This can be rationalized by arguing that, just because a collision has enough energy to be reactive, it may not actually result in a reaction because it may have the wrong orientation. This is illustrated for an S_N2 substitution reaction in Figure 4.14. For the non-reactive orientations, which is any orientation that does not approach the molecule from the back of the C-I σ-bond, the substitution product does not form regardless of how energetic the collision is.

To address this difficulty, the rate constant in collision theory can be modified by a **steric factor** p:

$$k = \underbrace{p}_{\text{steric requirement}} \underbrace{\sigma_{\text{BC}} N_A \left(\frac{8k_B T}{\pi\mu}\right)^{1/2}}_{\text{encounter rate}} \underbrace{e^{-\epsilon_0/k_B T}}_{\text{minimum-energy requirement}} \tag{4.191}$$

The steric factor, which in general has values between 0 and 1, takes into account that only a fraction of the collisions have the correct orientation. p measures the fraction of the solid angle for which molecular approaches in such orientations are successful. In most cases, p is several orders of magnitude smaller than one, and it tends to be smaller the more complex the molecules involved in the reaction.

There are certain reactions where the steric factor is greater than one, which indicates that collisions that should not be reactive because they do not reach the energy threshold actually result in a successful reaction. This occurs in reactions like:

$$\mathrm{K} + \mathrm{Br_2} \longrightarrow \mathrm{KBr} + \mathrm{Br}$$

and is explained by electron tunneling. An electron jumps from potassium (which is very electropositive) to the bromine molecule (electrophile) even if no direct collision takes place. This argument is sometimes referred to as the “harpoon mechanism”. The two reacting molecules do not collide but come close enough to each other. As a result, the electron tunnels from one to the other resulting in molecules with opposite electric charges, which attract each other and eventually collide, resulting in a reaction. Effectively, this is interpreted in collision theory as an increase in the reactive cross-section of both reactants beyond the collision cross-section.

The steric factor cannot be determined from collision theory alone, and it is usually derived from experiment by taking the ratio of the observed frequency factor and the factor predicted by collision theory. Furthermore, there is no way to predict the energy threshold ϵ_0 in collision theory, either, and therefore the predictive capabilities of this theory are limited. In order to have a theory that predicts activation energies and steric factors, we need to involve the structure and energy levels of the reacting molecules using statistical thermodynamics.

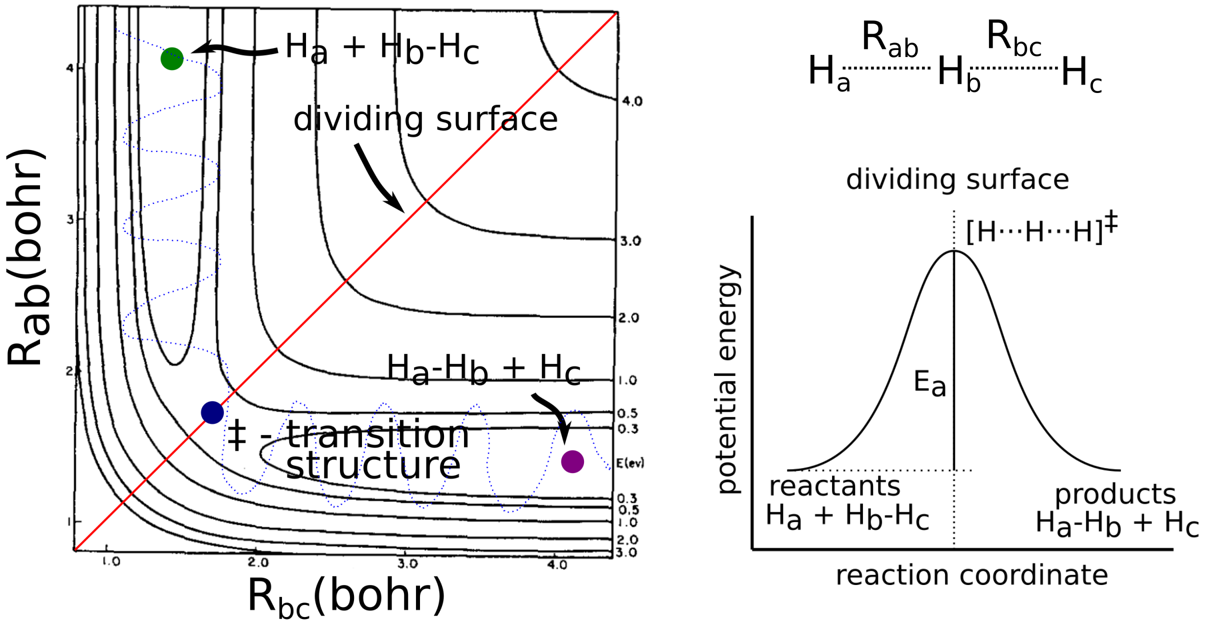
4.8 Transition-State Theory

In order to incorporate molecular details into the calculation of the rate of an elementary bimolecular reaction:

$$\mathrm{B} + \mathrm{C} \longrightarrow \mathrm{P} \tag{4.192}$$

we need to consider the energy of the complex formed by the reactants B and C as they approach each other. If B has n_B atoms and C has n_C atoms, then the energy of the B + C supermolecule is found by solving the corresponding Schrödinger equation with $n_B + n_C$ atoms. Under the Born-Oppenheimer approximation, we can write and solve one Schrödinger equation for every orientation of this supermolecule to obtain an energy. In particular, if the atomic positions of the atoms in the supermolecule are given by the coordinates $\boldsymbol{x}_1, \ldots, \boldsymbol{x}_{n_B}$ for the B molecule and $\boldsymbol{x}_{n_B+1}, \ldots, \boldsymbol{x}_{n_B+n_C}$ for the C molecule, then the energy of the supermolecule as a function of the atomic positions of B and C is $E(\boldsymbol{x}_1, \ldots, \boldsymbol{x}_{n_B+n_C})$, where this energy is obtained by solving the corresponding time-independent Schrödinger equation with the nuclei at those fixed positions.

Figure 4.15: Contour representation of the bidimensional potential energy surface for the H + H_2 reaction, indicating the dividing surface. Adapted, with permission, from R. N. Porter and M. Karplus, *J. Chem. Phys.*, **40** (1964) 1105.



The energy written as a function of the atomic positions is called the **potential energy surface** (PES) of the system. In general, we are not interested in translations of the whole supermolecule, which are determined by 3 coordinates (the position of its center of mass). Likewise, we do not need the variables associated with whole-body rotations of the supermolecule, amounting to three additional variables (two additional variable if the supermolecule is linear when it contains only two atoms). Therefore, the PES is a function of $3m - 6$ variables, where $m = n_B + n_C$, usually written:

$$E(q_1, \ldots, q_{3m-6}) \tag{4.193}$$

where the q_n coordinates can be constructed in a similar way to how vibrational normal modes in a molecule are obtained.

Let us consider as a simple example the following chemical reaction:

$$H_2 + H \longrightarrow H + H_2 \tag{4.194}$$

The supermolecule contains three hydrogen atoms, which we label as H_a, H_b, and H_c. Since it is the energetically most favorable approach, we consider only the orientation in which the three hydrogen atoms are aligned, and so the geometry of the supermolecule is determined by only two variables: the distance between H_a and H_b, R_{ab}, and the distance between H_b and H_c, R_{bc}. The potential energy surface in this reaction is a function of these two variables, $E(R_{ab}, R_{bc})$. At any given value for R_{ab} and R_{bc}, $E(R_{ab}, R_{bc})$ is obtained by solving the corresponding Schrödinger equation determined by the relative positions of the three hydrogen atoms.

A graphical representation of the potential energy surface for this reaction is shown in Figure 4.15 (left). The contours in this graph represent points of equal energy, same as pressure contours (isobars) on a weather map, or a topographical elevation map. The low-energy regions correspond to the reactants (the green circle, top left) and the products (purple circle, bottom right). For any given point in this diagram, we can follow the steepest descent route to either reactants or products. If we group the points in the diagram by whether following the steepest-descent path leads to reactants or products, we can divide the diagram into two **basins**, separated by a **dividing (or critical) surface**, indicated as a red line across the diagonal of the map. Points above and to the left of the dividing line descend to the reactants (green circle) and points below and to the right of the line descend to the products (purple circle). Any structure on or near the dividing surface is known as an **activated complex** and the set of all activated complexes is the **transition state**. The point with minimum energy on the dividing surface is the **transition structure**, and it is represented with a ‡ symbol. (There is disagreement in the literature regarding the definition of these terms and sometimes they are used interchangeably.)

The transition structure represents the lowest-energy point through which a trajectory going from reactants to products can cross. The steepest-descent path originating at the transition structure and going down to the reactants and products is the minimum-energy path linking them, and it is known as the **reaction coordinate**. If we plot the energy along the reaction coordinate through the transition structure, we obtain the **energy profile** for the reaction, shown in Figure 4.15 (right). When following the reaction coordinate, the dividing surface is crossed exactly at the transition structure.

Potential energy surfaces for more complicated reactions have many more dimensions, and in general it is not possible to represent them graphically. Mathematically, the transition structure always corresponds to a **first-order saddle point** on the PES. A first-order saddle point is a critical point, that is, the derivatives of the energy with respect to the coordinates are zero:

$$\frac{\partial E}{\partial q_i}(\boldsymbol{q}_{\mathbf{TS}}) = 0 \text{ for any } i \tag{4.195}$$

In addition, the matrix of second derivatives of the energy (the energy Hessian) at the transition structure:

$$H_{ij} = \frac{\partial E}{\partial q_i \partial q_j}(\boldsymbol{q}_{\mathbf{TS}}) \tag{4.196}$$

has eigenvalues that are all positive except for one. The eigenvector corresponding to the negative eigenvalue points towards the direction of steepest descent along the reaction coordinate.

The rate of the chemical reaction may be calculated by considering **trajectories** leading from the reactants to the products. One of these trajectories is shown in Figure 4.15 (left) for the $H + H_2$ reaction. Following the trajectory from the top left, the system starts as a vibrating $H_b{-}H_c$ molecule and an atom H_a approaching it. If the system has enough energy, the trajectory overcomes the barrier and crosses the dividing surface (generally at a point other than the transition structure) and moves over the product basin. The $H_a{-}H_b$ molecule forms and starts vibrating while the H_c atom moves away as the trajectory exits the bottom right part of the plot.

For a general reaction, if one does a statistical sampling of these trajectories it is possible to calculate accurate rate constants for bimolecular elementary steps. However, this requires a very detailed knowledge of the potential energy surface, which entails solving the Schrödinger equation for many different geometries of the supermolecule. Therefore, this is only feasible for the simplest reactions. The transition-state theory (TST), also called "activated-complex theory", is a theory that allows a much simpler calculation of the bimolecular rate constant because it only requires information about the reactants, products, and transition structure (i.e. the two minima and the first-order saddle point connecting them).

Transition-state theory is based on the assumption that molecules on the dividing surface are in thermal equilibrium with the reactant, i.e., that the relative population of reactants and transition state is governed by the Boltzmann distribution. In particular, the ratio in the number of transition state and reactant molecules is given by an expression analogous to the one we saw when we considered chemical equilibrium (Eq. 2.158):

$$\frac{N_\ddagger}{N_B N_C} = \frac{q_\ddagger}{q_B q_C} \tag{4.197}$$

This is equivalent to assuming there is a chemical equilibrium between the reactants and the transition state:

$$\mathrm{B} + \mathrm{C} \rightleftharpoons \ddagger \longrightarrow \mathrm{P} \tag{4.198}$$

However, note that a transition state is not a stable species (cannot be isolated) and has a life-time in the order of femtoseconds (10^{-15} s) so this is not a real chemical equilibrium. We have only assumed that the number of molecules at the transition state is given by the Boltzmann distribution. If we denote the ground-state energy of any of these molecules as ϵ_0, then the partition function can be written as:

$$q = q^0 \times e^{-\epsilon_0/k_BT} \tag{4.199}$$

where q^0 is the partition function referred to a ground-state with zero energy. Then, Eq. 4.197 can be rewritten as:

$$\frac{N_\ddagger}{N_B N_C} = \frac{q^0_\ddagger}{q^0_B q^0_C} e^{-\Delta\epsilon^\ddagger_0/k_BT} \tag{4.200}$$

where we have defined the energy difference between the ground-states of transition state and reactants as:

$$\Delta\epsilon^\ddagger_0 = \epsilon^\ddagger_0 - \epsilon^\mathrm{B}_0 - \epsilon^\mathrm{C}_0 \tag{4.201}$$

Dividing both sides of Eq. 4.200 by N_AV (same as we did in Section 2.3.5 to derive K_c in terms of partition functions), we find:

$$\frac{[\ddagger]}{[\mathrm{B}][\mathrm{C}]} = \frac{\left(\frac{q^0_\ddagger}{N_AV}\right)}{\left(\frac{q^0_B}{N_AV}\right)\left(\frac{q^0_C}{N_AV}\right)} e^{-\Delta\epsilon^\ddagger_0/k_BT} \tag{4.202}$$

where we have used that the number of moles is related to the number of molecules by $n_X = N_X/N_A$ and that the concentration is $[\mathrm{X}] = n_X/V$.

This expression is similar to that of an equilibrium constant in a chemical reaction (compare to Eq. 2.167), but this is not a chemical equilibrium, because the transition state is not stable. The partition function for the transition state is written as (Eq. 2.14):

$$q^0_\ddagger = q^{0,\mathrm{elec}}_\ddagger q^{0,\mathrm{vib}}_\ddagger q^{\mathrm{rot}}_\ddagger q^{\mathrm{trans}}_\ddagger \tag{4.203}$$

The electronic, rotational, and translational partition functions are calculated in the same way as in a stable molecule. The vibrational contribution in the harmonic approximation is (Eq. 2.69):

$$q^{0,\mathrm{vib}}_\ddagger = \prod_{i=1}^{3m-6} q^{0,\mathrm{vib},i}_\ddagger \tag{4.204}$$

where the partition function corresponding to each mode of motion involves the corresponding vibrational frequency (Eq. 2.65):

$$q^{0,\mathrm{vib},i}_\ddagger = \frac{1}{1 - e^{-\beta hc\tilde{\nu}_i}} \tag{4.205}$$

(Note we used the zero-energy ground-state expression for the partition function (Eq. 2.177).) The transition state is a saddle point and, therefore, there is a vibrational frequency that is imaginary because the energy decreases along one of the normal modes of the molecule. The eigenvector associated with the imaginary vibrational frequency points along the reaction coordinate and the beginning of the steepest descent path towards reactants and products. Because the molecule is not stable along this normal mode, applying the harmonic approximation makes no sense, and neither does the harmonic vibrational partition function above. Consequently, we separate the vibrational partition function into two contributions. One contribution corresponds to the movement along the reaction coordinate and the other contains the product of the partition functions for the rest of the normal modes, for which the harmonic approximation is still valid:

$$q_{\ddagger}^{0,\mathrm{vib}} = q_{\mathrm{rc}} \prod_{i=1}^{3m-5} q_{\ddagger}^{0,\mathrm{vib},i} \tag{4.206}$$

With this, we can single out the vibrational contribution from the reaction coordinate to the transition-state partition function in Eq. 4.202 and rewrite this equation as:

$$\frac{[\ddagger]}{[\mathrm{B}][\mathrm{C}]} = q_{\mathrm{rc}} \underbrace{\frac{\left(\frac{\bar{q}_{\ddagger}}{N_A V}\right)}{\left(\frac{q_B^0}{N_A V}\right)\left(\frac{q_C^0}{N_A V}\right)} e^{-\Delta\epsilon_0^{\ddagger}/k_B T}}_{K^{\ddagger}} = q_{\mathrm{rc}} K^{\ddagger} \tag{4.207}$$

where $\bar{q}_{\ddagger}$ does not contain the vibrational contribution from the reaction coordinate. We labeled the second factor in the right-hand side of this equation $K^{\ddagger}$ because of its similarity with an equilibrium constant. However, note $K^{\ddagger}$ contains one fewer vibrational contribution in the partition function $\bar{q}_{\ddagger}$.

From this last expression we can solve the transition-state concentration:

$$[\ddagger] = q_{\mathrm{rc}} K^{\ddagger} [\mathrm{B}][\mathrm{C}] \tag{4.208}$$

We can write the rate of generation of the products as (see Eq. 4.198):

$$r = k_{\ddagger}[\ddagger] = k_{\ddagger} q_{\mathrm{rc}} K^{\ddagger} [\mathrm{B}][\mathrm{C}] \tag{4.209}$$

where $k_{\ddagger}$ is the rate constant associated with the conversion of transition state to product. The rate constant for the bimolecular elementary reaction is:

$$r = k[\mathrm{B}][\mathrm{C}] \tag{4.210}$$

so we identify the rate constant as:

$$k = k_{\ddagger} q_{\mathrm{rc}} K^{\ddagger} \tag{4.211}$$

It is possible to show that, if we treat the movement along the reaction coordinate classically (either as a translation or a very floppy vibration) and we assume that all molecules that cross the dividing surface become products, then the first two factors in the right-hand side of this equation reduce to $k_B T/h$, where h is Planck constant. With this, the rate constant becomes:

$$k = \frac{k_B T}{h} K^{\ddagger} = \frac{k_B T}{h} \frac{\left(\frac{\bar{q}_{\ddagger}}{N_A V}\right)}{\left(\frac{q_B^0}{N_A V}\right)\left(\frac{q_C^0}{N_A V}\right)} e^{-\Delta\epsilon_0^{\ddagger}/k_B T} \tag{4.212}$$

This is the **Eyring equation**. It approximates the rate constant of a bimolecular elementary step from the knowledge of the reactants and the transition state, bypassing the requirement of calculating other parts of the potential energy surface. The Eyring equation gives a reasonable description of bimolecular rate constants, but it has serious limitations in two cases: i) when the assumption that a reactant molecule that crosses the dividing surface goes on to form the product is not valid, and ii) when there are substantial quantum tunneling effects such as, for instance, in hydrogen-transfer reactions. Extensions to conventional transition state theory have been proposed to address both limitations.

The equilibrium constant $K^\ddagger$ has units of concentration^{-1}. By analogy with our treatment the equilibrium constant K_c (Eq. 2.167), we can define an adimensional equivalent of $K^\ddagger$ by multiplying by c°:

$$K_c^\ddagger = c^\circ \frac{\left(\frac{\bar{q}_\ddagger}{N_A V}\right)}{\left(\frac{q_B^0}{N_A V}\right)\left(\frac{q_C^0}{N_A V}\right)} e^{-\Delta\epsilon_0^\ddagger/k_B T} = c^\circ K^\ddagger \tag{4.213}$$

This constant, however, has one vibrational contribution missing from the transition state partition function. Following the same procedure we used in Section 2.3.5 for the equilibrium constant K_c, we can relate $K_c^\ddagger$ with the **(standard) activation Gibbs energy in the concentration scale**, $\Delta G_c^{\circ\ddagger}$, which, again, is calculated by taking into account all contributions from all molecular modes of motion except the vibrational contribution of the transition state along the reaction coordinate:

$$\Delta G_c^{\circ\ddagger} = -RT \ln K_c^\ddagger \tag{4.214}$$

Likewise, we can define the **activation enthalpy** ($\Delta H_c^{\circ\ddagger}$) and the **activation entropy** ($\Delta S_c^{\circ\ddagger}$), and the three are related by:

$$\Delta G_c^{\circ\ddagger} = \Delta H_c^{\circ\ddagger} - T\Delta S_c^{\circ\ddagger} \tag{4.215}$$

all of them in the concentration scale. Substituting in the Eyring equation, we have:

$$k = \frac{k_B T}{h}\frac{K_c^\ddagger}{c^\circ} = \frac{k_B T}{h}\frac{1}{c^\circ} e^{-\Delta G_c^{\circ\ddagger}/RT} = \frac{k_B T}{h}\frac{1}{c^\circ} e^{\Delta S_c^{\circ\ddagger}/R} e^{-\Delta H_c^{\circ\ddagger}/RT} \tag{4.216}$$

From here, we can find the activation energy in transition-state theory by first calculating the logarithm of the rate constant:

$$\ln k = \ln\left(\frac{k_B}{h}\frac{1}{c^\circ}\right) + \ln T - \frac{\Delta G_c^{\circ\ddagger}}{RT} \tag{4.217}$$

and then using the definition of the activation energy (Eq. 4.135):

$$E_a = RT^2 \frac{d\ln k}{dT} = RT^2\left(\frac{1}{T} - \frac{1}{R}\frac{d(\Delta G_c^{\circ\ddagger}/T)}{dT}\right) = RT^2\left(\frac{1}{T} + \frac{\Delta H_c^{\circ\ddagger}}{RT^2}\right) = \Delta H_c^{\circ\ddagger} + RT \tag{4.218}$$

where we have applied the Gibbs-Helmholtz equation:

$$\left(\frac{\partial(G/T)}{\partial T}\right)_p = -\frac{H}{T^2} \tag{4.219}$$

to the activation free energy. In transition-state theory, the activation energy is related to the activation enthalpy (RT is 0.59 kcal/mol at room temperature, and therefore small compared with the activation energies of typical reactions). The exponential prefactor is (Eq. 4.136):

$$A = ke^{E_a/RT} = \frac{k_B T}{h}\frac{1}{c^\circ} e^{\Delta S_c^{\circ\ddagger}/R} \cancel{e^{-\Delta H_c^{\circ\ddagger}/RT}} \times e \times \cancel{e^{\Delta H_c^{\circ\ddagger}/RT}} = \frac{k_B T}{hc^\circ} e^{1+\Delta S_c^{\circ\ddagger}/R} \tag{4.220}$$

The entropy of activation is always negative because two species (B and C) combine into a single molecule (the transition state). However, the $\Delta S_c^{\circ\ddagger}$ is usually lower than the reduction in entropy corresponding to a simple merge between molecules B and C, which informs us of the fact that not only do B and C need to meet, they must do it with the correct orientation. This extra reduction in entropy can be used to calculate the steric factor from collision theory.

Finally, similar expressions can be derived for reactions in the gas phase, where we refer all activation quantities to a standard state of 1 bar, and the equilibrium constant is written in terms of pressures. In particular, the transition-state constant is written as:

$$K_p^\ddagger = \frac{p^\circ}{c^\circ RT} K_c^\ddagger \tag{4.221}$$

and the the Eyring equation for a gas phase reaction becomes:

$$k = \frac{k_B T}{h}\frac{RT}{p^\circ}K_p^\ddagger = \frac{k_B T}{h}\frac{RT}{p^\circ}e^{-\Delta G_p^{\circ\ddagger}/RT} = \frac{k_B T}{h}\frac{RT}{p^\circ}e^{\Delta S_p^{\circ\ddagger}/R}e^{-\Delta H_p^{\circ\ddagger}/RT} \tag{4.222}$$

where $\Delta G_p^{\circ\ddagger}$,... are the same thermodynamic quantities as before but referred to the gas-phase standard state (1 bar, ideal gas). The Arrhenius parameters in the gas phase can be derived in the same way as before, to find:

$$E_a = \Delta H_p^{\circ\ddagger} + 2RT \tag{4.223}$$

$$A = \frac{k_B T}{h}\frac{RT}{p^\circ}e^{2+\Delta S_p^{\circ\ddagger}/R} \tag{4.224}$$

The activation Gibbs energy, enthalpy and entropy can be calculated using quantum mechanical methods and the statistical thermodynamics formulas we have seen before, but one must take care not to include the reaction coordinate in the calculation of the transition state's vibrational quantities. The activation free energy, enthalpy and entropy that appear in transition-state theory are widely used to report experimental observations of reaction rates and rate constants, particularly for organic reactions in solution.

The activation quantities are also useful in the context of **correlation analysis** where the equilibrium constant $\ln K^\circ = -\Delta_r G^\circ/RT$ of a series of similar reactions is represented against $\ln k = -\Delta G^{\circ\ddagger}/RT$. In many cases, there is a linear correlation between these quantities in families of similar reactions, which indicates that, within that family, those reactions that are thermodynamically more favorable also occur faster. These correlations are usually referred to as **linear free energy relations**, because the reaction free energy ($\Delta_r G^\circ$) and the activation free energy ($\Delta G^{\circ\ddagger}$) are found to be linearly proportional to each other. One example of linear free energy relation is the **Bell-Evans-Polanyi** principle, which states that differences in activation energies of reactions in the same family are approximately the same as the differences between their enthalpies of reaction.

Another popular example of a linear free energy relation is the **Hammett equation**, in which the rate constants and the equilibrium constants of reactions involving para- and meta-substituted benzoic acid derivatives can be described by two parameters:

$$\log\frac{K}{K_0} = \log\frac{k}{k_0} = \sigma\rho \tag{4.225}$$

where K and k are the equilibrium constant and rate constant of the reaction under study and K_0 and k_0 are the equivalent quantities for a reference reaction with unsubstituted benzoic acid. The two constants are σ (the **substituent constant**), which depends on the substituents involved but not on the reaction, and ρ (the **reaction constant**), which depends on the reaction but not on the substituents. The fact that the Hammett equation can be used both for the equilibrium constants and rate constants implies, using our results from transition-state theory, that the Hammett equation is postulating a linear relationship between differences in Gibbs free energies of two reactions and differences in the corresponding activation free energies. The Hammett parameters have been determined for many reactions and substances and have been tabulated in the literature.

4.9 Reactions in Solution

Reactions that happen in solution have the reactants surrounded at all times by molecules of solvent. For this reason, molecular collisions happen at a much lower rate than in the gas phase and, once they happen, the reactants involved in the collision may become locked by the molecules of the solvent for a certain amount of time, increasing the chance that further collisions between the molecules trapped in the cage will happen again. This is called the **cage effect** and the complex made by the reactants surrounded by solvent molecules is an **encounter pair**, which may or may not react to become the products.

We can describe the formation and fate of the encounter pairs by the following mechanism:

$$\mathrm{B} + \mathrm{C} \xrightarrow{k_d} \mathrm{BC}$$
$$\mathrm{BC} \xrightarrow{k'_d} \mathrm{B} + \mathrm{C}$$
$$\mathrm{BC} \xrightarrow{k_a} \mathrm{P}$$

where B and C are reactant molecules and BC is the encounter pair. k_d is the diffusion rate constant, which depends on the diffusion velocities of both reactants in solution. The encounter pair may disgregate (with rate constant k'_d) or it may form the products with rate constant k_a, called the activation rate constant. The encounter pair is relatively short lived, so we can apply the steady-state approximation to it:

$$\frac{d[\mathrm{BC}]}{dt} = k_d[\mathrm{B}][\mathrm{C}] - k'_d[\mathrm{BC}] - k_a[\mathrm{BC}] = 0 \tag{4.226}$$

from where we solve the concentration of the encounter pair

$$[\mathrm{BC}] = \frac{k_d[\mathrm{B}][\mathrm{C}]}{k'_d + k_a} \tag{4.227}$$

The rate of formation of the products is therefore:

$$\frac{d[\mathrm{P}]}{dt} = k_a[\mathrm{BC}] = \frac{k_a k_d}{k'_d + k_a}[\mathrm{B}][\mathrm{C}] = k[\mathrm{B}][\mathrm{C}] \tag{4.228}$$

where the effective rate constant is:

$$k = \frac{k_a k_d}{k'_d + k_a} \tag{4.229}$$

This equation tells us that there are two important limits for reactions in solution. If the activation rate constant (k_a) is much higher than the diffusion rate constant (k'_d), then the rate constant for the reaction equals k_d, which is determined by the diffusion properties of both species. This is the case of a **diffusion-controlled reaction**. Using arguments related to the properties of diffusion transport in solution, it is possible to show that its value is approximately:

$$k_d = \frac{8RT}{3\eta} \tag{4.230}$$

where η is the viscosity of the solvent. Water at 20 °C has a viscosity of approximately $1\,\mathrm{cP} = 1\,\mathrm{mPa\,s}$, which gives a diffusion rate constant of $k_d = 6.61 \times 10^9\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$. This is the order of magnitude for the rate constants of the (usually very fast) diffusion-controlled reactions.

If, on the other hand, $k_a \ll k'_d$, then the effective rate constant is:

$$k \approx \frac{k_a k_d}{k'_d} = k_a K \tag{4.231}$$

where K is the equilibrium constant for the formation of the encounter pair. This case is an **activation-controlled reaction**. In this case, the overall rate constant of the reaction is determined by the stability of the encounter pair (k increases if the encounter pair is more stable) and by the rate constant of the elementary step involving the reaction between B and C.

4.10 Reactions Between Ions and the Kinetic Salt Effect

The transition-state theory can be applied to solutions in which interactions of reactant molecules with the solvent and with other molecules result in deviations from ideal behavior. In this case, we consider activities instead of concentrations. As in the ideal case, the rate of generation of products depends on the concentration of molecules in the transition state:

$$\frac{d[\mathrm{P}]}{dt} = k_\ddagger [\ddagger] \tag{4.232}$$

because the reaction rate, and therefore the rate law, is always expressed in terms of concentrations. The rate constant under ideal conditions is (Eq. 4.216):

$$k^\circ = \frac{k_B T}{h}\frac{K_c^\ddagger}{c^\circ} = \frac{k_B T}{h}\frac{1}{c^\circ} e^{-\Delta G_c^{\circ\ddagger}/RT} \tag{4.233}$$

and the activation equilibrium constant is given by (Eq. 4.207 and Eq. 4.213):

$$\frac{([\ddagger]/c^\circ)}{([\mathrm{B}]/c^\circ)\,([\mathrm{C}]/c^\circ)} = q_{\mathrm{rc}} K_c^\ddagger \tag{4.234}$$

Under non-ideal conditions, this activation equilibrium constant is written in terms of activities, so we have to modify the left-hand side of the last equation:

$$\frac{a_\ddagger}{a_\mathrm{B} a_\mathrm{C}} = \underbrace{\frac{\gamma_\ddagger}{\gamma_\mathrm{B}\gamma_\mathrm{C}}}_{K_\gamma} \frac{([\ddagger]/c^\circ)}{([\mathrm{B}]/c^\circ)\,([\mathrm{C}]/c^\circ)} = q_{\mathrm{rc}} K_c^\ddagger \tag{4.235}$$

where we defined K_γ in terms of the activity coefficients:

$$K_\gamma = \frac{\gamma_\ddagger}{\gamma_\mathrm{B}\gamma_\mathrm{C}} \tag{4.236}$$

(Note that both activities and activity coefficients are adimensional. These activities are in the concentration scale, because we are assuming a standard state with $c = c^\circ$.) Solving for the transition-state concentration:

$$[\ddagger] = q_{\mathrm{rc}} \frac{K_c^\ddagger}{K_\gamma c^\circ}[\mathrm{B}][\mathrm{C}] \tag{4.237}$$

and the rate is:

$$r = k_\ddagger [\ddagger] = k_\ddagger q_{\mathrm{rc}} \frac{K_c^\ddagger}{K_\gamma c^\circ}[\mathrm{B}][\mathrm{C}] \tag{4.238}$$

And finally we arrive at the rate constant of the reaction under non-ideal conditions:

$$k = \frac{k_BT}{h}\frac{K_c^\ddagger}{K_\gamma c^\circ} \tag{4.239}$$

If we compare this expression with the rate constant under ideal conditions (Eq. 4.233), we find that:

$$k = \frac{k^\circ}{K_\gamma} \tag{4.240}$$

which is the **Brønsted-Bjerrum equation**. In a non-ideal solution, the rate constant of an elementary bimolecular reaction is modified by the activity coefficients of reactants and transition state. In non-ionic reactions, this change is so small that it is not detectable with current experimental techniques. In ionic solutions, however, the change can be quite substantial.

To examine how the charges of reactants and transition state affect the rate constant, we take the logarithm of the rate constant:

$$\log k = \log k^\circ - \log K_\gamma \tag{4.241}$$

At low concentration, the activity coefficients can be expressed in terms of the ionic strength of the solution ($I = I_c/c^\circ$ with $I_c = \frac{1}{2}\sum_j c_j z_j^2$) using the Debye-Hückel limiting law, or some other suitable law appropriate for the experimental conditions (e.g. Davies' equation):

$$\log \gamma_i = -Az_i^2 I^{1/2} \tag{4.242}$$

$$\log \gamma_\pm = -A|z_+z_-|I^{1/2} \tag{4.243}$$

where $A = 0.509$ for water at 298 K, $\gamma_\pm$ is the mean activity coefficient, z_i are the (signed) charges of each species, and c_i are the molar concentrations. If reactants B and C have charges z_B and z_C, then the transition state has charge $z_\ddagger = z_B + z_C$ and therefore:

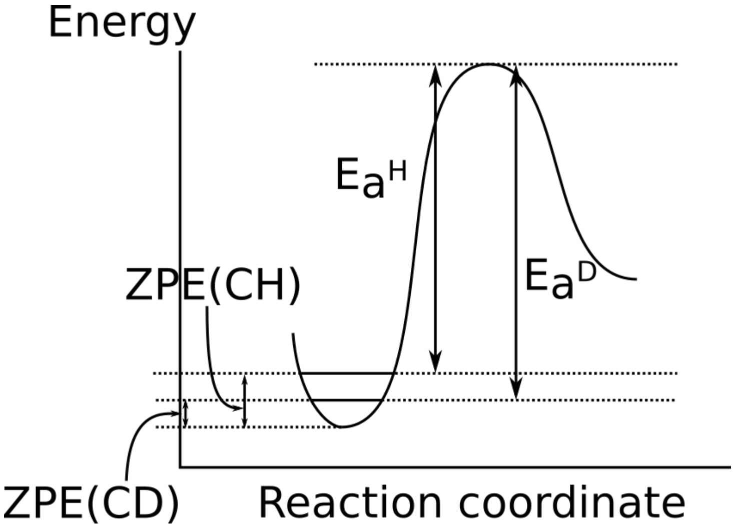
$$\log \gamma_\ddagger = -A(z_B + z_C)^2 I^{1/2} \tag{4.244}$$

Using these relations in Eq. 4.241, we have that:

$$\begin{aligned}\log k &= \log k^\circ - [\log\gamma_\ddagger - \log\gamma_B - \log\gamma_C] \\ &= \log k^\circ - \left[-A(z_B+z_C)^2 I^{1/2} + Az_B^2 I^{1/2} + Az_C^2 I^{1/2}\right] \\ &= \log k^\circ - A\left[-(z_B+z_C)^2 + z_B^2 + z_C^2\right] I^{1/2} = \log k^\circ + 2Az_Bz_C I^{1/2}\end{aligned} \tag{4.245}$$

This equation is the quantitative expression of the **(primary) kinetic salt effect**. The kinetic salt effect occurs when the rate of a reaction between ions in solution changes when an inert ion is added to the mixture. The rate constant depends on the ionic strength and therefore on the concentration of all ions in solution, regardless of whether they participate in the reaction or not. The change in the reaction rate on addition of an inert electrolyte informs us of the charge of the reactants and the transition state. If both reactants have the same charge sign (i.e. both cations or both anions), then the rate increases when inert salt is added. This is because the transition state interacts more strongly with the environment than the reactants, and is thus stabilized relative to them. The decrease in the activation enthalpy results in a smaller rate constant. On the contrary, if the reactants have opposite-signed charges (cation and anion) then the rate constant decreases when salt is added because the transition state interacts with the ionic environment less strongly than the reactants, and is relatively destabilized, increasing the activation enthalpy and decreasing the rate constant. The primary kinetic salt effect is also more noticeable the higher the charges of the reactants. (Note: the secondary kinetic salt effect, which is different from the primary kinetic salt effect, occurs when addition of the inert electrolyte changes the concentrations of the reactants themselves by altering the chemical equilibria in which they are involved.)

Figure 4.16: Effect of an isotopic change (H to D) in the activation energy of a reaction.



4.11 The Kinetic Isotope Effect

One important tool in the experimental elucidation of reaction mechanisms is the **kinetic isotope effect**. The kinetic isotope effect refers to the change in the rate of a chemical reaction when one of the atoms in one of the reactants is replaced by a heavier isotope. Typically, a hydrogen atom is replaced by deuterium because in that case the kinetic isotope effect is most noticeable (the mass of D is twice the mass of H). If the heavy isotope is directly involved in the bond-breaking event of the rate-determining step, then we have a **primary kinetic isotope effect**. Otherwise, the change in the reaction rate is caused by a **secondary kinetic isotope effect**. Since the chemical behavior of both isotopes is the same, the change in reaction rate results from a change in the rate constant that mostly originates from a change in the activation energy, which in turn comes from the modification of the vibrational energies resulting from the replacement of a light atom with a heavier atom.

Consider a reaction where a C−H bond is cleaved. If breaking this bond constitutes the rate-determining step, then the change in the activation energy can be roughly approximated by the change in zero-point energy of the stretching vibration of this bond (see Figure 4.16):

$$E_a^{\mathrm{D}} - E_a^{\mathrm{H}} = N_A \left[\frac{1}{2} h\nu(\mathrm{C{-}H}) - \frac{1}{2} h\nu(\mathrm{C{-}D}) \right] = \frac{1}{2} N_A h [\nu(\mathrm{C{-}H}) - \nu(\mathrm{C{-}D})] \tag{4.246}$$

where ν are the vibrational frequencies, which are calculated as:

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \tag{4.247}$$

with k the force constant for the harmonic oscillator and μ is the reduced mass for that particular vibration. The force constant is the same regardless of the isotope, because it is the second derivative of the electronic energy, which depends on the atomic numbers but not the atomic weights. Therefore, the ratio of the two frequencies is:

$$\frac{\nu(\mathrm{C{-}D})}{\nu(\mathrm{C{-}H})} = \sqrt{\frac{\mu_{\mathrm{C-H}}}{\mu_{\mathrm{C-D}}}} \tag{4.248}$$

where μ are the effective masses for the two pairs of atoms. Note that $\mu_{\mathrm{C-D}} > \mu_{\mathrm{C-H}}$ since D is heavier than H. From this, we obtain:

$$\begin{aligned} E_a^{\mathrm{D}} - E_a^{\mathrm{H}} &= \frac{1}{2}N_A h[\nu(\mathrm{C{-}H}) - \nu(\mathrm{C{-}D})] = \frac{1}{2}N_A h\nu(\mathrm{C{-}H})\left[1 - \frac{\nu(\mathrm{C{-}D})}{\nu(\mathrm{C{-}H})}\right] \\ &= \frac{1}{2}N_A h\nu(\mathrm{C{-}H})\left(1 - \sqrt{\frac{\mu_{\mathrm{C-H}}}{\mu_{\mathrm{C-D}}}}\right) \end{aligned} \tag{4.249}$$

If we further assume the pre-exponential factor does not change upon deuteration, then the ratio of the rate constants is:

$$\frac{k^{\mathrm{H}}}{k^{\mathrm{D}}} = e^{-(E_a^{\mathrm{H}} - E_a^{\mathrm{D}})/RT} = e^{(E_a^{\mathrm{D}} - E_a^{\mathrm{H}})/RT} \tag{4.250}$$

$$= \exp\left[\frac{h\nu(\mathrm{C{-}H})}{2k_B T}\left(1 - \sqrt{\frac{\mu_{\mathrm{C-H}}}{\mu_{\mathrm{C-D}}}}\right)\right] \tag{4.251}$$

because $\mu_{\mathrm{C-D}} > \mu_{\mathrm{C-H}}$ (deuterium is heavier than hydrogen), the factor in the parentheses is positive, and the whole exponent is positive, and therefore $k^{\mathrm{H}}/k^{\mathrm{D}} > 1$. This ratio between the rate constants for the two reactions with the light and the heavy atoms is itself known as the kinetic isotope effect:

$$\mathrm{KIE} = \frac{k_{\mathrm{L}}}{k_{\mathrm{H}}} \tag{4.252}$$

where L and H are the light and heavy atoms, respectively. From the discussion above, we expect the rate constant, and therefore the rate of the reaction, to decrease upon deuteration. Often, the experimentally observed isotope effect differs significantly from this rough estimate, particularly in the case of hydrogen replaced with deuterium, because tunneling effects in reactions involving hydrogen can be important. The probability of tunneling decreases as the mass of the particle increases and therefore deuterium tunnels much less efficiently through a barrier and, therefore, the deuterium rate constant is much lower than predicted by the above estimate.

Chapter 5

Surface Adsorption

5.1 Structure of Solid Surfaces

The study of adsorption to solid surfaces is important due to the technological and industrial applications of surface processes. One example application is the role that surfaces play in heterogeneous catalysis because—solid catalysts are very relevant in many chemical reactions of industrial importance. Another example is the manufacturing of layered materials for technological applications. For instance, liquid crystal displays (LCD) are formed by sandwiched layers of conductive transparent surfaces and molecular liquid crystals. Self-assembled monolayers (SAM) are structures in which molecules are chemically bonded to the surface of a solid forming an ordered single-layer. The molecules in a SAM are designed in such a way that their order can be modified, allowing control over the properties of the surface. For instance, a hydrophilic surface may be turned hydrophobic by coating it in molecules with long-chain alkyl substituents (e.g. thiols on a gold surface). Likewise, it is possible to functionalize a surface to have specific chemical reactivity or ligand-binding properties.

At a basic level, surfaces can be thought of as obtained by cleaving a periodic solid through one of its crystallographic planes. These planes are labeled by their Miller indices, (hkl), which correspond to the inverse of the intercept of the cleavage plane with the crystallographic axes of the solid. For the same solid material, the structure of a given surface changes depending on the cleavage plane chosen. Figure 5.1 shows an example of three surfaces with different structures corresponding to three crystallographic planes in an elemental metal with a face-centered cubic (fcc) structure.

The properties of a solid surface depend both on the underlying material as well as the structure structure, determined by the cleavage plane. One important surface property is its growth rate, which determines whether the surface is obtained spontaneously by crystallizing the solid. The activity of solid-state catalysts is also critically dependent on the surface structure, and therefore on the cleavage plane.

Because a surface is exposed to vacuum, the surface atoms are less stable than their bulk counterparts, i.e., it takes work to move an atom from the bulk to the surface. In addition, surface atoms move in order to minimize the free energy of the whole surface and, therefore, a surface rarely has the same structure as a clean cut of the bulk solid. The extent to which the surface structure differs from the bulk changes from material to material. In the case of metals, surfaces typically retain the bulk structure but the last layer is compressed, so that the distance to the next-to-last layer is lower than in the bulk. This process is called **surface relaxation**. In insulators and semiconductors, which typically contain anions and cations, the structure of the surface often changes dramatically relative to the bulk. This process is called

Figure 5.1: Three surfaces extracted from a solid that has a face-centered cubic (fcc) lattice. The surfaces are labeled by the corresponding Miller index of the crystallographic plane.

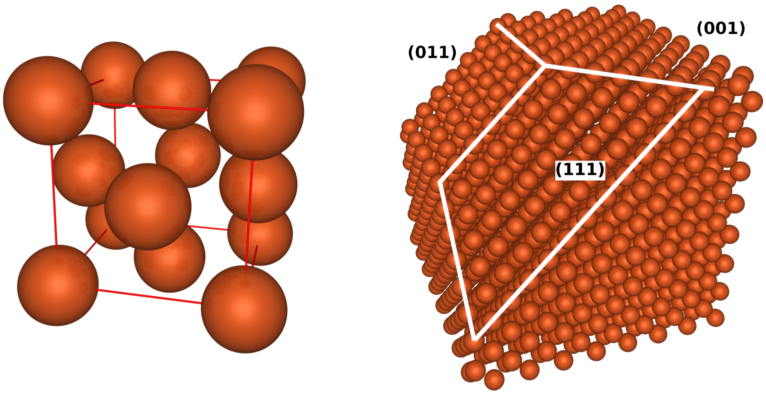
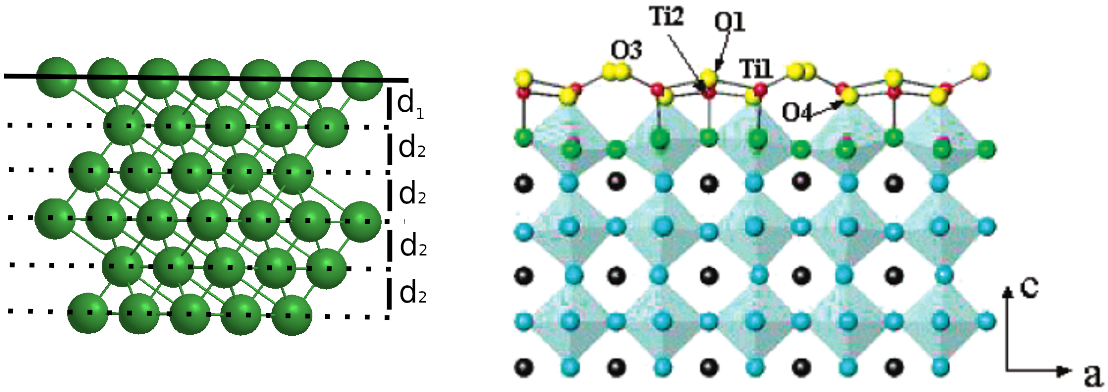


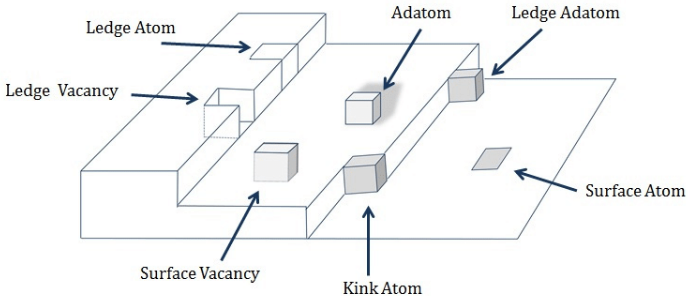
Figure 5.2: Left: Surface relaxation in a nickel surface. The distance d_1 is slightly lower than d_2. Right: Surface reconstruction in the (001) surface of $SrTiO_3$. (Reproduced, with permission, from Erdman et al. *J. Am. Chem. Soc.* **125** (2003) 10050.)



surface reconstruction and can affect several layers of the surface, not just the first one. The way in which a given surface reconstructs is difficult to predict, and usually has to be determined experimentally. Examples of surface relaxation and surface reconstruction are shown in Figure 5.2. Nickel undergoes surface relaxation, and the distance between the last and next-to-last layers (d_1) is slightly lower than the others (d_2. In the $SrTiO_3$ surface, it can be seen that the reconstruction disrupts the bulk perovskite structure up to three layers underneath the surface.

In addition to relaxation and reconstruction, the structure of a surface also contains a number of defects, which are energetically unfavorable but entropically favored. Some of the typical surface defects are shown in Figure 5.3. Flat tracts of clean surface are called **terraces**. These terraces contain defects such as **ledges** (also called **steps**; a line separating two terraces), **kinks** (the atom at which a ledge ends), **adatoms** (atoms that stick out of the surface), and **vacancies** (missing atoms). Defects play an essential role in adsorption and particularly in the catalytic activity of a surface because often these defects are the active sites for molecular dissociation. For instance, a mixture of carbon monoxide and hydrogen ("synthesis gas") can be used to synthesize liquid hydrocarbons using a cobalt catalyst (the Fischer-Tropsch process). The activity of this catalyst is known to increase with the number of steps on its surface.

Figure 5.3: Illustration of several kinds of defects on the surface: ledges, kinks, and adatoms. Reproduced, with permission, from Zangari, "Electrodeposition of Alloys and Compounds in the Era of Microelectronics and Energy Conversion Technology", *Coatings*, **5** (2015) (distributed under CC license).



5.2 Adsorption on Surfaces

We now consider the surface of a material in contact with a gas. The molecules of the gas are constantly colliding with the surface, and some of them become attached to it. This is a case of molecular **adsorption** (the molecule adsorbs onto the surface). After a while, an adsorbed molecule may gain enough energy to detach from the surface, a process known as **desorption** (the molecule desorbs). The substance in the gas phase is the **adsorbate** and the surface material is known as the **adsorbant** or **substrate**. (Do not confuse adsorption with absorption: the molecules, in general, are not absorbed and do not penetrate the bulk of the solid.) Common adsorbates include small species such as He, H_2, N_2, O_2, CO, CO_2, NH_3, SO_2, and small hydrocarbons (methane, ethane, ethene). Common substrates include elemental metals, metal oxides such as alumina (Al_2O_3) or silica (SiO_2), activated charcoal, and synthetic porous materials like zeolites (aluminosilicate structures with channels in the bulk that let molecules through).

In general, a clean surface exposed to a gas quickly becomes covered in adsorbed molecules. We can estimate the number of impacts per area per unit time on the surface using results from the kinetic theory of gases. For instance, a 1 bar pressure of N_2 at 298 K has a collision flux (Eq. 3.73) of $Z = 2.9 \times 10^{27}\,\mathrm{m^{-2}\,s^{-1}}$. A metal surface has a typical atom density of $1 \times 10^{19}\,\mathrm{m^{-2}}$ so, on average, each atom on the surface receives a molecular collision about 1×10^{8} times per second. The experimental characterization of surfaces usually requires a clean surface, and this is typically achieved by applying high vacuum (0.1 mPa) or ultra-high vacuum (between 0.1 μPa and 0.1 nPa) to the surface, which significantly reduces the number of molecular collisions on the surface and therefore the adsorption. Surfaces where molecules are already adsorbed can be cleaned by raising the temperature, a process known as **outgassing**. Since this procedure sometimes leaves contaminants on the surface, there are alternative methods, which include bombardment with Ar ions, or depositing or cleaving the surface under ultra-high vacuum.

5.2.1 Types of Adsorption

There are two types of surface adsorption: **physisorption** (short for "physical adsorption") and **chemisorption** ("chemical adsorption"). In physisorption, the interaction between molecule and surface is dominated by van der Waals (non-covalent) interactions. During physisorption, the mobility of the adsorbed molecule is impeded, but the electronic structure and the chemical bonds of substrate and adsorbate are not significantly distorted, and the interaction strength between the two is usually weak, in the order of 1 to 10 kcal/mol. In addition, physisorption is non-specific: any surface can effect physisorption with any molecule provided the temperature is low enough to prevent the adsorbate from returning to the gas phase. In fact, a characteristic of physisorption is that multiple layers of adsorbate can stack. The second and subsequent molecular layers physisorb onto other adsorbed molecular layers, in a process thermodynamically identical to the condensation of a vapor on a liquid.

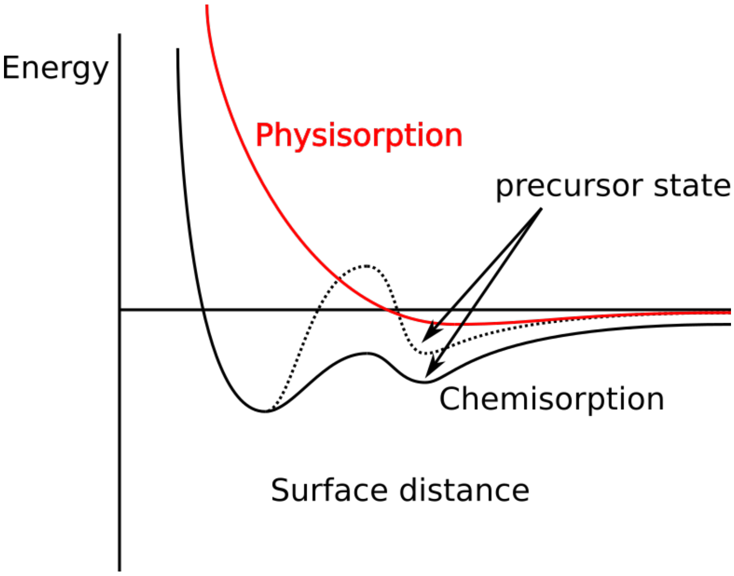
In contrast, chemisorption involves the formation of a chemical (covalent) bond between the adsorbate and the surface. The interaction strength between the two is much higher than in physisorption, typically in the order of tens to hundreds of kcal/mol. As a consequence of the formation of new bonds, the structure and electronic properties of substrate and surface are significantly distorted. In fact, in many cases, the chemisorbed molecule dissociates on the substrate, and the resulting molecular fragments chemisorb to the surface forming new chemical bonds, possibly after moving to a different location on the surface. Chemisorption is usually specific in that it only happens at certain sites on the surface (called **active sites** or **active centers**). These sites often coincide with surface defects. Chemisorption with molecular dissociation on the surface is known **dissociative chemisorption**. This typically happens in species with no free electron pairs with which they can bond to the surface (e.g. H_2, CH_4, and ethane). Molecules that do not dissociate on the surface effect **non-dissociative chemisorption**, which is typical of species like CO, NH_3, or ethene, which bond to the surface via unshared electron pairs. Another example is CO_2, which chemisorbs onto metal oxide surfaces by transforming into a carbonate (CO_3^{2-}). In general, whether a molecule physisorbs or chemisorbs depends on the nature of molecule and surface. For instance, N_2 chemisorbs onto Fe, W, Ca, and Ti but not onto Ni, Ag, Cu, or Pb. A clean Au surface can chemisorb O_2, C_2H_2, and CO, but physisorbs H_2, CO_2, and N_2.

Figure 5.4 shows the typical energy profiles for chemisorption and physisorption as a function of adsorbate distance from the surface. The interaction energy between molecule and surface in the case of physisorption is relatively weak, and therefore its energy profile only has a shallow minimum relatively away from the surface (red line in the figure). In contrast, chemisorption involves a covalent bond and a much higher interaction strength. Often, the chemisorption energy profile has two minima. A shallow minimum relatively far from the surface corresponding to a “precursor state”, similar to the physisorption minimum. In the precursor state, the adsorbate is not yet covalently bonded to the surface. A second minimum, much deeper and closer to the surface exists, and it corresponds to the true chemisorbed state with a chemical bond between adsorbate and substrate. The chemisorption minimum may be separated from the precursor state by an energy barrier. If this barrier is higher than the energy of the molecule in the gas phase (i.e. the energy at infinite substrate-molecule distance), then it is an **activated chemisorption** process. Otherwise, it is **non-activated chemisorption**. The rate of adsorption in physisorption and non-activated chemisorption processes is usually fast but activated chemisorption is slow because there is a significant activation energy that the molecule needs to overcome in order to bond to the surface.

5.2.2 Adsorption and Desorption Energetics

The process of adsorption is almost always exothermic because there is an entropy decrease associated to removing a molecule to the gas phase and attaching it to the surface. In order for the adsorption to be spontaneous ($\Delta G < 0$), it is necessary to have $\Delta H < 0$ to compensate for the decrease in entropy. However, there are rare exceptions like the endothermic adsorption of H_2 on glass, in which the molecule dissociates and the two H atoms are free to move on the surface, resulting in an increase in entropy. In general, the adsorption enthalpy and entropy depend on the number of molecules already adsorbed on the surface (the **coverage**). The molecules on the surface may be forming ordered structures, aggregates, or may be disordered,

Figure 5.4: Typical energy profiles for physisorption (red) and chemisorption (black). Chemisorption can be non-activated (full lines) or activated (dashed).



depending on coverage and temperature.

In both adsorption types, the energy released in the adsorption process is dissipated by the surface, typically via vibrations of the solid, a process that is known as **accommodation**. If not enough energy from the molecule is dissipated, then the molecule may migrate on the surface until it finds a defect (e.g. a kink or a vacancy) or move away from the surface and go back to the gas phase.

The **sticking probability** (or sticking coefficient) is the fraction of molecules that collide with the surface that result in a successful adsorption. It is calculated as the ratio between the rate of adsorption and the rate of molecular collisions with the surface:

$$s = \frac{\text{rate of adsorption}}{\text{rate of collision}} \tag{5.1}$$

The rate of collision can be calculated using the kinetic theory of gases (the collisional flux, Eq. 3.73), and the rate of adsorption can be measured experimentally as a decrease in gas pressure. The sticking coefficient is highest at low surface coverage, and can be as high as 0.1-1 (e.g. CO on transition metal surfaces) but it can also be relatively small (e.g. $s < 1 \times 10^{-2}$ for N_2 on Re). The value of s decreases non-linearly as the surface coverage increases, and also with an increase in temperature because more energy needs to be dissipated for a successful accommodation. An exception is the case of activated chemisorption, when temperature may increase s because the additional energy helps overcome the chemisorption barrier.

In contrast to adsorption, the process of desorption is always activated, since the molecule has to acquire enough energy to break away from the surface. The desorption process is usually modeled as a first-order kinetics (although in many cases this is not strictly correct), and the rate constant of desorption is:

$$k_d = Ae^{-E_{a,\text{des}}/RT} \tag{5.2}$$

where $E_{a,\text{des}}$ is the desorption activation energy. The **residence half-life** is the time it takes for half the molecules on the surface to desorb:

$$t_{1/2} = \frac{\ln 2}{k_d} = \tau_0 e^{E_{a,\text{des}}/RT} \tag{5.3}$$

The quantity τ_0 is the residence half-life in the limit of infinite temperature. It is related to the pre-exponential constant for desorption:

$$\tau_0 = \frac{\ln 2}{A} \tag{5.4}$$

The residence half-life at infinite temperature is a lower bound for the residence half-life itself. The higher the temperature or the lower the desorption activation energy, the lower the $t_{1/2}$.

Finally, the study of the kinetics of **molecular migration** on the surface is also important because, as we shall see, the most common mechanism for catalyzed reactions on a surface involves two molecules migrating on it and reacting with each other. The activation energy for migration on the surface is usually about 10% to 20% the adsorption enthalpy. This activation energy for migration determines the rate of molecular diffusion on the surface.

5.3 Adsorption Isotherms

The extent of surface adsorption is measured by the **fractional coverage**, an adimensional quantity defined as:

$$\theta = \frac{N_{\text{ads}}}{N_{\text{sites}}} = \frac{V}{V_{\text{mon}}} \tag{5.5}$$

where N_{ads} is the number of molecules adsorbed and N_{sites} is the total number of adsorption sites on the surface. It is customary to express this ratio as a quotient of volumes, as shown in the second equation. Here, V is the volume of gas adsorbed at the chosen pressure and temperature and V_{mon} is the volume of gas adsorbed that corresponds to a complete occupation of all adsorption sites by a single molecule (i.e. the complete formation of a monolayer). Note that these volumes have nothing to do with the volume of gas in contact with the surface at any given time. Instead, they are the volume the adsorbed molecules would occupy at a certain temperature and pressure if they were desorbed from the surface, calculated using the ideal gas law:

$$V = \frac{N_{\text{ads}} k_B T}{p} \quad ; \quad V_{\text{mon}} = \frac{N_{\text{sites}} k_B T}{p} \tag{5.6}$$

where T is the experimental temperature and p is some arbitrary pressure (e.g. 1 atm).

For a surface in contact with a gas of molecules, the **adsorption isotherm** is the value of the fractional coverage of the surface as a function of gas pressure at a fixed temperature, $\theta(p)$. The shape of the adsorption isotherm depends on the nature of the adsorption. In the case of pure chemisorption (e.g. O_2 on charcoal), the fractional occupation tends to one since, once the available sites on the surface are occupied ($V = V_{\text{mon}}$), chemisorption stops. This is a **type I isotherm** (Figure 5.5, although type I isotherms can also happen in some physisorption cases). In the case of physisorption, or chemisorption combined with physisorption, the adsorbed volume may increase indefinitely as successive molecular layers adsorb onto other molecular layers (e.g. N_2 on silica gel). This is a **type II isotherm** (Figure 5.6). The simplest models of type I and type II isotherms are the Langmuir and BET isotherms, respectively. Up to six types of adsorption isotherms for physisorption have been identified, the other four having more complicated forms (*Pure & Appl. Chem.*, **54** (1982) 2201).

5.3.1 Langmuir Isotherm

The simplest isotherm representing pure chemisorption can be built using the following assumptions:

- Only a single adsorption layer is formed.

- Molecules can only be adsorbed at vacant sites on the surface, and all surface sites are equivalent.
- The probability of adsorption does not depend on the coverage, i.e., molecules on the surface do not interact with each other.

Figure 5.5 (left) shows a graphical representation of adsorption on this surface. These assumptions are not very realistic because, as mentioned above, solids are not uniform surfaces so desorption and adsorption enthalpies also depend on the presence of defects. In addition, the adsorption enthalpy depends significantly on the fractional coverage because of the interactions between adsorbed molecules on the surface. (Some of these assumptions can be circumvented by using statistical mechanics to derive the Langmuir isotherm expression.)

Under these assumptions, the chemical reaction corresponding to the adsorption of a gas molecule A onto the surface M is:

$$\mathrm{A_{(g)}} + \mathrm{M_{(surf)}} \underset{k_d}{\overset{k_a}{\rightleftharpoons}} \mathrm{AM_{(surf)}} \tag{5.7}$$

where the adsorption rate constant (k_a) and the desorption rate constant (k_d) depend on temperature only and not on pressure or surface coverage.

The rate of adsorption is proportional to the rate of collision of A molecules with the surface, which, in turn, is proportional to its partial pressure. (The collisional flux, Eq. 3.73, is proportional to p.) The adsorption rate is also proportional to the number of available adsorption sites on the surface. If N is the total number of adsorption sites on the surface and θ is the fractional coverage, then the number of empty sites is $N(1-\theta)$. Therefore, the rate of adsorption is:

$$\left.\frac{d\theta}{dt}\right|_{\mathrm{ad}} = k_a p N(1-\theta) \tag{5.8}$$

Conversely, the rate of desorption is proportional to the number of adsorption sites that are currently occupied, $N\theta$. Therefore:

$$\left.\frac{d\theta}{dt}\right|_{\mathrm{des}} = k_d N\theta \tag{5.9}$$

Combining the two results, we find that the rate of change in the fractional coverage is:

$$\frac{d\theta}{dt} = \left.\frac{d\theta}{dt}\right|_{\mathrm{ad}} - \left.\frac{d\theta}{dt}\right|_{\mathrm{des}} = k_a p N(1-\theta) - k_d N\theta \tag{5.10}$$

When the surface and the gas are at equilibrium, the fraction coverage does not change, so we have:

$$\frac{d\theta}{dt} = k_a p N(1-\theta) - k_d N\theta = 0 \tag{5.11}$$

Solving for the fractional coverage we find:

$$k_a p N(1-\theta) = k_d N\theta \tag{5.12}$$

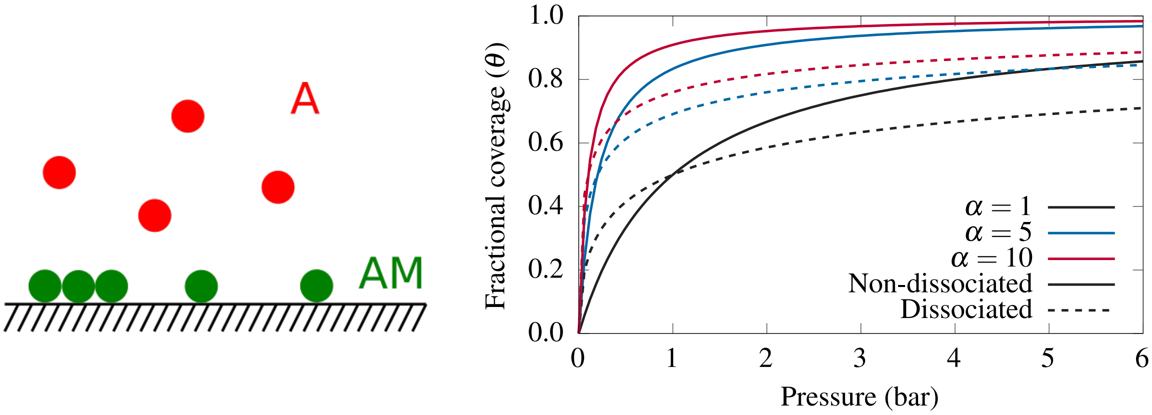
$$k_a p - k_a p\theta = k_d\theta \tag{5.13}$$

$$\theta = \frac{k_a p}{k_d + k_a p} \tag{5.14}$$

If we define α as the ratio of the adsorption and desorption rate constants:

$$\alpha = \frac{k_a}{k_d} \tag{5.15}$$

Figure 5.5: Left: model for a type I isotherm, with adsorption only in a single layer. Right: Langmuir isotherm (fractional coverage as a function of pressure) for different values of the α constant. Full lines = non-dissociated molecules. Dashed lines = dissociated molecules.



then the fractional coverage as a function of pressure can be written as:

$$\theta = \frac{\alpha p}{1 + \alpha p} \tag{5.16}$$

which is the expression of the **Langmuir isotherm**. The α constant has units of p^{-1}, because θ is adimensional.

A few examples of the Langmuir isotherm are shown in Figure 5.5. In the limit of $p \to 0$, the fractional coverage tends to zero (because there are no molecules to adsorb). In the limit of $p \to \infty$, we have $\theta \to 1$, reflecting the fact that the pressure is so high that all available adsorption sites on the surface are occupied. Since we are considering that only a single layer is formed (i.e. pure chemisorption), the fractional coverage never rises above one.

When determining the parameters of the Langmuir isotherm experimentally, one usually measures adsorbed volumes V as a function of gas pressure p at a constant temperature. These data can be used to obtain the α and V_{mon} in the Langmuir isotherm. For this, we first linearize the isotherm and then we use a linear least-squares fit to the experimental data. Writing the fractional coverage in terms of volume, we have:

$$\frac{V}{V_{\mathrm{mon}}} = \frac{\alpha p}{1 + \alpha p} \tag{5.17}$$

and then multiplying by $(1 + \alpha p)$:

$$\frac{V}{V_{\mathrm{mon}}} + \frac{V \alpha p}{V_{\mathrm{mon}}} = \alpha p \tag{5.18}$$

and dividing by αV,

$$\underbrace{\frac{p}{V}}_{y} = \frac{1}{\alpha V_{\mathrm{mon}}} + \frac{1}{V_{\mathrm{mon}}} \times \underbrace{p}_{x} \tag{5.19}$$

If the Langmuir isotherm is valid, a representation of p/V vs. p gives a straight line, and the α and V_{mon} parameters can be obtained from the slope and the intercept.

The expression for the Langmuir isotherm changes in the case when the gas molecule dissociates upon adsorption (dissociative chemisorption). In this case, the reaction for the adsorption process is:

$$\mathrm{A}_{2(\mathrm{g})} + 2\,\mathrm{M}_{(\mathrm{surf})} \underset{k_d}{\overset{k_a}{\rightleftharpoons}} 2\,\mathrm{AM}_{(\mathrm{surf})} \tag{5.20}$$

The adsorption rate is given by:

$$\left.\frac{d\theta}{dt}\right|_{\text{ad}} = 2k_a p[N(1-\theta)]^2 \tag{5.21}$$

where we add a 2 prefactor to take into account that each adsorption step occupies two adsorption sites. The square represents the requirement of having two empty adsorption sites in order to bind a single molecule. Conversely, the desorption rate in a dissociative chemisorption is:

$$\left.\frac{d\theta}{dt}\right|_{\text{des}} = 2k_d(N\theta)^2 \tag{5.22}$$

where the 2 factor appears because every desorption step liberates two adsorption sites, and the square reflects the fact that two fragments on the surface need to meet to regenerate the molecule.

At equilibrium, the rate of adsorption and the rate of desorption balance:

$$\frac{d\theta}{dt} = 2k_a p[N(1-\theta)]^2 - 2k_d(N\theta)^2 = 0 \tag{5.23}$$

Rearranging and using the definition $\alpha = k_a/k_d$:

$$\alpha p(1-\theta)^2 = \theta^2 \tag{5.24}$$

$$\sqrt{\alpha p}(1-\theta) = \theta \tag{5.25}$$

$$\theta = \frac{\sqrt{\alpha p}}{1+\sqrt{\alpha p}} \tag{5.26}$$

which is the expression for the Langmuir isotherm with dissociation.

This isotherm is compared with the non-dissociative isotherm (Eq. 5.16) in Figure 5.5. The fractional coverage is higher at low pressure if the molecule dissociates, which happens because a single molecule adsorbing on the surface occupies two sites. Conversely, the pressure required to saturate the surface is much higher if the molecule dissociates, because two empty adsorption sites are involved in each adsorption step, and at high pressure the empty sites on the surface are scarce.

The temperature dependence of the α constant that characterizes the Langmuir isotherm can be related to the **isosteric adsorption enthalpy** ($\Delta_{\text{ad}}H^\circ$), i.e. the enthalpy associated with adsorbing a molecule onto the surface at constant fractional coverage. The α parameter is similar to an equilibrium constant but it has units of p^{-1}. To convert α into an equilibrium constant for the adsorption process, we multiply by p°:

$$K = \frac{k_a}{k_d}p^\circ = \alpha p^\circ \tag{5.27}$$

and this equilibrium constant can be related with the standard free energy for adsorption:

$$\Delta_{\text{ad}}G^\circ = -RT\ln K \tag{5.28}$$

Rearranging:

$$-R\ln K = \frac{\Delta_{\text{ad}}G^\circ}{T} \tag{5.29}$$

and taking the derivative with respect to temperature at constant coverage:

$$\frac{d(-R\ln K)}{dT} = \frac{d}{dT}\left(\frac{\Delta_{\text{ad}}G^\circ}{T}\right) = -\frac{\Delta_{\text{ad}}H^\circ}{T^2} \tag{5.30}$$

where we have used the Gibbs-Helmholtz equation (Eq. 4.219). Using $K = \alpha p^\circ$, we find:

$$\frac{d(\ln \alpha p^\circ)}{dT} = \frac{\Delta_{\text{ad}} H^\circ}{RT^2} \tag{5.31}$$

Note that the derivatives are taken at constant coverage.

This expression can be used to determine adsorption enthalpies from adsorption data. Let us assume an adsorption process that follows the Langmuir isotherm, and we determine the pressure required to maintain a constant adsorption volume (i.e. constant fractional coverage) at different temperatures, $p(T)$. In order to find $\Delta_{\text{ad}} H^\circ$ from these data, we first rearrange the Langmuir isotherm to give:

$$\theta = \frac{\alpha p}{1 + \alpha p} \tag{5.32}$$

$$\alpha p \theta + \theta = \alpha p \tag{5.33}$$

$$\alpha = \frac{\theta}{p(1 - \theta)} \tag{5.34}$$

Multiplying by p° and taking logarithms:

$$\ln(\alpha p^\circ) = \ln\left(\frac{p^\circ}{p}\right) + \ln\left(\frac{\theta}{1 - \theta}\right) \tag{5.35}$$

where p and α depend on temperature but θ does not. Therefore:

$$\frac{d}{dT}\left[\ln(\alpha p^\circ)\right] = \frac{d}{dT}\left[\ln\left(\frac{p^\circ}{p}\right)\right] \tag{5.36}$$

Inverting the argument inside the logarithm and replacing the left-hand-side with Eq. 5.31, we find:

$$\frac{d}{dT}\left[\ln\left(\frac{p}{p^\circ}\right)\right] = -\frac{d}{dT}\left[\ln(\alpha p^\circ)\right] = -\frac{\Delta_{\text{ad}} H^\circ}{RT^2} = \frac{\Delta_{\text{des}} H^\circ}{RT^2} \tag{5.37}$$

where $\Delta_{\text{des}} H^\circ = -\Delta_{\text{ad}} H^\circ$ is the isosteric enthalpy of desorption (the process opposite to adsorption, Eq. 5.7). Note the similarity of this equation with the Clausius-Clapeyron equation that gives the change in vapor pressure of a solid or liquid in equilibrium with its gas:

$$\frac{d \ln\left(\frac{p_v}{p^\circ}\right)}{dT} = \frac{\Delta_{\text{vap}} H^\circ}{RT^2} \tag{5.38}$$

where the pressure in contact with the surface (p) is replaced by the pressure in contact with the liquid (p_v) and the enthalpy of desorption (the heat associated with a molecule going from the surface to the gas) is replaced with the enthalpy of vaporization (a molecule going from the liquid to the gas).

Finally, Eq. 5.37 can be written in a more useful form using the chain rule:

$$-\frac{\Delta_{\text{ad}} H^\circ}{RT^2} = \frac{d\left[\ln\left(\frac{p}{p^\circ}\right)\right]}{dT} = \frac{d\left[\ln\left(\frac{p}{p^\circ}\right)\right]}{d(1/T)} \times \frac{d(1/T)}{dT} = -\frac{1}{T^2}\frac{d\left[\ln\left(\frac{p}{p^\circ}\right)\right]}{d(1/T)} \tag{5.39}$$

from where:

$$\frac{\Delta_{\text{ad}} H^\circ}{R} = \frac{d\left[\ln\left(\frac{p}{p^\circ}\right)\right]}{d(1/T)} \tag{5.40}$$

The slope of the p/p° plot against $1/T$ at constant coverage, both experimentally available quantities, can be used to find the adsorption enthalpy from constant-coverage adsorption data.

5.3.2 BET Isotherm

The Langmuir isotherm is not a good model for cases in which multiple molecular layers adsorb on the surface. Braunauer, Emmett, and Teller proposed an isotherm specifically for multilayer adsorption (type II), the **BET isotherm**. In this case, we assume that the molecules adsorb to the clean surface (either via physisorption or chemisorption) following the process:

$$\mathrm{A_{(g)}} + \mathrm{M_{(surf)}} \underset{k_{d,0}}{\overset{k_{a,0}}{\rightleftharpoons}} \mathrm{AM_{(surf)}} \tag{5.41}$$

Unlike in the Langmuir isotherm, we now consider that additional gas phase molecules can adsorb onto the first layer, thus creating a second, third,... layers (see Figure 5.6, left). We assume that the second and subsequent layers have the same adsorption and desorption rate constants:

$$\mathrm{A_{(g)}} + \mathrm{M'_{(surf)}} \underset{k_{d,1}}{\overset{k_{a,1}}{\rightleftharpoons}} \mathrm{AM'_{(surf)}} \tag{5.42}$$

Because of the multilayer adsorption, in the BET isotherm the volume of adsorbed gas can increase indefinitely and the fractional coverage θ can be greater than one.

It is possible to show that the BET isotherm is:

$$\theta = \frac{V}{V_{\mathrm{mon}}} = \frac{cz}{(1-z)[1-(1-c)z]} \tag{5.43}$$

where V is the volume of adsorbed gas, V_{mon} is the volume corresponding to a complete monolayer (same as V_{mon} in the Langmuir isotherm) and:

$$z = \frac{p}{p^*} \tag{5.44}$$

with p the gas pressure and p^* the vapor pressure of the liquid formed by the gas molecules at that temperature. In addition, the c parameter is:

$$c = \frac{\alpha_0}{\alpha_1} \tag{5.45}$$

where:

$$\alpha_0 = \frac{k_{a,0}}{k_{d,0}} \tag{5.46}$$

is the equilibrium constant related to the adsorption directly onto the surface, and:

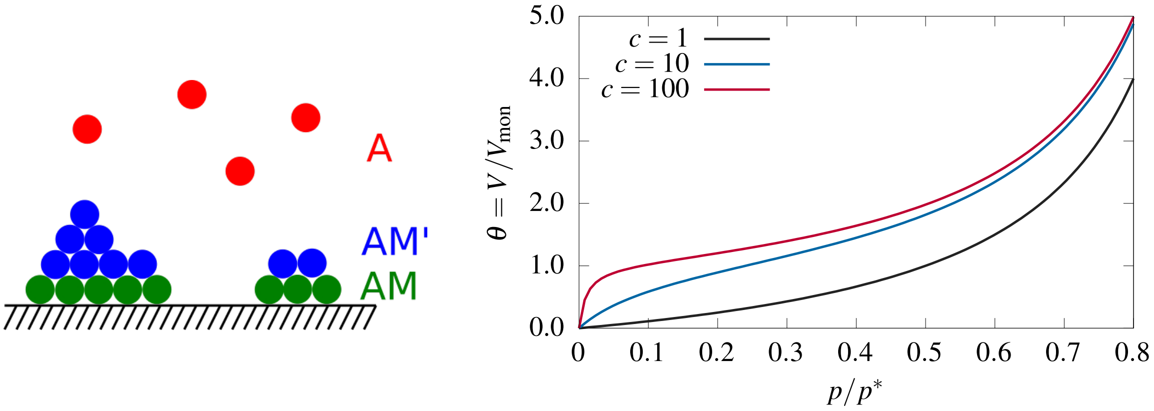
$$\alpha_1 = \frac{k_{a,1}}{k_{d,1}} \tag{5.47}$$

is the equilibrium constant for the adsorption and desorption to and from the molecular layers (i.e. the equilibrium constant for adsorption on the second and subsequent layers). A value of $c > 1$ is common, and it indicates that adsorption onto the surface is more favorable than adsorption on the molecular layers.

Figure 5.6 shows the BET isotherm for several values of the c parameter. Because the limitation that molecules must occupy a single layer has been lifted, the fractional occupation ($\theta = V/V_{\mathrm{mon}}$) can be greater than one. In the case of $c = 1$, there is no difference between the molecules adsorbing directly on the surface or on top of other molecules, and the fractional occupation increases as $z/(1-z)$, with no particular features around $\theta = 1$. If $c > 1$, then the molecule prefers unoccupied adsorption sites on the surface to adsorbing onto the molecular layers.

The higher c, the greater the affinity of the molecule for the adsorbant surface, and the BET isotherm shows a correspondingly more pronounced plateau around $\theta = 1$. This happens

Figure 5.6: Left: model for a type II isotherm, with adsorption on several layers. Right: The BET isotherm (fractional coverage as a function of pressure) for different values of the c parameter.



because, at moderate pressures, a competition is established between occupying the few empty adsorption sites on the surface, which greatly stabilizes the molecule, and adsorbing on the molecular layer, with a comparatively weaker adsorption energy. Once past this plateau (i.e. when all sites on the surface are occupied), the behavior of all isotherms is similar regardless of c.

The BET isotherm can be linearized, which is useful when determining the BET isotherm parameters from experimental data. Inverting the isotherm expression (Eq. 5.43) we find:

$$\frac{V_{\mathrm{mon}}}{V} = \frac{(1-z)[1-(1-c)z]}{cz} \tag{5.48}$$

and multiplying by $z/(1-z)V_{\mathrm{mon}}$,

$$\frac{z}{(1-z)V} = \frac{1-(1-c)z}{cV_{\mathrm{mon}}} = \frac{1}{cV_{\mathrm{mon}}} - \frac{1-c}{cV_{\mathrm{mon}}}z \tag{5.49}$$

so it is possible to determine the parameters in the BET isotherm (c and V_{mon}) from the intercept and slope of a linear least-squares fit of $y = \frac{z}{(1-z)V}$ against $x = z$. Specifically, the ratio between the slope and intercept is $c - 1$.

The c parameter in the BET isotherm can be related to relevant thermodynamic quantities in the adsorption processes. In contrast to the Langmuir isotherm, now we have two different processes: the adsorption of a molecule on the clean surface, with an equilibrium constant related to α_0, and the adsorption onto molecules corresponding to the second and subsequent layers, with equilibrium constant related to α_1. Specifically, the α_0 equilibrium constant is related to the free energy of adsorption of a molecule onto the substrate ($\Delta_{\mathrm{ad}}G^\circ$):

$$\Delta_{\mathrm{ad}}G^\circ = -RT\ln(\alpha_0 p^0) \tag{5.50}$$

This is the same expression as in the Langmuir isotherm (Eq. 5.28). On the other hand, the α_1 equilibrium constant is related to the condensation of a molecule on top of a layer of molecules of the same kind. This is equivalent to a gas molecule condensing into the liquid phase, so α_1 can be written in terms of the condensation free energy:

$$\Delta_{\mathrm{con}}G^\circ = -RT\ln(\alpha_1 p^0) \tag{5.51}$$

Now we define the vaporization free energy and desorption free energy as minus the condensation and adsorption free energies, respectively:

$$\Delta_{\mathrm{vap}}G^\circ = -\Delta_{\mathrm{con}}G^\circ \quad ; \quad \Delta_{\mathrm{des}}G^\circ = -\Delta_{\mathrm{ad}}G^\circ \tag{5.52}$$

With these definitions, the α_0 and α_1 can be written in terms of desorption and vaporization free energies as:

$$\Delta_{\text{des}}G^\circ = RT\ln(\alpha_0 p^0) \tag{5.53}$$

$$\Delta_{\text{vap}}G^\circ = RT\ln(\alpha_1 p^0) \tag{5.54}$$

and the c parameter is:

$$c = \frac{\alpha_0}{\alpha_1} = \frac{e^{\Delta_{\text{des}}G^\circ/RT}}{e^{\Delta_{\text{vap}}G^\circ/RT}} = \frac{e^{\Delta_{\text{des}}H^\circ/RT}e^{-\Delta_{\text{des}}S^\circ/R}}{e^{\Delta_{\text{vap}}H^\circ/RT}e^{-\Delta_{\text{vap}}S^\circ/R}} \tag{5.55}$$

The entropy of vaporization and the entropy of desorption are approximately the same. The two processes increase entropy in about the same amount because both correspond to a molecule going from a condensed phase, with restricted movements, into the gas phase. Therefore, this equation approximately simplifies to:

$$c \approx \frac{e^{\Delta_{\text{des}}H^\circ/RT}}{e^{\Delta_{\text{vap}}H^\circ/RT}} = e^{(\Delta_{\text{des}}H^\circ - \Delta_{\text{vap}}H^\circ)/RT} \tag{5.56}$$

In the case where $\Delta_{\text{des}}H^\circ \gg \Delta_{\text{vap}}H^\circ$, the molecule is much more stabilized by adsorption on the adsorbent surface compared to adsorption onto other molecules, and therefore $c \gg 1$. In this case, there is a strong preference for the formation of a monolayer at low pressures, and this is reflected as a plateau in the BET isotherm (see Figure 5.6).

5.3.3 Other Isotherms

The BET isotherm is widely used in the description of adsorption to real surfaces, and it works reasonably well for intermediate pressures. However, the BET isotherm underestimates adsorption at low pressure and it overestimates adsorption at high pressure. Alternatives to the Langmuir and BET isotherms have been proposed purely on empirical grounds to try to take into account that the adsorption enthalpy does depend on surface coverage. These isotherms are often reliable and quite useful, so they are used in practical studies of heterogeneous catalysis. In addition, they can also be applied to the adsorption of solutes onto solid surfaces submerged in liquid solutions.

Dozens of empirical models for adsorption isotherms exist. For instance, the **Temkin isotherm** assumes that $\Delta_{\text{ad}}H^\circ$ changes linearly with pressure. It is:

$$\theta = c_1 \ln(c_2 p) \tag{5.57}$$

where c_1 and c_2 are empirically determined parameters. Another common model is the **Freundlich isotherm**:

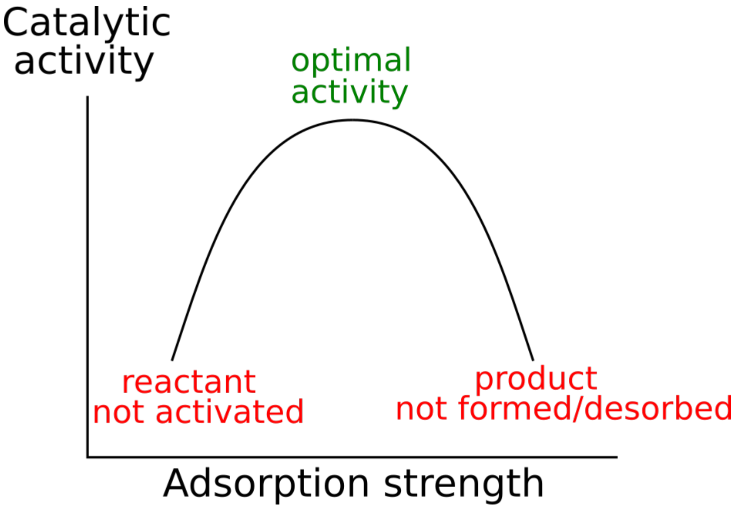
$$\theta = c_1 p^{1/c_2} \tag{5.58}$$

which, instead, assumes that $\Delta_{\text{vap}}H^\circ$ changes logarithmically with pressure. The c_2 parameter is assumed to be greater than one. The Freundlich isotherm is applied to type I adsorption only (i.e. pure chemisorption). It is not valid at very high pressure, but it is usually more accurate than the Langmuir isotherm at low and intermediate pressures.

5.4 Heterogeneous Catalysis

The phenomenon of surface adsorption is fundamental in the study of heterogeneous catalysis by solids. Solid catalysts are often used to speed up chemical reactions of industrial relevance. Most industrially used catalysts are metals, metal oxides, or acids such as H_3PO_4 or H_2SO_4 immobilized on a metal oxide surface (e.g. silica). Examples of important industrial reactions

Figure 5.7: The "volcano curve" exemplifying the Sabatier principle. Optimal catalytic activity is achieved when the reactant is bound neither too weakly nor too strongly to the surface.



in which heterogeneous catalysis are used include: i) the synthesis of ammonia from N_2 and H_2, catalyzed by partially oxidized iron; ii) the oxidation of SO_2 to SO_3, important in the production of sulfuric acid and catalyzed by V_2O_5; iii) the cracking of hydrocarbons (i.e. breaking down long-chain hydrocarbons into simpler molecules), catalyzed by porous aluminosilicate materials known as zeolites; iv) the polymerization of olefins, catalyzed by Ziegler-Natta catalysts (titanium chlorides with organoaluminum compounds); and v) hydrogenation reactions, catalyzed by transition metals such as Ni, Ru, Pt, or Pd.

In all these examples, heterogeneous catalysts substantially increase the reaction rate of the corresponding reaction. This is typically achieved by decreasing the energy barrier of the slow step, which usually coincides with the dissociation of the reactants (hence, at least one of the reactants must chemisorb on the surface for the catalyst to be effective). For instance, in the case of the hydrogenation reactions, H_2 dissociates on the metal surface. The resulting H atoms can move on the surface and, in the presence of an unsaturated organic compound, they can attack the organic molecule, resulting in its hydrogenation. Solid catalysts are usually employed in a form in which their surface area is maximized. The surface area of a catalyst is measured by its **specific surface**, the surface area per gram of catalyst. In the hydrogenation reactions, maximizing the surface involves either using a very fine metal powder or sponge (Raney nickel, platinum black, palladium black) or particles on the metal deposited on a porous **support** or **carrier** such as silica gel, diatomaceous earth, or activated charcoal (Pt/C, Pd/C). In the case of zeolites, the pore diameter in the catalyst can be controlled, such that it is active only for molecules with a specific size.

The catalytic activity of a solid surface is also usually improved by defects and some crystallographic planes of the bulk solid are more active than others. For this reason, solid catalysts used in practice usually undergo a very specific empirically developed manufacturing process aimed at maximizing their activity. Solid catalysts are also affected by the presence of other substances that either enhance (**promoters**) or impede (**poisons**) their catalytic activity. A common example is the poisoning of catalytic converters in cars. These converters catalyze the elimination of CO, NO_x, and unreacted hydrocarbons, and can be poisoned by lead from gasoline additives. In some cases, catalytic poisons are used to improve the reaction selectivity. For instance, the Lindlar catalyst (Pd on $CaCO_3$ poisoned with lead or quinoline) is used to selectively hydrogenate alkyne to alkenes.

Which catalyst is efficient for which reaction is difficult to predict but a guiding rule is the qualitative **Sabatier principle**. This principle states that, in order to have good catalytic activity, chemisorption of the reactant on the surface should be neither too weak nor too strong. If the reactant adsorbs too weakly on the surface, then the reaction barrier does not decrease sufficiently. If the adsorption is too strong, then the reactant is immobilized and the product cannot desorb from the surface. The Sabatier principle can be presented in the form of a plot of catalytic activity against interaction strength, the so-called "volcano plot" (Figure 5.7). Optimal catalytic activity is achieved with substrates that bind the reactant with intermediate strength.

We now consider specific mechanisms for heterogeneous catalysis on solid surfaces: first the case of unimolecular reactions and then two model mechanisms for bimolecular reactions (the Langmuir-Hinshelwood and Eley-Rideal mechanisms). In general, the mechanisms involve three potentially slow steps: adsorption of the reactants on the surface, the transformation of reactants to products, and desorption of products from the surface. For simplicity, we will assume the chemical transformation is always the slow step, so we can use the adsorption isotherm expressions derived previously. In the study of reactions at an interface, the definition of the rate of a reaction is sightly modified. Instead of using an expression similar to (Eq. 4.7):

$$r = \frac{1}{V}\frac{dn_X}{dt} \tag{5.59}$$

as in the bulk, for a surface we use the **product flux**:

$$r = \frac{1}{A}\frac{dn_X}{dt} \tag{5.60}$$

which measures the change in the number of moles of a reactant or product per unit time per unit area. The units of rate and the associated rate constants on a surface change appropriately. In particular, r has units of $\mathrm{mol\,m^{-2}\,s^{-1}}$ in the SI.

5.4.1 Unimolecular Reactions

In the case of a unimolecular elementary reaction,

$$\mathrm{A_{(g)}} \longrightarrow \mathrm{P_{(g)}}$$

the surface-catalyzed reaction mechanism is:

$$\begin{gathered}
\mathrm{A_{(g)}} + \mathrm{M_{(surf)}} \underset{k_{d,1}}{\overset{k_{a,1}}{\rightleftharpoons}} \mathrm{AM_{(surf)}} \\
\mathrm{AM_{(surf)}} \xrightarrow{k} \mathrm{PM_{(surf)}} \\
\mathrm{PM_{(surf)}} \underset{k_{a,2}}{\overset{k_{d,2}}{\rightleftharpoons}} \mathrm{P_{(g)}} + \mathrm{M_{(surf)}}
\end{gathered}$$

where $k_{a,1}$ and $k_{a,2}$ are the adsorption rate constants and $k_{d,1}$ and $k_{d,2}$ are the desorption rate constants, and k is the rate constant for the chemical transformation. Assuming the chemical transformation (step 2) is the rate-determining step, then the rate of the reaction is proportional to the fractional coverage:

$$r = k\theta \tag{5.61}$$

and we can assume the adsorption process (first step) is in a state of pre-equilibrium, so we can use the expression for the fractional coverage from the Langmuir (chemisorption) isotherm (Eq. 5.16):

$$r = k\theta = \frac{k\alpha p}{1+\alpha p} \tag{5.62}$$

where, in this case,

$$\alpha = \frac{k_{a,1}}{k_{d,1}} \tag{5.63}$$

In the limit of low pressure, $\alpha p \ll 1$ and the rate becomes first-order in the partial pressure of the reactant:

$$r \approx k\alpha p \tag{5.64}$$

Conversely, at high pressure, $\alpha p \gg 1$ and the reaction is approximately zeroth order:

$$r \approx k \tag{5.65}$$

The zeroth order behavior in the high-pressure limit arises from the fact that, at high pressure, the entire surface is covered in molecules and increasing the pressure further has no effect on the reaction rate. Instead, the rate is determined purely by the catalytic activity of the surface. Note the similarity between a surface-catalyzed unimolecular reaction and an enzymatic reaction controlled by the Michaelis-Menten mechanism (Eq. 4.149). The rate law of the two have the same form because they correspond to a process in which there is a limited number of reaction sites (adsorption centers on the surface or enzyme active sites) and the maximum rate is limited by the catalytic activity of the surface or the enzyme. An example of reaction that follows this mechanism is the W-catalyzed decomposition of phosphine (PH_3) at 700 °C.

5.4.2 Bimolecular Reactions: the Langmuir-Hinshelwood Mechanism

There are two commonly used mechanisms to model a surface-catalyzed elementary bimolecular reaction:

$$\mathrm{A_{(g)}} + \mathrm{B_{(g)}} \longrightarrow \mathrm{P_{(g)}}$$

The first model is the **Langmuir-Hinshelwood mechanism** in which both reactants first adsorb on the surface, then react with each other to form the product:

$$\begin{aligned}
\mathrm{A_{(g)}} + \mathrm{M_{(surf)}} &\underset{k_{d,\mathrm{A}}}{\overset{k_{a,\mathrm{A}}}{\rightleftharpoons}} \mathrm{AM_{(surf)}} \\
\mathrm{B_{(g)}} + \mathrm{M_{(surf)}} &\underset{k_{d,\mathrm{B}}}{\overset{k_{a,\mathrm{B}}}{\rightleftharpoons}} \mathrm{BM_{(surf)}} \\
\mathrm{AM_{(surf)}} + \mathrm{BM_{(surf)}} &\xrightarrow{k} \mathrm{PM_{(surf)}} \\
\mathrm{PM_{(surf)}} &\underset{k_{a,\mathrm{P}}}{\overset{k_{d,\mathrm{P}}}{\rightleftharpoons}} \mathrm{P_{(g)}} + \mathrm{M_{(surf)}}
\end{aligned}$$

The first two steps in this mechanism correspond to the adsorption of the reactants A and B. These two species then migrate on the surface until they collide and react, forming the product P. Finally, the product desorbs and returns to the gas phase.

Assuming the chemical transformation on the surface (step 3) is the rate-determining step, we have that the rate of the reaction is proportional to the coverage of both A and B:

$$r = k\theta_a\theta_b \tag{5.66}$$

where θ_A and θ_B is the fractional coverage of each molecule.

We can find the fractional coverages in the case of multiple chemisorption on a surface using a procedure similar to the one we used to derive the Langmuir isotherm. The rate of adsorption of A is given by:

$$\left.\frac{d\theta_A}{dt}\right|_{\mathrm{ad}} = k_{a,A}p_A N(1-\theta_A-\theta_B) \tag{5.67}$$

where p_A is the partial pressure of A. This differs from the equivalent expression in the one-component Langmuir isotherm (Eq. 5.8) by the appearance of θ_B. The rate of desorption is:

$$\left.\frac{d\theta_A}{dt}\right|_{\text{des}} = k_{d,A}N\theta_A \tag{5.68}$$

Equivalent relations are valid for the B molecule:

$$\left.\frac{d\theta_B}{dt}\right|_{\text{ad}} = k_{a,B}p_BN(1-\theta_A-\theta_B) \tag{5.69}$$

$$\left.\frac{d\theta_B}{dt}\right|_{\text{des}} = k_{d,B}N\theta_B \tag{5.70}$$

At equilibrium, the rate of adsorption and desorption equalizes:

$$k_{a,A}p_AN(1-\theta_A-\theta_B) = k_{d,A}N\theta_A \tag{5.71}$$

$$k_{a,B}p_BN(1-\theta_A-\theta_B) = k_{d,B}N\theta_B \tag{5.72}$$

If we define the equilibrium constants $\alpha_A = k_{a,A}/k_{d,A}$ and $\alpha_B = k_{a,B}/k_{d,B}$, then:

$$\alpha_Ap_A(1-\theta_A-\theta_B) = \theta_A \tag{5.73}$$

$$\alpha_Bp_B(1-\theta_A-\theta_B) = \theta_B \tag{5.74}$$

and rearranging:

$$(\alpha_Ap_A+1)\theta_A + \alpha_Ap_A\theta_B = \alpha_Ap_A \tag{5.75}$$

$$(\alpha_Bp_B+1)\theta_B + \alpha_Bp_B\theta_A = \alpha_Bp_B \tag{5.76}$$

Multiplying the first equation by α_Bp_B and the second by (α_Ap_A+1),

$$\alpha_Bp_B(\alpha_Ap_A+1)\theta_A + \alpha_Ap_A\alpha_Bp_B\theta_B = \alpha_Ap_A\alpha_Bp_B \tag{5.77}$$

$$\alpha_Bp_B(\alpha_Ap_A+1)\theta_A + (\alpha_Ap_A+1)(\alpha_Bp_B+1)\theta_B = \alpha_Bp_B(\alpha_Ap_A+1) \tag{5.78}$$

and subtracting:

$$[\alpha_Ap_A\alpha_Bp_B - (\alpha_Ap_A+1)(\alpha_Bp_B+1)]\theta_B = -\alpha_Bp_B \tag{5.79}$$

$$(-\alpha_Ap_A-\alpha_Bp_B-1)\theta_B = -\alpha_Bp_B \tag{5.80}$$

Finally, solving for the fractional coverage of B gives:

$$\theta_B = \frac{\alpha_Bp_B}{1+\alpha_Ap_A+\alpha_Bp_B} \tag{5.81}$$

We can rearrange Eq. 5.73 to give:

$$\alpha_Ap_A(1-\theta_B) = (1+\alpha_Ap_A)\theta_A \tag{5.82}$$

and now we solve for the fractional coverage of A:

$$\theta_A = \frac{\alpha_Ap_A}{1+\alpha_Ap_A}\theta_B = \frac{\alpha_Ap_A}{1+\alpha_Ap_A}\times\left[1-\frac{\alpha_Bp_B}{1+\alpha_Ap_A+\alpha_Bp_B}\right] = \frac{\alpha_Ap_A}{1+\alpha_Ap_A}\times\frac{1+\alpha_Ap_A}{1+\alpha_Ap_A+\alpha_Bp_B}$$
$$= \frac{\alpha_Ap_A}{1+\alpha_Ap_A+\alpha_Bp_B} \tag{5.83}$$

In the general case when we have n components, it is possible to show that the fractional coverage for component i in the Langmuir model is:

$$\theta_i = \frac{\alpha_ip_i}{1+\sum_{j=1}^{n}\alpha_jp_j} \tag{5.84}$$

where $\alpha_j = k_{a,j}/k_{d,j}$ is the ratio of the corresponding adsorption and desorption constants.

Substituting the isotherm for each component in the rate law (Eq. 5.66), we find:

$$r = k\theta_A\theta_B = \frac{k\alpha_A p_A \alpha_B p_B}{(1 + \alpha_A p_A + \alpha_B p_B)^2} \tag{5.85}$$

Note that the maximum rate is achieved if the two reactants are adsorbed on the surface to approximately the same extent. Increasing the pressure of one or the other reactant may result in inhibition of the reaction, if this increase results in a greater imbalance of A and B on the surface. The rate constant and the two α constants in this equation both depend on temperature so reactions in this model do not follow the Arrhenius equation. Modifications of the Langmuir-Hinshelwood mechanism exist for reactions with dissociation. An example of a reaction controlled by this mechanism is the oxidation of CO to CO_2 in the presence of O_2 catalyzed by Pt.

5.4.3 Bimolecular Reactions: the Eley-Rideal Mechanism

The second model of a surface-catalyzed elementary bimolecular reaction:

$$\mathrm{A_{(g)} + B_{(g)} \longrightarrow P_{(g)}}$$

is the **Eley-Rideal mechanism**:

$$\begin{aligned}
\mathrm{A_{(g)} + M_{(surf)}} &\underset{k_{d,\mathrm{A}}}{\overset{k_{a,\mathrm{A}}}{\rightleftharpoons}} \mathrm{AM_{(surf)}} \\
\mathrm{B_{(g)} + AM_{(surf)}} &\xrightarrow{k} \mathrm{PM_{(surf)}} \\
\mathrm{PM_{(surf)}} &\underset{k_{a,\mathrm{P}}}{\overset{k_{d,\mathrm{P}}}{\rightleftharpoons}} \mathrm{P_{(g)} + M_{(surf)}}
\end{aligned}$$

In the Eley-Rideal mechanism, one of the reactants (A) chemisorbs on the surface first. Then, the second reactant (B) from the gas phase reacts with the adsorbed molecule to form the product. Finally, the product desorbs and goes back into the gas phase. Assuming the chemical transformation (step 2) is the rate-determining step, the rate is proportional to the fractional coverage of A and the partial pressure of B:

$$r = kp_B\theta_A \tag{5.86}$$

Since the adsorption of A is in a state of pre-equilibrium, we can substitute the fractional coverage with the Langmuir isotherm expression:

$$r = k\frac{\alpha p_A p_B}{1 + \alpha p_A} \tag{5.87}$$

At high pressure of A ($\alpha p_A \gg 1$), a reaction that follows the Eley-Rideal mechanism is first order in the partial pressure of B:

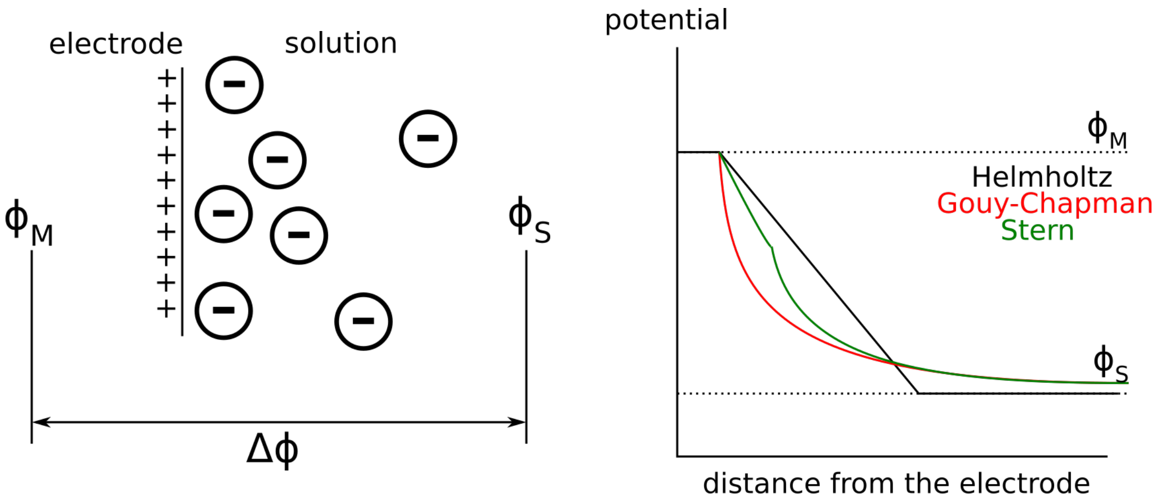
$$r \approx kp_B \tag{5.88}$$

Conversely, at low pressure of A ($\alpha p_A \ll 1$), the reaction is first-order in A and B and second order overall:

$$r = k\alpha p_A p_B \tag{5.89}$$

Most solid-catalyzed chemical reactions are thought to occur via the Lindemann-Hinshelwood mechanism but a few of them are thought to follow the Eley-Rideal model. Most notably, the formation of HD from H_2 and D_2 is thought to occur via the Eley-Rideal mechanism. Both

Figure 5.8: Left: Depiction of an electrical double layer. In this case, the electrode is positively charged and in equilibrium with the solution, which has negative charges close to the electrode. The Galvani potential difference ($\Delta\phi$) for this electrode is indicated. Right: different models for the potential and structure of a charged interface.



mechanisms are best thought as limits, as combinations of the two can happen simultaneously for the same reaction.

In some cases, the dissociative chemisorption of one of the reactants is the rate-determining step. This is the case, for instance, in the synthesis of ammonia from N_2 and H_2. In that case, the kinetics of the reaction is dominated by the kinetics of the adsorption process.

5.5 Redox Reactions at Solid Surfaces (Electrodes)

Surface adsorption is important in the study of redox reactions happening at electrodes. The rate of oxidation or reduction at an electrode in contact with an electrolyte solution is determined by the nature and characteristics of the solid-liquid interface. In any electrochemical cell, there is a difference in electrical potential at every interface in the system. In particular, any conducting solid in contact with an electrolytic solution establishes a potential difference ($\Delta\phi$) whose value is determined by its microscopic structure. As a result of this, charges migrate to the surface of the electrode and ions move in solution in order to compensate for the electrical potential difference. At equilibrium, a double layer of opposite-sign charges is established on both sides of the interface, in a manner similar to the charges in a capacitor (see Figure 5.8, left).

There are several mathematical models used to describe the structure and potential profile of an electrode in contact with an electrolytic solution. These models have varying degrees of sophistication, and they are important when applied to quantifying the concentration in solution as a function of distance from the electrode. In the **Helmholtz double-layer model**, there is a layer of ions on the surface of the electrode that are held away from the metal surface by the hydration spheres (i.e. the solvent molecules that accompany the ions in solution). These ions form a layer in the solution side of the interface known as the **outer Helmholtz plane** (OHP). A slightly more sophisticated Helmholtz model is possible in which there is an **inner Helmholtz plane** (IHP), formed by the ions that have been stripped of their hydration spheres and are directly in contact with the electrode. In this model, the potential changes linearly between the metal (ϕ_M) and the bulk of the solution (ϕ_S), see Figure 5.8 (right). More complex interface models include the Gouy-Chapman, Stern, and Grahame models.

The potential difference between the electrode and the bulk of the solution is known as the **Galvani potential difference**, $\Delta\phi = \phi_M - \phi_S$. If there is no current through the electrode, the Galvani potential difference coincides with the electrode potential, E. The Galvani potential can be altered by the application of an external potential difference. In that case, current passes through the electrode.

The **current density** at the electrode (j) is the amount of electrical current that flows through the electrode per surface area. In the SI, the units of current density are $\mathrm{A/m^2} = \mathrm{C\,m^{-2}\,s^{-1}}$. The current density measures the rate of electron transfer at an electrode. We can distinguish two types of current density depending on the direction of the electron flow. The **cathodic current density** (j_c) is the flow of electrons from the electrode to a species in solution, which is reduced. The **anodic current density** (j_a) is the flow of electrons from the electrolytic solution to the electrode; a species in solution is oxidized. Both the cathodic and the anodic current densities happen at the same time and the difference between them is the **net current density**:

$$j = j_a - j_c \tag{5.90}$$

If $j_c > j_a$, then $j < 0$, and we have a net cathodic current. In that case, the electrode behaves as a cathode and there is net reduction of species in solution. Conversely, if $j_a < j_c$, then $j > 0$, and we have a net anodic current. In this case, the electrode behaves as an anode and there is net oxidation of species in solution. In the case when j is exactly zero, the electrode is at equilibrium with the solution and $\Delta\phi = E$, where E is the electrode potential. However, this equilibrium is dynamic, since there are always non-zero cathodic and anodic currents, which are equal in magnitude. The amount of current at equilibrium:

$$j_0 = j_a = j_c \tag{5.91}$$

is called the **exchange current density** (j_0). When $\Delta\phi \neq E$, then net current flows through the electrode. We define the **overpotential** (η) as:

$$\eta = \Delta\phi - E \tag{5.92}$$

By our previous discussion, the electrode is at equilibrium if $\eta = 0$.

The chemical potential of species on both sides of the electrode-solution interface depends on the Galvani potential. Without loss of generality, let us assume we have the following redox half-reaction associated to the interface:

$$\mathrm{Ox}^{+}_{(\mathrm{sol})} + \mathrm{e}^{-}_{(\mathrm{surf})} \underset{k_a}{\overset{k_c}{\rightleftharpoons}} \mathrm{Red}_{(\mathrm{sol})} \tag{5.93}$$

(The choice of whether we have oxidation or reduction or the charge of each species is not important for this derivation.) The cathodic current density is related to the rate of the forward reaction, with rate constant k_c:

$$j_c = Fk_c[\mathrm{Ox}^+] \tag{5.94}$$

where F is Faraday's constant (the charge of a mole of electrons, $F = 96\,485.34\,\mathrm{C/mol}$). Note that the rate of the cathodic reaction $r = k_c[\mathrm{Ox}^+]$ has units of product flux ($\mathrm{mol\,m^{-2}\,s^{-1}}$) and therefore k_c has units of $\mathrm{m\,s^{-1}}$ in the SI. The combination of F (C/mol), k_c ($\mathrm{m\,s^{-1}}$), and $[\mathrm{Ox}^+]$ ($\mathrm{mol\,m^{-3}}$) gives the correct units for j_c ($\mathrm{C\,m^{-2}\,s^{-1}}$, also in the SI). Similarly, the anodic current density is:

$$j_a = Fk_a[\mathrm{Red}] \tag{5.95}$$

Therefore, the net current density is:

$$j = j_a - j_c = Fk_a[\mathrm{Red}] - Fk_c[\mathrm{Ox}^+] \tag{5.96}$$

Applying transition-state theory to both rate constants (Eq. 4.216), we can write the current density as:

$$j = \underbrace{FBe^{-\Delta G_a^{\circ\ddagger}/RT}[\mathrm{Red}]}_{j_a} - \underbrace{FBe^{-\Delta G_c^{\circ\ddagger}/RT}[\mathrm{Ox}^+]}_{j_c} \tag{5.97}$$

where in this case the a subindex indicates the activation energy for the anodic reaction and c the cathodic reaction (both standard activation free energies are in the concentration scale). The B constant contains the prefactor from the Eyring equation and have the same units as k_a and k_c.

The standard chemical potential of a species with charge z in a region with electric potential ϕ is:

$$\mu^\circ = \mu_0^\circ + zF\phi \tag{5.98}$$

where μ_0° is the standard chemical potential in absence of electric potential ($\phi = 0$). For the species in our redox half-reaction, the chemical potentials are:

$$\mu^\circ(\mathrm{Ox}^+) = \mu_0^\circ(\mathrm{Ox}^+) + F\phi_S \tag{5.99}$$

$$\mu^\circ(\mathrm{Red}) = \mu_0^\circ(\mathrm{Red}) \tag{5.100}$$

$$\mu^\circ(\mathrm{e}^-) = \mu_0^\circ(\mathrm{e}^-) - F\phi_M \tag{5.101}$$

and the standard molar free energy of the reactants is:

$$\begin{aligned} G_m^\circ(\mathrm{r}) &= \mu^\circ(\mathrm{Ox}^+) + \mu^\circ(\mathrm{e}^-) = \mu_0^\circ(\mathrm{Ox}^+) + F\phi_S + \mu_0^\circ(\mathrm{e}^-) - F\phi_M \\ &= G_{m,0}^\circ(\mathrm{r}) - F\Delta\phi \end{aligned} \tag{5.102}$$

where $G_{m,0}^\circ(\mathrm{r})$ is the standard molar Gibbs free energy of the reactants in absence of an electric potential. The product standard molar Gibbs free energy is equal to the free energy at zero potential difference because the reduced species has zero charge:

$$G_m^\circ(\mathrm{p}) = \mu^\circ(\mathrm{Red}) = G_{m,0}^\circ(\mathrm{p}) \tag{5.103}$$

where $G_{m,0}^\circ(\mathrm{p})$ is the molar standard Gibbs free energy of the products at zero potential.

For the transition state, if it is similar to the reactants, then its Gibbs free energy is affected by the potential in a manner similar to the reactants (Eq. 5.102):

$$G_m^\circ(\ddagger) \approx G_{m,0}^\circ(\ddagger) - F\Delta\phi \qquad (\alpha \approx 0) \tag{5.104}$$

Conversely, if the transition state resembles the product, then its free energy is approximately independent of $\Delta\phi$, because the reduced species has zero charge (Eq. 5.103):

$$G_m^\circ(\ddagger) \approx G_{m,0}^\circ(\ddagger) \qquad (\alpha \approx 1) \tag{5.105}$$

In general, the transition state is intermediate between those two situations, and we measure this with a **transfer coefficient**, α, which is zero if the transition state is identical to the reactants and one if it is identical to the products. The transfer coefficient can be used to interpolate between the two situations (Eqs. 5.104 and 5.105):

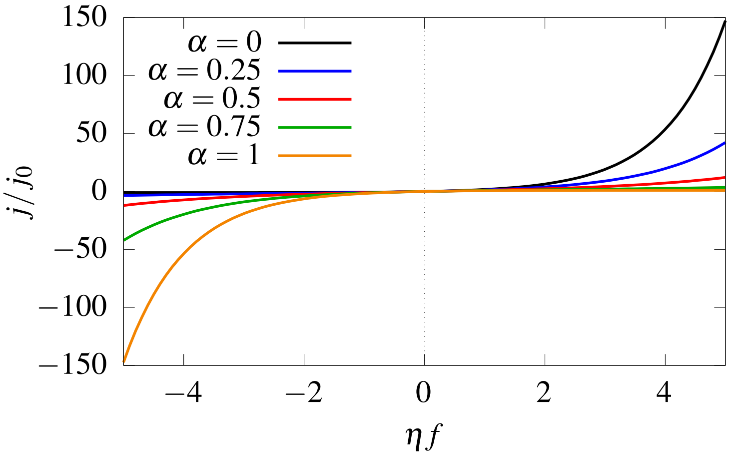
$$G_m^\circ(\ddagger) = G_{m,0}^\circ(\ddagger) - (1-\alpha)F\Delta\phi \tag{5.106}$$

In general α values are often around 0.5, but they are very dependent on the nature of the redox reaction taking place.

With this assumption, we can now calculate the activation free energy of the cathodic reaction:

$$\begin{aligned} \Delta G_c^{\circ\ddagger} &= G_m^\circ(\ddagger) - G_m^\circ(\mathrm{r}) = G_{m,0}^\circ(\ddagger) - (1-\alpha)F\Delta\phi - \left[G_{m,0}^\circ(\mathrm{r}) - F\Delta\phi\right] \\ &= \Delta G_{c,0}^{\circ\ddagger} + \alpha F\Delta\phi \end{aligned} \tag{5.107}$$

Figure 5.9: The current density (j) as a function of applied overpotential (η) according to the Butler-Volmer equation (Eq. 5.115).



where $\Delta G^{\circ\ddagger}_{c,0}$ is the activation free energy for the cathodic reaction at zero potential. Employing the same argument, the activation free energies for the anodic reaction is:

$$\begin{aligned}\Delta G^{\circ\ddagger}_{a} &= G^{\circ}_{m}(\ddagger) - G^{\circ}_{m}(\mathrm{p}) = \left[G^{\circ}_{m,0}(\ddagger) - (1-\alpha)F\Delta\phi\right] - G^{\circ}_{m,0}(\mathrm{p}) \\ &= \Delta G^{\circ\ddagger}_{a,0} - (1-\alpha)F\Delta\phi \qquad (5.108)\end{aligned}$$

where $\Delta G^{\circ\ddagger}_{a,0}$ is the activation free energy for the anodic reaction at zero potential. Substituting these expressions for the activation free energies in the equations for the cathodic and anodic current densities (Eq. 5.97), we have:

$$j_a = FBe^{-\Delta G^{\circ\ddagger}_{a,0}/RT}[\mathrm{Red}]e^{(1-\alpha)f\Delta\phi} \qquad (5.109)$$

$$j_c = FBe^{-\Delta G^{\circ\ddagger}_{c,0}/RT}[\mathrm{Ox}^+]e^{-\alpha f\Delta\phi} \qquad (5.110)$$

where we defined $f = F/RT$. At equilibrium, we have $j_0 = j_a = j_c$, and $\Delta\phi = E$:

$$j_a = FBe^{-\Delta G^{\circ\ddagger}_{a,0}/RT}[\mathrm{Red}]e^{(1-\alpha)fE} = j_0 \qquad (5.111)$$

$$j_c = FBe^{-\Delta G^{\circ\ddagger}_{c,0}/RT}[\mathrm{Ox}^+]e^{-\alpha fE} = j_0 \qquad (5.112)$$

where E is the electrode potential. (Note that the two equalities could be combined to relate the electrode potential E with the standard reaction Gibbs free energy $\Delta_r G^{\circ} = -FE$.) In the case when an overpotential η is applied, we have $\Delta\phi = E + \eta$ and:

$$j_a = FBe^{-\Delta G^{\circ\ddagger}_{a,0}/RT}[\mathrm{Red}]e^{(1-\alpha)fE}e^{(1-\alpha)f\eta} = j_0 e^{(1-\alpha)f\eta} \qquad (5.113)$$

$$j_c = FBe^{-\Delta G^{\circ\ddagger}_{c,0}/RT}[\mathrm{Ox}^+]e^{-\alpha fE}e^{-\alpha f\eta} = j_0 e^{-\alpha f\eta} \qquad (5.114)$$

The net current density is therefore:

$$j = j_a - j_c = \underbrace{j_0 e^{(1-\alpha)f\eta}}_{j_a} - \underbrace{j_0 e^{-\alpha f\eta}}_{j_c} = j_0\left[e^{(1-\alpha)f\eta} - e^{-\alpha f\eta}\right] \qquad (5.115)$$

This is the **Butler-Volmer equation**, which gives the current density through the electrode as a function of the overpotential. The plot of j vs. η for various values of the α parameter is shown in Figure 5.9.

There are several important things to note about the Butler-Volmer equation. If $\eta = 0$, then $j_a = j_c = j_0$ and there is no net current through the electrode, although there are non-zero anodic and cathodic currents, equal in magnitude. When $0 < \alpha < 1$, if the overpotential is positive ($\eta > 0$), then $j_a > j_c$, $j > 0$, and oxidation takes place. Conversely, if the overpotential is negative ($\eta < 0$), then $j_c > j_a$, $j < 0$, and reduction happens.

Note also that the sign of the exponential arguments in the j_a and j_c terms depends on the sign of η. For $\eta > 0$, j_a is an exponential with positive sign and j_c has negative sign. This means that for sufficiently high values of η, the contribution from j_c is negligible and the net current density is dominated by j_a. Conversely, for negative values of the overpotential ($\eta < 0$), j_a is an exponential with negative sign and j_c is an exponential with positive sign. For sufficiently low values of the overpotential ($\eta \ll 0$), j_a is negligible compared to j_c, and the net current density is dominated by j_c.

Lastly, note that if $\alpha = 1$, then $j_a = j_0$ and the anodic current is independent of η and, if $\alpha = 0$, then $j_c = j_0$ and the cathodic current is independent of η.

It is also interesting to consider the case when the overpotential is relatively small ($f\eta \ll 1$, typically with η less than 10 mV). In this case, we can Taylor-expand the exponentials around zero, to give:

$$j = j_0 \left[e^{(1-\alpha)f\eta} - e^{-\alpha f\eta}\right] = j_0 \left[1 + (1-\alpha)f\eta + \ldots - (1 - \alpha f\eta + \ldots)\right] \approx j_0 f\eta \tag{5.116}$$

Therefore, at very low overpotential the interface obeys Ohm's law because the current is proportional to the applied potential.

The exchange current density (j_0) is related to the reversibility of an electrode half-reaction. In general, j_0 is large if the electrode process involves no bond breaking or formation, or if the bonds being disrupted are weak. In this case, the Butler-Volmer equation indicates that a modest overpotential leads to a large current density, and we say this is a **reversible electrode**. (Note this has to do with the reversibility of the redox half-reaction, not with thermodynamic reversibility.) The exchange current density (j_0) is small if strong bonds are broken or formed, or if more than one electron is being transferred. In the case of a small j_0, a large overpotential is required to observe a significant net current density, and at the value of η when this happens, only one of j_a or j_c gives a significant contribution to the current. This is an **irreversible electrode**. Typical values of the exchange current are $j_0 = 6.3 \times 10^{-6}\,\mathrm{A/cm^2}$ for the $\mathrm{Ni_{(s)}|H_{2(g)}|H^+_{(aq)}}$ electrode and $j_0 = 2.5 \times 10^{-3}\,\mathrm{A/cm^2}$ for the $\mathrm{Pt_{(s)}|Fe^{2+}_{(aq)}|Fe^{3+}_{(aq)}}$ electrode.

If the applied overpotential is relatively large ($\eta \geq 0.12\,\mathrm{V}$), then the current density contains only one contribution from either j_a or j_c and the other one is negligible due to the corresponding exponential term in Eq. 5.115 having a negative sign. For instance, in the case of a positive overpotential:

$$j \approx j_a = j_0 e^{(1-\alpha)f\eta} \tag{5.117}$$

Taking logarithms, we find:

$$\ln j = \ln j_0 + (1-\alpha)f\eta \tag{5.118}$$

A representation of the logarithm of the current against the applied overpotential gives a linear plot, provided η is high enough to be in the linear regime. This representation is known as a **Tafel plot**. An example is shown in Figure 5.10. The Tafel plot can be used to determine the exchange current density and transfer coefficient of an electrode process experimentally. Extrapolation of a linear least-squares fit in the Tafel plot to $\eta = 0$ gives the exchange current density j_0 and, from the slope of the linear fit, it is possible to derive the α coefficient. Note that the Tafel plot is non-linear for small η because in that case the contribution from the opposite current density is not negligible.

The Butler-Volmer equation is very important in the application of electrochemical analytical techniques. The analytical method known as **voltammetry** is based on measuring an electrode

Figure 5.10: A Tafel plot, with $\ln j$ being represented against the overpotential. The plot is non-linear at low values of η.

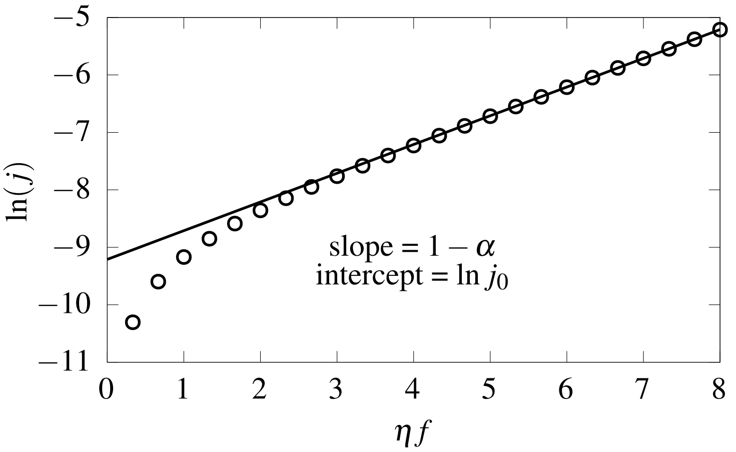
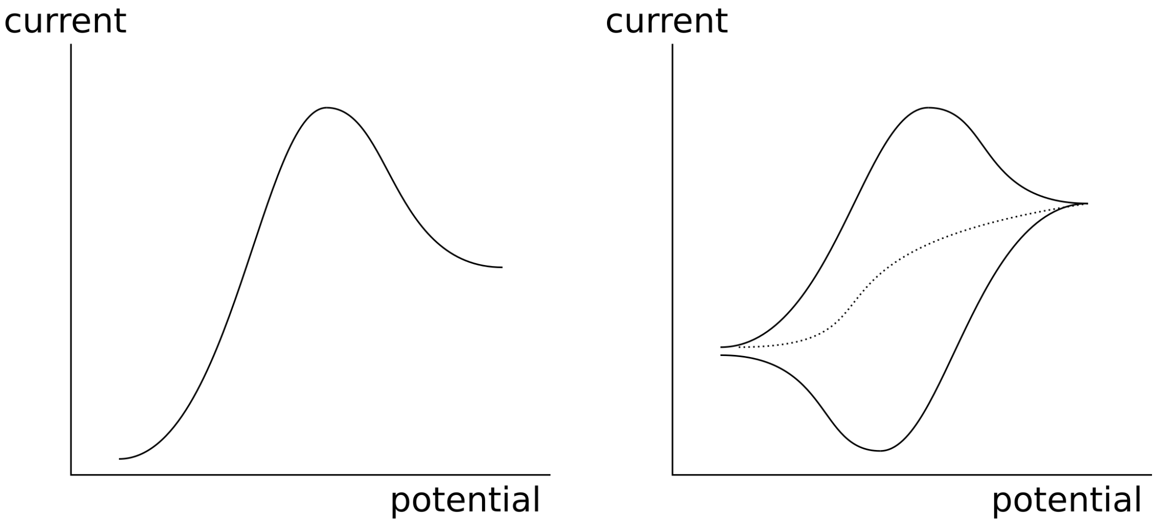


Figure 5.11: Left: a linear-sweep voltammogram. Right: a cyclic voltammogram for a reversible electrode (full lines) and an irreversible electrode (dotted lines).



current as a function of the applied overpotential and then relating the features in the corresponding voltammogram with the concentration of the electroactive species in solution. In a **linear-sweep voltammetry**, the applied potential is increased linearly with time, resulting in a current versus potential plot with a characteristic profile, shown in Figure 5.11 (left). The initial part of the plot shows an exponential increase in the current with applied potential, and corresponds almost exactly to the predictions of the Butler-Volmer equation (Eq. 5.115 and Figure 5.9). In our derivation, we considered that the concentration of electroactive species at the electrode is the same as in the solution bulk. As the redox reaction progresses, the electroactive species at the electrode is depleted and, at some point, it is reduced to zero. This causes a departure from the Figure 5.9: the current shows a maximum and starts decreasing as the rate of the redox reaction is dominated by the rate at which the redox-active species diffuses from the solution to the surface of the electrode. This effect is called **concentration polarization**. The maximum current in the voltammogram can be shown to be proportional to the concentration of electroactive species and to the sweep rate.

In a **cyclic voltammetry** experiment, the potential is first increased linearly, then decreased linearly with time. The current vs. potential plot in a cyclic voltammetry with a reversible electrode has a characteristic double peak structure, shown in Figure 5.11 (right). In the case of an irreversible electrode, the second peak corresponding to a decrease in potential is missing as the reverse reaction requires a significant overpotential to happen.

Chapter 6

Transport Phenomena

6.1 Transport Kinetics

In a **transport process**, mass or energy is transferred from one part of the system to another or between the system and its environment. A transport process is irreversible and the systems that we will study in this chapter are not in equilibrium. However, we will often assume that thermodynamic variables such as T, U, S, or p, can be locally defined at any point in the system, and can therefore be made dependent on the position (the **principle of local state** or **hypothesis of local equilibrium**). The field of study that deals with transport processes is **physical kinetics**, as opposed to chemical kinetics, which we have already studied, and it is essential in many fields of science and technology. In some cases, like in the study of continuous-flow reactors used in chemical engineering, there is an interplay between physical and chemical kinetics.

There are several different types of transport, depending on the property being transferred within the system. However, regardless of their type, all of these transport processes share the same fundamental characteristic: that the rate of transport is proportional to the gradient within the system of a related intensive property that acts as the driving force for the transport. For instance, a gradient in concentration in the system results in a mass transfer from the region with high concentration to the region with low concentration, resulting in the phenomenon known as **diffusion**.

In order to describe transport in a system, we use the concept of **flux**, which is the amount of property transferred per unit area per unit time. For instance, in the case of diffusion, the mass flux (J_{mass}) measures the amount of matter transferred per unit time per unit area, and therefore has units of $\mathrm{mol\,m^{-2}\,s^{-1}}$ in the SI. In general, the flux depends on the position in the system, and it is a vector quantity, pointing in the direction of transport ($\boldsymbol{J}(\boldsymbol{r})$). However, for the sake of simplicity, we will only consider one-dimensional transport, so the direction of the flux is indicated by the sign of J (positive means flux to the right and negative means flux to the left, see Figure 6.1). For a flux J, the total amount of property transferred through an area A and during a time t is $|J| \times A \times t$, where the absolute value ensures that we get rid of the sign indicating the direction of the flux.

Experiments have shown that the flux of a transport property at a certain point in the system is proportional to the gradient of its complementary property whose inhomogeneity acts as the driving force for the transport process. For instance, in the case of mass transfer, this property is the concentration. The mass flux at a given point is proportional to the concentration gradient at that point:

$$J_{\text{mass}} = -D\frac{dc}{dz} \tag{6.1}$$

Figure 6.1: Direction of the flux as a function of concentration profile in a one-dimensional diffusion process.

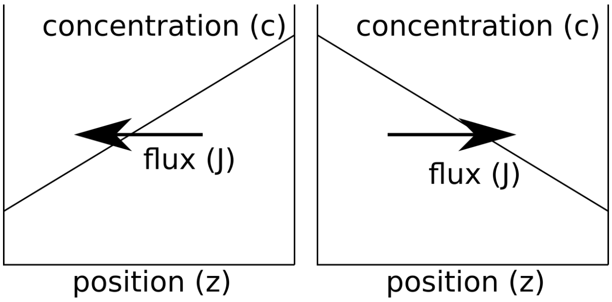


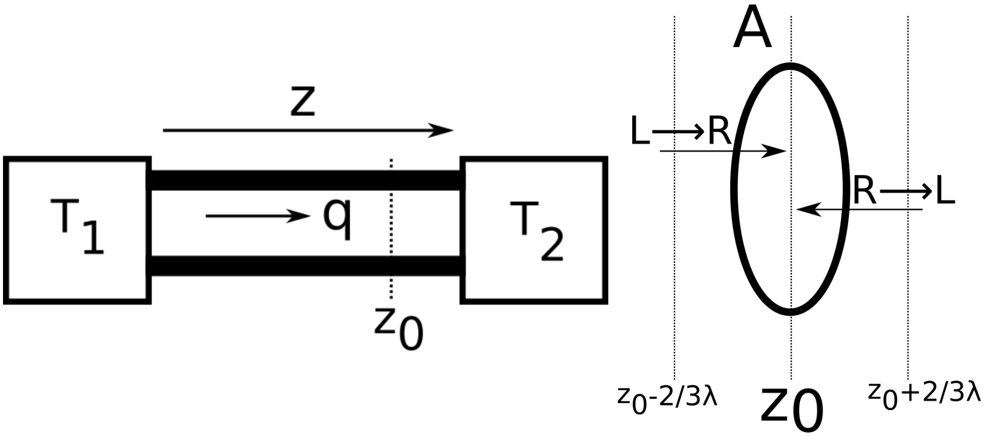
Table 6.1: List of transport properties, driving forces, and transport equations.

Quantity	Driving force	Proportionality constant	Equation	Name
Particles	Concentration (c)	Diffusion coefficient (D)	$J = -D\frac{dc}{dz}$	Fick's law
Heat	Temperature (T)	Thermal conductivity (κ)	$J = -\kappa\frac{dT}{dz}$	Fourier's law
Momentum	Velocity (v_x)	Viscosity (η)	$J = -\eta\frac{dv_x}{dz}$	Newton's law
Fluid mass	Pressure (p)	Poiseuille constant (C)	$J = -C\frac{dp}{dz}$	Poiseuille's law
Charge	Potential (ϕ)	Conductivity (κ)	$J = -\kappa\frac{d\phi}{dz}$	Ohm's law

where we assume that the diffusion process occurs along the z coordinate, and $c(z)$ is the concentration as a function of z. The proportionality constant D is a property of the medium and independent of the concentration (in this case, the diffusion coefficient). Note the minus sign in this equation, which indicates that the flux occurs opposite to the concentration gradient. In the three-dimensional case, we would have a vector flux ($\boldsymbol{J}_{\text{mass}}$) with its direction pointing opposite to the gradient of the concentration ($-D\boldsymbol{\nabla}c$).

Similar relations exist for other transport properties. They are listed in Table 6.1. The quantities that appear in these equations (including their units) are different, but the equations governing the transport phenomena are the same. We study a few of them in detail now.

Figure 6.2: Left: Diagram for a heat transport process along the z direction between two heat reservoirs at temperatures $T_1 > T_2$. Right: Cross-section of the system at a point z_0.



6.2 Thermal Conductivity

When **thermal conduction** takes place, heat is transferred between parts of the system due to a difference in temperature. A simple system portraying thermal conduction in one dimension is shown in Figure 6.2 (left). In this system, there are two reservoirs at temperatures T_1 and T_2 (with $T_1 > T_2$) and the temperature changes along the z direction, so we can write T as a function of the position, $T(z)$. As a consequence of the temperature difference, heat flows from the hot reservoir (T_1) to the cold reservoir (T_2). The heat flux is related to the temperature gradient by the equation:

$$J_{\text{heat}} = -\kappa \frac{dT}{dz} \tag{6.2}$$

which is known as **Fourier's law**. The κ is an intensive quantity characteristic of the material and is known as the **coefficient of thermal conductivity** (or simply **thermal conductivity**). The heat flux has units of $\mathrm{J\,m^{-2}\,s^{-1}}$ and the temperature gradient has units of $\mathrm{K\,m^{-1}}$ in the SI. Therefore, the units of κ are $\mathrm{J\,K^{-1}\,m^{-1}\,s^{-1}} = \mathrm{W\,K^{-1}\,m^{-1}}$ in the SI. (Note that heat transfer can also be achieved by **convection**, when heat is carried along with mass between regions at different temperatures, or by **radiation**, when the system emits electromagnetic radiation. We do not consider these two other sources of heat transport for now.)

The thermal conductivity of a material can arise from different heat transport mechanisms. Metals are typically good conductors of heat ($\kappa(\mathrm{Fe}) = 79.5\,\mathrm{W\,K^{-1}\,m^{-1}}$, $\kappa(\mathrm{Al}) = 205\,\mathrm{W\,K^{-1}\,m^{-1}}$) because the valence electrons are relatively free to move across the metal and act as energy carriers. In insulators, heat transport is dominated by atomic vibrations travelling throughout the crystal (phonons), and most insulators are poor thermal conductors, with the notable exception of diamond, which has the highest thermal conductivity of any material (κ in the range of $2400\,\mathrm{W\,K^{-1}\,m^{-1}}$). In solids, the thermal conductivity typically depends strongly on temperature, and it can either increase or decrease with T.

In gases, molecules in high-temperature regions have higher kinetic energy than those in low-temperature regions. Heat conduction is effected by the exchange of kinetic energy during molecular collisions and, consequently, gases are very poor heat conductors. Transport in an ideal gas can be rigorously derived from the kinetic theory of gases using the Chapman-Enskog theory, which provides expressions for its thermal conductivity, among other properties. We now derive an expression for κ using a hard sphere model and other crude assumptions used when we studied our simplified version of the kinetic theory of gases.

Consider a cross-section of the system in Figure 6.2 (left) with area A at position z_0. This cross-section is shown in Figure 6.2 (right). Molecules are constantly crossing this section of the system from the left to the right and from the right to the left. Because heat is being transported and the temperature changes with the position in the system ($T(z)$), molecules also have different average energies depending on their position ($\epsilon(z)$). Because the hot reservoir is on the left, molecules that cross this area from the left have slightly higher energies than those that cross it from the right. The number of molecules that impact this section per unit time per area is given by the collisional flux (Eq. 3.71):

$$Z_c = \frac{nN_A v_{\text{mean}}}{4V} \tag{6.3}$$

The energy flux is therefore the number of molecular collisions per time per area times the average energy that each molecule carries.

On average, the molecules in the gas travel a distance λ (the mean free path, Eq. 3.56) before crossing z_0. (As we have seen, the mean free path is independent of temperature.) However, these molecules need not travel perpendicular to the cross-section at z_0, and it is possible to show that the molecules crossing z_0 have traveled an average of 2/3 of the mean free path in the direction perpendicular to the surface. Therefore, an average molecule coming from the left has the energy corresponding to the $z_0 - \frac{2}{3}\lambda$ plane and an average molecule from the right has an energy corresponding to the $z_0 + \frac{2}{3}\lambda$ plane. Consequently, the energy flux from left to right and from right to left at z_0 are:

$$J(\mathrm{L} \to \mathrm{R}) = \frac{nN_A v_{\mathrm{mean}}}{4V} \times \epsilon(z_0 - \frac{2}{3}\lambda) \tag{6.4}$$

$$J(\mathrm{R} \to \mathrm{L}) = \frac{nN_A v_{\mathrm{mean}}}{4V} \times \epsilon(z_0 + \frac{2}{3}\lambda) \tag{6.5}$$

The net flux through the section is:

$$J_{\mathrm{heat}} = J(\mathrm{L} \to \mathrm{R}) - J(\mathrm{R} \to \mathrm{L}) = \frac{nN_A v_{\mathrm{mean}}}{4V} \left[\epsilon(z_0 - \frac{2}{3}\lambda) - \epsilon(z_0 + \frac{2}{3}\lambda)\right] \tag{6.6}$$

The term in square brackets can be simplified by using the Taylor expansion of the energy to first order, which is a reasonable approximation if the variation in the average molecular energy is not too large over a molecular mean free path:

$$\epsilon(z_0 - \frac{2}{3}\lambda) - \epsilon(z_0 + \frac{2}{3}\lambda) = \epsilon(z_0) - \frac{2}{3}\lambda \left.\frac{d\epsilon}{dz}\right|_{z_0} - \left[\epsilon(z_0) + \frac{2}{3}\lambda \left.\frac{d\epsilon}{dz}\right|_{z_0}\right] = -\frac{4}{3}\lambda \left.\frac{d\epsilon}{dz}\right|_{z_0} \tag{6.7}$$

Using the chain rule, this derivative can be written in terms of temperature:

$$\frac{d\epsilon}{dz} = \frac{d\epsilon}{dT}\frac{dT}{dz} \tag{6.8}$$

Because this is an ideal gas, the molar internal energy of the gas, which is a function of temperature only, equals N_A times the energy of a single molecule:

$$U_m = U_m(T) = N_A\epsilon \tag{6.9}$$

Therefore, the position-derivative of the molecular energy becomes:

$$\frac{d\epsilon}{dz} = \frac{1}{N_A}\frac{dU_m}{dT}\frac{dT}{dz} \tag{6.10}$$

And, since U is a function of T only, the temperature-derivative of U equals the constant-volume heat capacity:

$$\frac{d\epsilon}{dz} = \frac{C_{v,m}}{N_A}\frac{dT}{dz} \tag{6.11}$$

from where:

$$\epsilon(z_0 - \frac{2}{3}\lambda) - \epsilon(z_0 + \frac{2}{3}\lambda) = -\frac{4C_{v,m}\lambda}{3N_A} \times \frac{dT}{dz} \tag{6.12}$$

and finally the energy flux through the section at z_0 is:

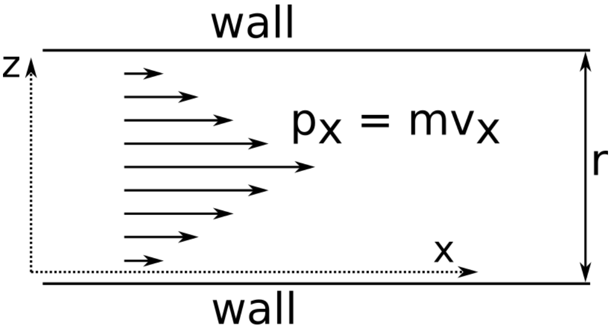
$$J = \frac{nN_A v_{\mathrm{mean}}}{4V} \times \left(-\frac{4C_{v,m}\lambda}{3N_A} \times \frac{dT}{dz}\right) = -\frac{nv_{\mathrm{mean}}C_{v,m}\lambda}{3V}\frac{dT}{dz} \tag{6.13}$$

Comparing to Fourier's law (Eq. 6.2), we identify the thermal conductivity as:

$$\kappa = \frac{1}{3}v_{\mathrm{mean}}C_{v,m}\lambda c \tag{6.14}$$

where $c = n/V$ is the molar concentration. The thermal conductivity of a gas increases with temperature at constant volume, because $C_{v,m}$ increases with temperature. The mean free path

Figure 6.3: A diagram exemplifying viscosity. The fluid is moving from left to right under the effect of a pressure difference. The fluid layers closer to the wall move more slowly due to internal friction within the fluid.



(Eq. 3.56) is inversely proportional to p but c is proportional to p, so both pressures cancel in the product λc, and the thermal conductivity of a gas is approximately independent of pressure at constant temperature (except at very high or very low pressure). This is reasonable because an increase in concentration increases the density of available carriers for energy transport but also decreases the mean free path of each molecule.

Although our expression is qualitatively correct, the multiplicative factor is wrong due to the crude assumptions used. By relaxing some of these assumptions, a more accurate estimate can be found for the thermal conductivity of a monoatomic ideal gas:

$$\kappa = \frac{25\pi}{64} v_{\text{mean}} C_{v,m} \lambda c \tag{6.15}$$

This expression has to be modified in the case of polyatomic molecules, to account for energy being transferred via the rotational and vibrational energy levels during molecular encounters (although the contribution from the translational levels is dominant).

6.3 Viscosity

Viscosity is the resistance of a fluid (a liquid or gas) to flow. Consider a fluid subjected to a pressure differential under which it is flowing through a tube, as shown in Figure 6.3. Due to friction with the wall, the fluid layers that are at the center move more quickly, whereas those closer to the wall are slowed down, to the point where layers in contact with the wall have exactly zero velocity (the **no-slip condition**). Each layer slides over the layers above and below and, in doing so, experiences friction. The slow-down effect in the fluid caused by this internal friction is the origin of viscosity.

Alternatively, viscosity can also be seen as the ability of the fluid to transfer momentum between adjacent layers parallel to the flow direction. The reason viscosity can be interpreted in this way is that the higher the internal friction between layers, the greater the transfer of momentum between them. For the fluid flowing in the x direction shown in Figure 6.3, all fluid layers parallel to the flow have molecules with different values of momentum along x (p_x). Layers closer to the wall contain slower molecules. Because of the gradient in v_x, there is a flux of momentum (p_x) in the z direction (J_z) as molecules move between the different layers. Experimentally, it has been determined that the momentum flux in the z direction is proportional to the velocity gradient:

$$J(p_x) = -\eta \frac{dv_x}{dz} \tag{6.16}$$

where v_x is the velocity in the x direction, which is a function of the distance from the wall of the tube ($v_x(z)$), and η is the **coefficient of viscosity** (also **dynamic viscosity** or simply **viscosity**). This is **Newton's law of viscosity**. The momentum flux has units of pressure ($\mathrm{kg\,m^{-1}\,s^{-2}}$ in the SI) and the velocity derivative has units of $\mathrm{s^{-1}}$. Therefore, the units of viscosity are $\mathrm{kg\,m^{-1}\,s^{-1}}$ in the SI. A very common non-SI unit is the poise ($1\,\mathrm{P} = 0.1\,\mathrm{kg\,m^{-1}\,s^{-1}}$) or the centipoise ($1\,\mathrm{P} = 100\,\mathrm{cP}$). The viscosity of liquid water at room temperature is approximately 1 cP. For other fluids the viscosity is: O_2 (0.021 cP), H_2SO_4 (19 cP), olive oil (80 cP), glycerol (954 cP). Gases are typically much less viscous than liquids.

Unlike in gases, the viscosity in liquids depends strongly on intermolecular interactions and on the shape of the molecules (e.g. polymer liquids are very viscous because the molecules tangle with each other). The viscosity in liquids increases with increasing pressure and, in general, decreases with increasing temperature. The latter is explained by the fact that molecular movement in the liquid is an activated process, i.e., for a molecule to move in the liquid it has to acquire a certain energy. This results in the temperature-dependence of the viscosity being expressed with an Arrhenius-like equation, $\eta = \eta_0 e^{E_a/RT}$. (Note the positive sign in the exponent; the viscosity decreases exponentially with temperature.) The calculation of this activation energy is currently an unsolved problem, but E_a corresponds approximately to the mean potential energy of the intermolecular interactions in the liquid. The change in the density of the liquid with temperature also makes an important contribution to its change in viscosity.

All gases and most liquids obey Newton's law of viscosity, but this law only holds in the case when the rate of flow is not too high. If Newton's law applies, then the flow is called **laminar**, because the motion consists of layers of fluid sliding over each other, as in Figure 6.3. At higher flow rates, these layers are disrupted and the flow becomes chaotic, with local changes in fluid pressure and the appearance of vortices. This is known as a **turbulent** flow. The distinction between these two types of flow is essential in fluid dynamics and its multiple applications in engineering (e.g. aerodynamics, hydraulics,...).

Another violation of Newton's law of viscosity occurs when the viscosity coefficient is not a constant. In a **Newtonian fluid**, the viscosity is independent of the velocity gradient (dv_x/dz). Gases and most liquids are Newtonian. A characteristic feature of a Newtonian fluid is that a sphere of radius r moving through a liquid with speed v experiences a friction force (a **drag**) that is proportional to the speed of the movement and the viscosity of the fluid:

$$F = fv = 6\pi\eta r v \tag{6.17}$$

The proportionality constant is the **friction coefficient** (f) and this equation is called **Stokes' law**. Some liquids are **non-Newtonian fluids**, and their viscosity changes with the rate of flow, the previous history of the liquid, as well as other properties such as applied stress. Non-Newtonian liquids are typically complex in composition and include some polymers, either molten or in solution, concentrated salt solutions, and suspensions. Examples include corn starch-water suspensions (oobleck), honey, blood, molasses, custard, and shampoo.

The viscosity of an ideal gas can be estimated using the same assumptions as those used for the calculation of the thermal conductivity. It is found to be:

$$\eta = \frac{1}{3} v_{\mathrm{mean}} \lambda \rho \tag{6.18}$$

where $\rho = \frac{Nm}{V} = \frac{nM}{V} = cM$ is the gas density. The derivation is analogous to that of the thermal conductivity, except that in this case momentum is being transferred rather than energy. Also, we consider molecules entering and exiting a layer parallel to the flow of the gas from above and from below. Molecules coming from other layers have different velocities and the net flow of momentum can be found and, from it, the viscosity coefficient. As in the case of the thermal conductivity, the dependence on the mean velocity, mean free path, and density is correct, but the multiplicative factor is wrong due to the crudeness of the assumptions. A more rigorous result is:

$$\eta = \frac{5\pi}{32} v_{\text{mean}} \lambda \rho \tag{6.19}$$

Viscosity measurements combined with this expression under the assumption of a hard sphere model can be used to determine molecular diameters experimentally. These equations correctly predict that, rather surprisingly, the viscosity of a gas increases with temperature at constant volume (because v_{mean} goes as $T^{1/2}$) and it is independent of pressure (because the p from λ cancels with the p^{-1} from ρ).

Finally, viscosity also determines the rate of laminar flow of a fluid in a tube under applied pressure (Figure 6.3). It is possible to show that the velocity of a fluid inside a tube of radius r at a distance s from the center of the tube is:

$$v_x = \frac{1}{4\eta}(r^2 - s^2)\left(-\frac{dp}{dz}\right) \tag{6.20}$$

where dp/dz is the pressure gradient along the tube. This equation says that the profile for the velocities of the different layers inside the tube is parabolic, with a maximum velocity exactly at the center and zero velocity in the layer that is in contact with the tube walls. Using this expression, the volume that passes through the tube in time t (the **volumetric flow rate**) can be shown to be:

$$\frac{dV}{dt} = \frac{\pi r^4}{8\eta} \frac{dp}{dz} \tag{6.21}$$

This is **Poiseuille's law**. If the pressure gradient is linear and the tube has constant radius, then the volume of fluid that passes through the tube in time Δt is obtained by direct integration:

$$V = \frac{\pi r^4}{8\eta} \frac{\Delta p}{L} \Delta t \tag{6.22}$$

where Δp is the pressure drop between both ends and L is the length of the tube. Note that the volume of fluid that flows through depends very strongly on the radius of the tube.

6.4 Diffusion

In the transport process known as **diffusion**, there is a transfer of molecules from one part of the system to another due to a difference in concentration. It is found empirically that the flux of matter in the system is proportional to the concentration gradient (see Figure. 6.1):

$$J_{\text{mass}} = -D \frac{dc}{dz} \tag{6.23}$$

where J_{mass} is the mass flux (units: $\text{mol}\,\text{m}^{-2}\,\text{s}^{-1}$), $\frac{dc}{dz}$ is the concentration gradient (units: $\text{mol}\,\text{m}^{-4}$), and D is the **diffusion coefficient** (or **diffusivity**) with units of $\text{m}^2\,\text{s}^{-1}$ in the SI. This equation is known as **Fick's first law of diffusion**.

Diffusion is a relatively slow process, and the order of magnitude of the diffusion coefficient depends mainly on the aggregation state of the medium. For gases, D is typically in the order of $0.1\,\text{cm}^2/\text{s}$. Examples: H_2 ($1.5\,\text{cm}^2/\text{s}$) and CO_2 ($0.10\,\text{cm}^2/\text{s}$). In the case of liquids, D is significantly smaller than in gases, in the order of $1 \times 10^{-5}\,\text{cm}^2/\text{s}$ ($2.4 \times 10^{-5}\,\text{cm}^2/\text{s}$ in H_2O and $2.2 \times 10^{-5}\,\text{cm}^2/\text{s}$ in benzene). The diffusion coefficient in solids is extremely small, in the order of $1 \times 10^{-20}\,\text{cm}^2/\text{s}$.

The reason why diffusion is so slow is that, despite the relative fast movements of molecules in a liquid or a gas, these molecules are constantly colliding with each other and they emerge from these collisions moving in a random direction. Indeed, the path of a given molecule through a gas or a liquid can be approximated as a series of steps in random directions: the molecule travels a distance comparable to the mean free path, then collides and acquires a new random direction. After that event, the same molecule travels some more, collides again, and its direction changes at random once more. This stochastic process in which a path is built as a succession of steps in random directions is known as a **random walk**. The random walks caused by molecular collisions in a fluid can be used to explain **Brownian motion**: the random movement of particles, such as pollen, suspended in a liquid.

Focussing on a single molecule undergoing a random walk, it is possible to show that its root-mean-square displacement over a period of time t is related to the diffusion coefficient (D):

$$(\Delta x)_{\mathrm{rms}} = \langle (\Delta x)^2 \rangle^{1/2} = \sqrt{2Dt} \tag{6.24}$$

This equation is known as the **Einstein-Smoluchowski relation**. If we consider a diffusion process that happens over a time span of $t = 1\,\mathrm{min}$ at room temperature and pressure then, using the typical orders of magnitude for D mentioned above, we find that a molecule travels on average $3\,\mathrm{cm}$ in a gas, $0.03\,\mathrm{cm}$ in a liquid, and $1\,\mathrm{Å}$ in a solid. (Note that we are considering only diffusion, not convection. The transfer of mass occurs only at the molecular level through collisions.)

In ideal gases, the same argument that we used to estimate the thermal conductivity can be used to calculate the diffusion coefficient. In this case, we would consider a section of the system with area A perpendicular to the flow, and the number of molecules traversing this section from left to right and from right to left. Since there is a concentration gradient, there are more molecules crossing this area from one side than from the other, resulting in a net flux. The proof is entirely analogous otherwise and the resulting expression for the diffusion coefficient is:

$$D = \frac{1}{3} v_{\mathrm{mean}} \lambda \tag{6.25}$$

As usual, the crudeness of our approximations does not yield a very accurate estimate but correctly captures the dependence on v_{mean} and λ. A better estimate obtained using a more rigorous approach is:

$$D = \frac{3\pi}{16} v_{\mathrm{mean}} \lambda \tag{6.26}$$

The mean free path decreases with increasing pressure, and therefore molecules diffuse more slowly at higher pressure. The mean speed increases with temperature, and so does the diffusion coefficient. Lastly, the mean free path increases for molecules with a lower diameter—smaller molecules diffuse faster.

Note that the diffusion coefficient in an ideal gas (Eq. 6.25) can be related to the viscosity (Eq. 6.18) and the thermal conductivity (Eq. 6.14):

$$D = \frac{1}{3} v_{\mathrm{mean}} \lambda \tag{6.27}$$

$$\eta = \frac{1}{3} v_{\mathrm{mean}} \lambda \rho = D\rho \tag{6.28}$$

$$\kappa = \frac{1}{3} v_{\mathrm{mean}} C_{v,m} \lambda c = D C_{v,m} c \tag{6.29}$$

Similar relations exist using the more rigorous estimates given, but with different multiplicative constants.

6.4.1 Thermodynamic View of Diffusion

We have seen that Fick's first law of diffusion can be justified by analyzing the particle flux across a section of the system. We now give an alternative derivation based on the second law of thermodynamics. At constant temperature and pressure, the maximum work that can be effected by a system undergoing a thermodynamic process equals the change in Gibbs free energy for that process (this maximum work is achieved when the process is reversible). In the case of a solute diffusing through a solution, this work equals the change in the chemical potential of the solute. If the chemical potential depends on the position in the system (z, see Figure 6.1):

$$dw_m = d\mu = \mu(z + dz) - \mu(z) = \left(\frac{\partial \mu}{\partial z}\right)_{T,p} dz \tag{6.30}$$

The work done by a solute particle moving in solution is:

$$dw_m = -F_{\text{therm}} dz \tag{6.31}$$

Comparing these two equations, we can identify the gradient of the chemical potential as a **thermodynamic force**:

$$F_{\text{therm}} = -\left(\frac{\partial \mu}{\partial z}\right)_{T,p} \tag{6.32}$$

The thermodynamic force is not an actual force. Instead, it is a measure of the tendency of the solute to spread in the solution, a process that is spontaneous and results in an entropy gain.

In a solution, the chemical potential of the solute is related to its activity:

$$\mu = \mu^\circ + RT \ln a \tag{6.33}$$

from where the thermodynamic force is:

$$F_{\text{therm}} = -\left(\frac{\partial \mu}{\partial z}\right)_{T,p} = -RT\left(\frac{\partial \ln a}{\partial z}\right)_{T,p} \tag{6.34}$$

Assuming an ideal behavior of the solute, we have $a = c/c^\circ$ and therefore:

$$F_{\text{therm}} = -RT\left(\frac{\partial \ln(c/c^\circ)}{\partial z}\right)_{T,p} = -\frac{RT}{c}\left(\frac{\partial c}{\partial z}\right)_{T,p} \tag{6.35}$$

The thermodynamic force accelerates the solute particles until the drag from the solution balances its effect. When the two forces balance each other exactly, the solute molecule moves with a constant **drift speed** (s) through the solution. In this situation, the friction force is proportional to the molecular speed:

$$F_{\text{friction}} = N_A f s \tag{6.36}$$

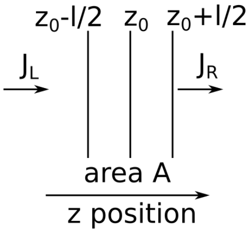
where f is a friction constant that depends on solution and solvent, and N_A is introduced in order to calculate the force experienced by a mole of molecules. When the friction force balances the thermodynamic force:

$$N_A f s = -\frac{RT}{c}\frac{dc}{dz} \tag{6.37}$$

from where we can solve the drift speed:

$$s = -\frac{k_B T}{cf}\frac{dc}{dz} \tag{6.38}$$

Figure 6.4: A section of a system undergoing diffusion mass transport. The section shown has area A and thickness l. There is a mass flux from the left (J_L) and from the right (J_R) entering the section.



The number of moles that pass through a cross-section of the solution with area A during a time interval Δt is $cAs\Delta t$, and therefore the mass flux through that area is:

$$J_{\text{mass}} = \frac{cAs\Delta t}{A\Delta t} = sc = -\frac{k_BT}{f}\frac{dc}{dz} \tag{6.39}$$

which proves Fick's first law of diffusion and shows that the diffusion coefficient can be written as:

$$D = \frac{k_BT}{f} \tag{6.40}$$

In a Newtonian liquid, the friction coefficient is related to the viscosity of the medium by Stokes' law (Eq. 6.17). Substituting:

$$D = \frac{k_BT}{6\pi\eta r} \tag{6.41}$$

where η is the viscosity and r is the hydrodynamic radius of the solute molecules. (Note the difference with a gas, where $D = \rho/\eta$, with ρ the gas density.) This is known as the **Stokes-Einstein equation**. The thermodynamic force that the solute molecules experience is related to the drift speed:

$$F = N_Afs = \frac{RTs}{D} \tag{6.42}$$

so measurements of s can be used to determine the magnitude of the thermodynamic force experimentally.

6.5 The Diffusion Equation and the Continuity Equation

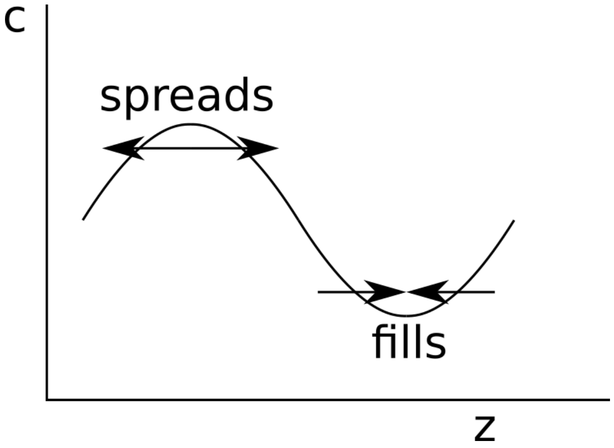
Consider a system undergoing diffusion mass transport and a cross-section in this system with area A and thickness l, as shown in Figure 6.4. Assuming l is sufficiently small, the change in concentration within this region can be written as the number of molecules that flow into this region divided by its volume. The number of molecules that enter from the left is J_LA, where J_L is the corresponding flux. Therefore, the contribution to the change in concentration from the left flux of molecules (J_L) is:

$$\left(\frac{\partial c}{\partial t}\right)_L = \frac{J_LA}{V} = \frac{J_L}{l} \tag{6.43}$$

where we have used that the volume of the region is $V = Al$. Note that the concentration increases because $J_L > 0$, i.e., the molecules enter the region. Similarly, the change in concentration due to the flux on the right is:

$$\left(\frac{\partial c}{\partial t}\right)_R = -\frac{J_RA}{V} = -\frac{J_R}{l} \tag{6.44}$$

Figure 6.5: A diagram illustrating the change in concentration over time predicted by the diffusion equation. Regions of positive curvature (the neighborhood of a minimum) fill over time. Regions of negative curvature (maxima) spread over time.



In this case, there is a minus sign because a positive J_R means that molecules are leaving the region under consideration. The net change in concentration inside the region is the sum of both contributions:

$$\left(\frac{\partial c}{\partial t}\right) = \left(\frac{\partial c}{\partial t}\right)_L + \left(\frac{\partial c}{\partial t}\right)_R = \frac{J_L}{l} - \frac{J_R}{l} = \frac{J_L - J_R}{l} \tag{6.45}$$

Using Fick's first law of diffusion (Eq. 6.23), we write both fluxes in terms of position derivative of the concentration:

$$\left(\frac{\partial c}{\partial t}\right) = \frac{D}{l}\left[\left(\frac{\partial c}{\partial z}\right)_R - \left(\frac{\partial c}{\partial z}\right)_L\right] \tag{6.46}$$

where z is the position coordinate along the system. Since we are assuming l is small compared to the change in concentration, we can apply Taylor expansions to both position derivatives around the center of the volume ($z_0 = z + l/2$):

$$\left(\frac{\partial c}{\partial t}\right) = \frac{D}{l}\left\{\left(\frac{\partial c}{\partial z}\right)_{z_0} + \left(\frac{\partial^2 c}{\partial z^2}\right)_{z_0}\frac{l}{2} - \left[\left(\frac{\partial c}{\partial z}\right)_{z_0} - \left(\frac{\partial^2 c}{\partial z^2}\right)_{z_0}\frac{l}{2}\right]\right\} \tag{6.47}$$

where the zero subscript indicates that the derivative is taken at the center of the region. This equation simplifies to:

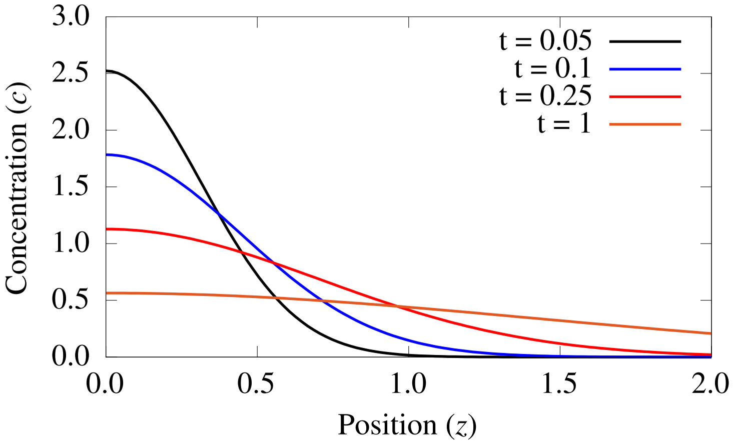
$$\left(\frac{\partial c}{\partial t}\right) = D\left(\frac{\partial^2 c}{\partial z^2}\right) \tag{6.48}$$

where we dropped the 0 subscript by making l infinitely small. This is the **diffusion equation** (or, less commonly, Fick's second law of diffusion).

The diffusion equation relates the change in concentration over time at any point in the system with the curvature of the concentration profile at that point. It predicts that the "wrinkles" in the concentration profile disappear over time. This is illustrated in Figure 6.5. If the curvature is positive (for instance, near a minimum in the concentration), then the $\partial c/\partial t > 0$ and the concentration increases, filling the minimum. If the curvature is negative (e.g. near a maximum), then $\partial c/\partial t < 0$ and the maximum disappears with time. If the curvature is zero, because c is a straight line, then the concentration does not change with time.

The diffusion equation is a partial differential equation. Finding a solution to this differential equation requires specifying the boundary conditions and the initial condition of the system. In all but the simplest cases, the solution of the diffusion equation requires numerical techniques

Figure 6.6: Concentration as a function of time and position given by the solution of the diffusion equation for an initial condition in which all the concentration is located at $z = 0$ when $t = 0$.



and a discretization of the system (i.e. partitioning the system into small fragments, each having a different, but uniform, concentration).

However, analytical solutions of the diffusion equation can be found in simple cases. For instance, consider a tall beaker of water with base area A and n_0 moles of solute in it. We assume that all solute molecules are at the bottom of the beaker ($z = 0$) at $t = 0$. In this case, the solution of the diffusion equation is:

$$c(z,t) = \frac{n_0}{A\sqrt{\pi D t}} \times e^{-z^2/4Dt} \tag{6.49}$$

This solution is illustrated in Figure 6.6. At time zero, all molecules are at $z = 0$ and, as time passes, the concentration spreads out further into the system. In doing this, the curvature in the concentration profile is progressively removed, as demanded by the diffusion equation.

The diffusion equation can be generalized with additional terms that take into account other processes that may affect the concentration profile in the system (convection, existence of chemical reactions that generate or consume the species, etc.) In addition, the diffusion equation can be generalized to three dimensions, where the change in concentration with time is given by the sum of the contributions from each direction:

$$\frac{\partial c(\boldsymbol{r})}{\partial t} = D\left[\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial z^2}\right] = D\nabla^2 c(\boldsymbol{r}) \tag{6.50}$$

where we have used the Laplacian operator (compare to Eq. 6.48).

Since the mathematical formalism behind diffusion is the same as for the other transport properties, the diffusion equation is a particular case of a more general expression that controls the transport of a conserved quantity (mass, energy, etc.) called the **continuity equation**:

$$\frac{\partial c}{\partial t} + \boldsymbol{\nabla} \cdot \boldsymbol{J} = 0 \tag{6.51}$$

where the flux in the case of diffusion is given by Fick's first law, $\boldsymbol{J} = -D\boldsymbol{\nabla} c$. Substitution of this expression for $\boldsymbol{J}$ in Eq. 6.51 and assuming D is constant yields the three-dimensional diffusion equation, Eq. 6.50. However, the continuity equation can be used to describe the transport of any of the other quantities in Table 6.1. For instance, in the case of thermal conductivity, transport occurs via differences in temperature (T) and J is the heat flux ($\boldsymbol{J} = -\kappa\boldsymbol{\nabla} T$, Eq. 6.2). The continuity equation in this case is known as the **heat equation**:

$$\frac{\partial T(\boldsymbol{r})}{\partial t} = \kappa\nabla^2 T(\boldsymbol{r}) \tag{6.52}$$

As in the case of the diffusion equation, to which it is entirely analogous, the solution of this partial differential equation gives the evolution in time of the temperature in a system out of thermal equilibrium. Similarly, application of the continuity equation to a viscous fluid results in the Navier-Stokes equations.

The continuity equation is a local (and stronger) version of the usual conservation laws. Not only does it reflect that mass or energy cannot be created or destroyed in the system as a whole but also that mass or energy cannot be instantly transported from one part of the system to another. Continuity equations are fundamental in the study of fluid dynamics and electromagnetism.

6.6 Transport in Electrolytic Solutions

If a potential difference is applied between two electrodes in an electrolytic solution, a current flows through them. The ratio between the applied potential and the resulting current is the **resistance**:

$$R = \frac{V}{I} \tag{6.53}$$

which is measured in ohms ($1\,\Omega = 1\,\mathrm{V/A}$). The **conductance** is the inverse of the resistance:

$$G = \frac{1}{R} = \frac{I}{V} \tag{6.54}$$

and it is measured in siemens ($1\,\mathrm{S} = 1\,\Omega^{-1} = 1\,\mathrm{A/V}$). Both the resistance and the conductance depend on the geometry of the system. In contrast, the (electrical) **conductivity** (κ) is defined as:

$$\kappa = \frac{Gl}{A} \tag{6.55}$$

where l is the length of the conductor and A is its area. The SI unit of conductivity is $\mathrm{S\,m^{-1}}$. The **resistivity** is the inverse of the conductivity:

$$\rho = \frac{1}{\kappa} = \frac{AR}{l} \tag{6.56}$$

Unlike R and G, which depend on the shape of the conductor, resistivity and conductivity are properties inherent to the conducting material.

The conductivity depends on the concentration of charge carriers in the conductor. In the case of an electrolytic solution, the carriers are the ions, so it makes sense to introduce the **molar conductivity**:

$$\Lambda_m = \frac{\kappa}{c} \tag{6.57}$$

where c is the molar concentration of added electrolyte. The SI unit of Λ_m is $\mathrm{S\,m^2\,mol^{-1}}$. Solutions of strong electrolytes have molar conductivities typically in the range of $10\,\mathrm{mS\,m^2\,mol^{-1}}$.

The conductivity of a solution is not proportional to the concentration of added electrolyte, which results in the molar concentration being itself a function of concentration. If the electrolyte is weak, then the number of ions in solution depends on the degree of the dissociation, which is a complicated function of the concentration. Even if the electrolyte is strong and dissociation is complete, there are interactions between the ions in solution. These interactions result in the formation of ionic pairs, which prevent κ from being proportional to c. In fact, for strong electrolytes, it has been experimentally determined that the molar conductivity is proportional to the square root of the electrolyte concentration:

$$\Lambda_m = \Lambda_m^\circ - Kc^{1/2} \tag{6.58}$$

This is **Kohlrausch law**. The Λ_m° is the molar conductivity in the limit $c \to 0$ and is therefore known as the **limiting molar conductivity** and K is the Kohlrausch's coefficient, which depends only on the stoichiometry of the electrolyte but not on the nature of the ions or their concentration. In the zero-concentration limit, ions move independently from one another, and therefore Λ_m° can be written as a sum of contributions from each of the ions:

$$\Lambda_m^\circ = \nu_+\lambda_+^\circ + \nu_-\lambda_-^\circ \tag{6.59}$$

which is the **law of the independent migration of ions** for a strong electrolyte that dissociates into ν_+ cations and ν_- anions:

$$A_{\nu+}B_{\nu-} \longrightarrow \nu_+A^{z+} + \nu_-B^{z-} \tag{6.60}$$

The λ_+° and λ_-° are the limiting molar conductivities of the corresponding cations and anions, respectively.

The conductivity of an ion can be related to how fast it moves in solution, i.e., its mobility. An ion in solution accelerates under the electric field created by the potential difference but it is slowed down because it is impeded by the solvent molecules (the **viscous drag**). After a while, the electric and the viscous friction forces balance each other and the ion achieves its drift speed (s), which can be calculated by a procedure similar to how we derived the drift speed of a non-charged particle using the Stokes-Einstein equation (Eq. 6.41). The electric force on a single ion is:

$$f_{\text{electric}} = q\mathcal{E} = ze\mathcal{E} \tag{6.61}$$

where $q = ze$ is the charge of the ion (in Coulomb), e is the electron charge, z is the charge of the ion (in number of electrons), $\mathcal{E} = -\Delta\phi/l$ is the electric field, and $\Delta\phi$ is the potential difference between the two electrodes, situated at a distance l from each other. From Stokes' law (Eq. 6.17), the friction force on a single ion is:

$$f_{\text{friction}} = 6\pi\eta rs \tag{6.62}$$

where η is the viscosity of the solvent and r is the hydrodynamic radius of the ion. Equating the two gives the drift speed in terms of the applied field and the viscosity of the solvent:

$$6\pi\eta rs = ze\mathcal{E} \tag{6.63}$$

$$s = \frac{ze}{6\pi\eta r} \times \mathcal{E} \tag{6.64}$$

Therefore, the drift speed is proportional to the applied field. We define the **ion mobility** (u) as the proportionality constant between the two:

$$s = u\mathcal{E} \tag{6.65}$$

$$u = \frac{ze}{6\pi\eta r} \tag{6.66}$$

The SI unit of $\mathcal{E}$ is V/m and the drift speed is in m/s, so the mobility unit is $\mathrm{m^2\,V^{-1}\,s^{-1}}$.

Eq. 6.66 says that ion mobility decreases with the viscosity of the solvent and with the radius r. Note that the r in this equation is the hydrodynamic radius: the radius of the ion plus its coordinated solvent shell. For small ions (e.g. single atoms), r is determined more by their polarizing ability than by the size of the ions themselves. For instance, the mobility of the alkali ions in water at room temperature increases down the group: $\mathrm{Li^+}$ ($4.01\,\mathrm{m^2\,V^{-1}\,s^{-1}}$), $\mathrm{Na^+}$ ($5.19\,\mathrm{m^2\,V^{-1}\,s^{-1}}$), $\mathrm{K^+}$ ($7.62\,\mathrm{m^2\,V^{-1}\,s^{-1}}$), and $\mathrm{Rb^+}$ ($7.92\,\mathrm{m^2\,V^{-1}\,s^{-1}}$). This is because small ions are more polarizing (put out stronger electric fields) and their solvation shells are correspondingly larger. The ionic mobility of the $\mathrm{OH^-}$ ($20.64\,\mathrm{m^2\,V^{-1}\,s^{-1}}$) and $\mathrm{H^+}$

($36.23\,\mathrm{m^2\,V^{-1}\,s^{-1}}$) ions in water is much higher than any other ion. One explanation for this observation is that, in water, protons can move by jumping from one molecule to the other through hydrogen bonds, resulting in a coordinated motion of protons throughout the liquid (this is known as the **Grotthuss mechanism**).

The mobility of an ion can be related to its diffusion coefficient in solution. The Stokes-Einstein law (Eq. 6.41) says that the ionic diffusion coefficient is:

$$D = \frac{k_BT}{6\pi\eta r} \tag{6.67}$$

so we have:

$$6\pi\eta r = \frac{k_BT}{D} \tag{6.68}$$

and therefore the mobility (Eq. 6.66) can be written as:

$$u = \frac{ze}{6\pi\eta r} = \frac{zeD}{k_BT} = \frac{zFD}{RT} \tag{6.69}$$

where in the last step we multiplied and divided by Avogadro's number and used that $F = eN_A$ and $R = k_BN_A$. This is the **Einstein relation**, which indicates that the mobility of an ion is proportional to its diffusion coefficient.

The limiting molar conductivity of an ion can now be calculated from its mobility. Consider a section of the system with area A between the two electrodes at a potential difference $\Delta\phi$. In a time interval Δt, all ions in a volume equal to $s\Delta tA$ traverse this section, where s is the drift speed. If the molar concentration is c and each ion carries a charge equal to ze, then the total charge that crosses this section in that time interval is:

$$Q = s\Delta tA \times c \times ze \times N_A = s\Delta tAczF \tag{6.70}$$

where we have used that the definition Faraday constant again ($F = eN_A$). The current intensity is the electrical charge that goes through the section divided by the time interval:

$$I = \frac{Q}{\Delta t} = sAczF \tag{6.71}$$

The conductance (Eq. 6.54) is:

$$G = \frac{I}{V} = \frac{sAczF}{\Delta\phi} \tag{6.72}$$

The conductivity (Eq. 6.55) is:

$$\kappa = \frac{Gl}{A} = \frac{slczF}{\Delta\phi} \tag{6.73}$$

where l is the distance between the electrodes. Finally, the limiting molar conductivity of the ion can be calculated simply as κ/c, since we are not considering interactions between ions:

$$\lambda^\circ = \frac{\kappa}{c} = \frac{slzF}{\Delta\phi} \tag{6.74}$$

This is equivalent to the experimental ionic molar conductivity in the $c \to 0$ limit.

Equation 6.74 can be rewritten by noting that the electric field is $\mathcal{E} = \Delta\phi/l$ and, therefore, the mobility (Eq. 6.65) can be written as:

$$u = \frac{s}{\mathcal{E}} = \frac{sl}{\Delta\phi} \tag{6.75}$$

Substituting this result in Eq. 6.74, we find:

$$\lambda^\circ = zuF \tag{6.76}$$

The limiting molar ionic conductivity is proportional to the mobility and the ionic charge. In a solution of a strong electrolyte that dissociates into ν_+ ions of charge z_+ and ν_- ions of charge z_-, substitution of the limiting molar conductivities into Eq. 6.59 gives:

$$\Lambda_m^\circ = \nu_+\lambda_+^\circ + \nu_-\lambda_-^\circ = (\nu_+z_+u_+ + \nu_-z_-u_-)F \tag{6.77}$$

which is the molar conductivity of a strong electrolyte in the infinite dilution limit.

Finally, using the Einstein relation for the ion mobilities (Eq. 6.69), we can write the limiting molar conductivity of an ion in terms of its diffusion coefficient:

$$\lambda^\circ = zuF = \frac{z^2F^2D}{RT} \tag{6.78}$$

With this, the limiting molar conductivity becomes:

$$\Lambda_m^\circ = \nu_+\lambda_+^\circ + \nu_-\lambda_-^\circ = (\nu_+z_+^2D_+ + \nu_-z_-^2D_-)\frac{F^2}{RT} \tag{6.79}$$

which is known as the **Nernst-Einstein equation**. This equation is used in the experimental determination of ionic diffusion coefficients and in the prediction of conductivities based on diffusion models.

Appendix A

Physical Constants and Energy Conversion Factors

Physical Constants

The following table contains the values for some fundamental physical constants published by the CODATA in 2018. The full list is available online at:
`https://physics.nist.gov/cuu/Constants/Table/allascii.txt`

Electron mass	$m_e = 9.109\,383\,701\,5 \times 10^{-31}\,\mathrm{kg}$
Electron charge	$e = 1.602\,176\,634 \times 10^{-19}\,\mathrm{C}$
Planck constant	$h = 6.626\,070\,15 \times 10^{-34}\,\mathrm{J\,s}$
Reduced Planck constant	$\hbar = h/2\pi = 1.054\,571\,817 \times 10^{-34}\,\mathrm{J\,s}$
Boltzmann constant	$k_B = 1.380\,649 \times 10^{-23}\,\mathrm{J/K}$
Avogadro constant	$N_A = 6.022\,140\,76 \times 10^{23}\,\mathrm{mol^{-1}}$
Molar gas constant	$R = 8.314\,462\,618\,\mathrm{J\,K^{-1}\,mol^{-1}}$
Speed of light in vacuum	$c = 299\,792\,458\,\mathrm{m/s}$
Standard pressure	$p^\circ = 1\,\mathrm{bar} = 100\,000\,\mathrm{Pa}$
Room temperature	$T_{\mathrm{RT}} = 298.15\,\mathrm{K}$

Some useful conversion factors:

J/cal conversion factor	$1\,\mathrm{cal} = 4.184\,\mathrm{J}$
Pressure conversion factor	$1\,\mathrm{atm} = 101\,325\,\mathrm{Pa}$
Temperature conversion	K = °C +273.15
Atomic mass unit conversion	$1\,\mathrm{amu} = 1.660\,539\,066\,60 \times 10^{-27}\,\mathrm{kg}$

Table A.1: List of energy conversion factors. One row unit equals the table value in column units.

	Hartree	eV	cm^{-1}	kcal/mol
Hartree	1	27.211 386 245 988	219 474.631 38	627.509 474 06
eV	0.036 749 322 175 655	1	8065.543 937 95	23.060 547 830
cm^{-1}	$4.556\,335\,252 \times 10^{-6}$	$1.239\,841\,984 \times 10^{-4}$	1	$2.859\,143\,537\,995\,42 \times 10^{-3}$
kcal/mol	$1.593\,601\,437\,6 \times 10^{-3}$	$4.336\,410\,424\,1 \times 10^{-2}$	349.755 088 09	1
kJ/mol	$3.808\,798\,847\,1 \times 10^{-4}$	$1.036\,426\,965\,6 \times 10^{-2}$	83.593 472 297	0.239 005 736 13
J	$2.293\,712\,278\,4 \times 10^{17}$	$6.241\,509\,074\,5 \times 10^{18}$	$5.034\,116\,567\,9 \times 10^{22}$	$1.439\,326\,185\,5 \times 10^{20}$
Hz	$1.519\,829\,846\,0 \times 10^{-16}$	$4.135\,667\,696\,9 \times 10^{-15}$	$3.335\,640\,952\,2 \times 10^{-11}$	$9.537\,076\,273\,6 \times 10^{-14}$
K	$3.166\,811\,563\,5 \times 10^{-6}$	$8.617\,333\,262\,1 \times 10^{-5}$	0.695 034 800 54	$1.987\,204\,258\,6 \times 10^{-3}$

	kJ/mol	J	Hz	K
Hartree	2625.499 639 4	$4.359\,744\,722\,207\,1 \times 10^{-18}$	$6.579\,683\,920\,502 \times 10^{15}$	315 775.024 804 07
eV	96.485 332 123	$1.602\,176\,634 \times 10^{-19}$	$2.417\,989\,242 \times 10^{14}$	$1.160\,451\,812 \times 10^{4}$
cm^{-1}	$1.196\,265\,656\,297\,28 \times 10^{-2}$	$1.986\,445\,857 \times 10^{-23}$	$2.997\,924\,58 \times 10^{10}$	1.438 776 877
kcal/mol	4.184	$6.947\,695\,457\,1 \times 10^{-21}$	$1.048\,539\,375\,5 \times 10^{13}$	503.219 533 499
kJ/mol	1	$1.660\,539\,067\,2 \times 10^{-21}$	$2.506\,069\,253\,1 \times 10^{12}$	120.272 355 04
J	$6.022\,140\,76 \times 10^{20}$	1	$1.509\,190\,179\,6 \times 10^{33}$	$7.242\,970\,516\,0 \times 10^{22}$
Hz	$3.990\,312\,712\,8 \times 10^{-13}$	$6.626\,070\,15 \times 10^{-34}$	1	$4.799\,243\,073\,4 \times 10^{-11}$
K	$8.314\,462\,618\,2 \times 10^{-3}$	$1.380\,649 \times 10^{-23}$	$2.083\,661\,912\,3 \times 10^{10}$	1

Appendix B

Numerical Precision and Least-Squares Fits

Numerical Precision

In scientific writing, the number of significant figures of a number is an expression of our degree of confidence in its precision. Typically, experimental measurements are reported with a number of significant digits corresponding to the resolution of the experimental apparatus and include the uncertainty, calculated from a set of measurements, between parentheses. However, **enough significant figures need to be preserved in the intermediate values when performing numerical calculations**. Not doing so introduces entirely preventable roundoff errors in our calculations, and the final result will be wrong. Digital calculators and computers usually store numbers with a precision of about 14 significant digits. Enough significant figures must be preserved up to the point when the final result is written, at which point the number should be rounded.

Least-Squares Fits

A common mathematical operation in physical chemistry is to fit a straight line to a set of data derived from experimental observations:

$$y = mx + b$$

where m is the slope and b is the intercept. This is usually done by finding the m and b that minimize the sum of the squares of the residuals:

$$S = \sum_i (y_i - mx_i - b)^2$$

where x_i and y_i are the experimental data and the sum runs over data points.

Often, the observed quantities do not follow a linear relationship but can be transformed into one by a suitable change of variable. For instance, the Arrhenius law:

$$k = Ae^{-E_a/RT}$$

can be linearized simply by taking logarithms:

$$\ln k = \ln A - \frac{E_a}{R} \times \frac{1}{T}$$

If the rate constant is measured as a function of temperature, then a plot of $\ln k$ *versus* $1/T$ should be approximately straight. Because of experimental error, the relation is not exactly linear and therefore if we want to find E_a and A, we can do a linear least-squares fit as specified above. However, by doing this, what we actually minimize is:

$$S_{\text{wrong}} = \sum_i (\ln k_i - m\frac{1}{T_i} - b)^2$$

instead of:

$$S_{\text{right}} = \sum_i (k_i - Ae^{-E_a/RT_i})^2$$

which is what we want. In cases where the original expression can be linearized in more than one way (as in the Langmuir isotherm, for instance), this can yield the disconcerting result that different parameters can be obtained from fits using two different linearized forms of the same equation, and there is no way of choosing one over the other.

There are two ways of working around this problem. The first and more appropriate is to conduct a non-linear least-squares fit. This can be done with octave (the `leasqr` function in the `optim` package). This approach minimizes S_{right} above. The drawbacks is that it is more complicated than a linear least-squares fit because there is no analytical solution to this problem in general, so the solution has to be found numerically. Consequently, one must be careful that the parameters are sane once the minimization of S is finished. Several examples of how to do this in `octave` are provided with this TG.

The other way uses linear least-squares fits but where the statistical weights of data point change to reflect the fact that there has been a change of variable. In particular, one could consider a generalized version of the linear least-squares problem where we associate a weight (w_i) to each point:

$$S = \sum_i w_i (y_i - mx_i - b)^2$$

This weight is calculated as the inverse of the square of the uncertainty in the y_i:

$$w_i = \frac{1}{\sigma_i^2}$$

This σ_i can either reflect the inherent uncertainty in our measuring apparatus or can be calculated as the standard deviation of a series of repeated measurements at the same x_i. If we perform a change of variable such that we fit to $y' = f(y)$ instead of y, the uncertainty in the new variable is calculated using:

$$\sigma_{f(y)}^2 = \left(\frac{\partial f}{\partial y}\right)^2 \sigma_y^2$$

For instance, in the case of the linearized Arrhenius equation, we have $y = k$ and $y' = \ln k$, so the uncertainty in the new variable is:

$$\sigma_{\ln k}^2 = \left(\frac{\partial(\ln k)}{\partial k}\right)^2 \sigma_k^2 = \frac{\sigma_k^2}{k^2}$$

If we assume the uncertainties of all the original points are equal (and therefore $w_i = 1$ for all i), then the new statistical weights for the linear least-squares fit are:

$$w_{\ln k,i} = k_i^2$$

Analytical expressions exist for solving weighted linear least-squares optimizations (see references at the end).

Compared to a non-linear least-squares fit, this approach has several downsides. First, this method is not exact, because even with the statistical weights selected as above, the function that is being minimized is not exactly the same as in the non-linear case. However, for small residuals, this approximation is usually quite good. Second, if x also has uncertainty, which is often the case, then a minimization of the residual in y is no longer appropriate. Furthermore, the statistical weights will also depend on the uncertainty in the x. In those cases, there are iterative approaches like the York-Williamson method to perform the minimization. Lastly, and perhaps more importantly, weighted linear least-squares fits are not implemented in Microsoft Excel.

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