PHYSICAL



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This text was compiled on 09/26/2026

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1: SYSTEMS AND VARIABLES

1.1: Thermodynamic Systems
1.2: Thermodynamic Variables

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1.1: Thermodynamic Systems

A thermodynamic system—or just simply a system—is a portion of space with defined boundaries that separate it from its surroundings (see also the title picture of this book). The surroundings may include other thermodynamic systems or physical systems that are not thermodynamic systems. A boundary may be a real physical barrier or a purely notional one. Typical examples of systems are reported in Figure 1.1.1 below. [1]



Figure 1.1.1: Examples of Thermodynamic Systems.

In the first case, a liquid is contained in a typical Erlenmeyer flask. The boundaries of the system are the glass walls of the beaker. The second system is represented by the gas contained in a balloon. The boundary is a physical barrier also in this case, being the plastic of the balloon. The third case is that of a thunder cloud. The boundary is not a well-defined physical barrier, but rather some condition of pressure and chemical composition at the interface between the cloud and the atmosphere. Finally, the fourth case is the case of an open flame. In this case, the boundary is again non-physical, and possibly even harder to define than for a cloud. For example, we can choose to define the flame based on some temperature threshold, color criterion, or even some chemical one. Despite the lack of physical boundaries, the cloud and the flame—as portions of space containing matter—can be defined as a thermodynamic system.

A system can exchange exclusively mass, exclusively energy, or both mass and energy with its surroundings. Depending on the boundaries' ability to transfer these quantities, a system is defined as open, closed, or isolated. An open system exchanges both mass and energy. A closed system exchanges only energy, but not mass. Finally, an isolated system does not exchange mass nor energy.

When a system exchanges mass or energy with its surroundings, some of its parameters (variables) change. For example, if a system loses mass to the surroundings, the number of molecules (or moles) in the system will decrease. Similarly, if a system absorbs some energy, one or more of its variables (such as its temperature) increase. Mass and energy can flow into the system or out of the system. Let's consider mass exchange only. If some molecules of a substance leave the system, and then the same amount of molecules flow back into the system, the system will not be modified. We can count, for example, 100 molecules leaving a system and assign them the value of –100 in an outgoing process, and then observe the same 100 molecules going back into the system and assign them a value of +100. Regardless of the number of molecules present in the system in the first place, the overall balance will be –100 (from the outgoing process) +100 (from the ingoing process) = 0, which brings the system to its initial situation (mass has not changed). However, from a mathematical standpoint, we could have equally assigned the label +100 to the outgoing process and –100 to the ingoing one, and the overall total would have stayed the same: +100–100 = 0. Which of the two labels is best? For this case, it seems natural to define a mass going out of the system as negative (the system is losing it), and a mass going into the system as positive (the system is gaining it), but is it as straightforward for energy?

Table 1.1.1

Type of System	Mass	Energy (either heat or work)
Open	Y	Y
Closed	N	Y
Isolated	N	N

Here is another example. Let's consider a system that is composed of your body. When you exercise, you lose mass in the form of water (sweat) and CO2 (from respiration). This mass loss can be easily measured by stepping on a scale before and after exercise. The number you observe on the scale will go down. Hence you have lost weight. After exercise, you will reintegrate the lost mass by drinking and eating. If you have reinstated the same amount you have lost, your weight will be the same as before the exercise (no weight loss). Nevertheless, which label do you attach to the amounts that you have lost and gained? Let's say that you are running a 5 km race without drinking nor eating, and you measure your weight dropping 2 kg after the race. After the race, you drink 1.5 kg of water and eat a 500 g energy bar. Overall you did not lose any weight, and it would seem reasonable to label the 2 kg that you've lost as negative (–2) and the 1.5 kg of water that you drank and the 500 g bar that you ate as positive (+1.5 +0.5 = +2). But is it the only way? After all, you didn't gain nor lose any weight, so why not calling the 2 kg due to exercise +2 and the 2 that you've ingested as –2? It might seem silly, but mathematically it would not make any difference, the total would still be zero. Now, let's consider energy instead of mass. To run the 5km race, you have spent 500 kcal, which then you reintegrate precisely by eating the energy bar. Which sign would you put in front of the kilocalories that you "burned" during the race? In principle, you've lost them, so if you want to be consistent, you should use a negative sign. But if you think about it, you've put quite an effort to "lose" those kilocalories, so it might not feel bad to assign them a positive sign instead. After all, it's perfectly OK to say, "I've done a 500 kcal run today", while it might sound quite awkward to say, "I've done a –500 kcal run today." Our previous exercise with mass demonstrates that it doesn't really matter which sign you put in front of the quantities. As long as you are consistent throughout the process, the signs will cancel out. If you've done a +500 kcal run, you've eaten a bar for –500 kcal, resulting in a total zero loss/gain. Alternatively, if you've done a –500 kcal run, you would have eaten a +500 kcal bar, for a total of again zero loss/gain.

These simple examples demonstrate that the sign that we assign to quantities that flow through a boundary is arbitrary (i.e., we can define it any way we want, as long as we are always consistent with ourselves). There is no best way to assign those signs. If you ask two different people, you might obtain two different answers. But we are scientists, and we must make sure to be rigorous. For this reason, chemists have established a convention for the signs that we will follow throughout this course. If we are consistent in following the convention, we are guaranteed to never make any mistake with the signs.

Definition: System-centric

The chemistry convention of the sign is system-centric:[2]

- If something (energy or mass) goes into the system it has a positive sign (the system is gaining)
- If something (energy or mass) goes out of the system it has a negative sign (the system is losing)

If you want a trick to remember the convention, use the weight loss/gain during the exercise example above. You are the system, if you lose weight, the kilograms will be negative (–2 kg), while if you gain weight, they will be positive (+2 kg). Similarly, if you eat an energy bar, you are the system, and you will have increased your energy by +500 kcal (positive). In contrast, if you burned energy during exercise, you are the system, and you will have lost energy, hence –500 kcal (negative). If the system is a balloon filled with gas, and the balloon is losing mass, you are the balloon, and you are losing weight; hence the mass will be negative. If the balloon is absorbing heat (likely increasing its temperature and increasing its volume), you are the system, and you are gaining heat; hence heat will be positive.

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1. The photos depicted in this figure are taken from Wikipedia: the Erlenmeyer flasks photo was taken by user Maytouch L., and distributed under CC-BY-SA license; the cloud photo was taken by user Mathew T Rader, and distributed under CC-BY-SA license; the flame picture was taken by user Oscar, and distributed under CC-BY-SA license; the balloon photo is in the public domain.
2. Notice that physicists use a different sign convention when it comes to thermodynamics. To eliminate confusion, I will not describe the physics convention here, but if you are reading thermodynamics on a physics textbook, or if you are browsing

the web and stumble on thermodynamics formula (e.g., on Wikipedia), please be advised that some quantity, such as work, might have a different sign than the one that is used in this textbook. Obviously, the science will not change, but you need to be *always* consistent, so if you decide that you want to use the physics convention, make sure to *always* use the physics convention. In this course, on the other hand, we will *always* use the chemistry one, as introduced above.

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1.2: Thermodynamic Variables

The system is defined and studied using parameters that are called variables. These variables are quantities that we can measure, such as pressure and temperature. However, don't be surprised if, on some occasions, you encounter some variable that is a little harder to measure directly, such as entropy. The variables depend only on the current state of the system, and therefore they define it. If I know the values of all the "relevant variables" of a system, I know the state of the system. The relationship between the variables is described by mathematical functions called state functions, while the "relevant variables" are called natural variables.

What are the "relevant variables" of a system? The answer to this question depends on the system, and it is not always straightforward. The simplest case is the case of an ideal gas, for which the natural variables are those that enter the ideal gas law and the corresponding equation:

$$PV = nRT \tag{1.2.1}$$

Therefore, the natural variables for an ideal gas are the pressure P, the volume V, the number of moles n, and the temperature T, with R being the ideal gas constant. Recalling from the general chemistry courses, R is a universal dimensional constant which has the values of R = 8.31 kJ/mol in SI units.
We will use the ideal gas equation and its variables as an example to discuss variables and functions in this chapter. We will analyze more complicated cases in the next chapters. Variables can be classified according to numerous criteria, each with its advantages and disadvantages. A typical classification is:

- **Physical variables** (P, V, T in the ideal gas law): independent of the chemical composition of the system.
- **Chemical variables** (n in the ideal gas law): dependent on the chemical composition of the system.

Another useful classification is:

- **Intensive variables** (P, T in the ideal gas law): independent of the physical size (extension) of the system.
- **Extensive variables** (V, n in the ideal gas law): dependent on the physical size (extension) of the system.

When we deal with thermodynamic systems, it is more convenient to work with intensive variables. Luckily, it is relatively easy to convert extensive variables into intensive ones by just taking the ratio between the two of them. For an ideal gas, by taking the ratio between V and n, we obtained the intensive variable called molar volume:

$$\overline{V} = \frac{V}{n}. \tag{1.2.2}$$

We can then recast Equation 1.2.1 as:

$$P\overline{V} = RT, \tag{1.2.3}$$

which is the preferred equation that we will use for the remainder of this course. The ideal gas equation connects the 3 variables pressure, molar volume, and temperature, reducing the number of independent variables to just 2. In other words, once 2 of the 3 variables are known, the other one can be easily obtained using these simple relations:

$$P(T, \overline{V}) = \frac{RT}{\overline{V}}, \tag{1.2.4}$$

$$\overline{V}(T, P) = \frac{RT}{P}, \tag{1.2.5}$$

$$T(P, \overline{V}) = \frac{P\overline{V}}{R}. \tag{1.2.6}$$

These equations define three state functions, each one expressed in terms of two independent natural variables. For example, Equation 1.2.4 defines the state function called "pressure", expressed as a function of temperature and molar volume. Similarly, Equation 1.2.5 defines the "molar volume" as a function of temperature and pressure, and Equation 1.2.6 defines the "temperature" as a function of pressure and molar volume. When we know the natural variables that define a state function, we

can express the function using its total differential, for example for the pressure $P(T, \overline{V})$:

$$dP = \left(\frac{\partial P}{\partial T}\right) dT + \left(\frac{\partial P}{\partial \overline{V}}\right) d\overline{V} \tag{1.2.7}$$

Recalling Schwartz's theorem, the mixed partial second derivatives that can be obtained from Equation 1.2.7 are the same:

$$\frac{\partial^2 P}{\partial T \partial \overline{V}} = \frac{\partial}{\partial \overline{V}} \frac{\partial P}{\partial T} = \frac{\partial}{\partial T} \frac{\partial P}{\partial \overline{V}} = \frac{\partial^2 P}{\partial \overline{V} \partial T} \tag{1.2.8}$$

Which can be easily verified considering that:

$$\frac{\partial}{\partial \overline{V}} \frac{\partial P}{\partial T} = \frac{\partial}{\partial \overline{V}} \left(\frac{R}{\overline{V}}\right) = -\frac{R}{\overline{V}^2} \tag{1.2.9}$$

and

$$\frac{\partial}{\partial T} \frac{\partial P}{\partial \overline{V}} = \frac{\partial}{\partial T} \left(\frac{-RT}{\overline{V}^2}\right) = -\frac{R}{\overline{V}^2} \tag{1.2.10}$$

While for the ideal gas law, all the variables are "well-behaved" and always satisfy Schwartz's theorem, we will encounter some variable for which Schwartz's theorem does not hold. Mathematically, if the Schwartz's theorem is violated (i.e., if the mixed second derivatives are not equal), then the corresponding function cannot be integrated, hence it is not a state function. The differential of a function that cannot be integrated cannot be defined exactly. Thus, these functions are called path functions; that is, they depend on the path rather than the state. The most typical examples of path functions that we will encounter in the next chapters are heat (Q) and work (W). For these functions, we cannot define exact differentials dQ and dW, and we must introduce a new notation to define their "inexact differentials" $đQ$ and $đW$.

We will return to exact and inexact differential when we discuss heat and work, but for this chapter, it is crucial to notice the difference between a state function and a path function. A typical example to understand the difference between state and path function is to consider the distance between two geographical locations. Let's, for example, consider the distance between New York City and Los Angeles. If we fly straight from one city to the other, there are roughly 4,000 km between them. This "air distance" depends exclusively on the geographical location of the two cities. It stays constant regardless of the method of transportation that I have accessibility to travel between them. Since the cities' positions depend uniquely on their latitudes and longitudes, the "air distance" is a state function, i.e., it is uniquely defined from a simple relationship between measurable variables. However, the "air distance" is not the distance that I will practically have to drive when I go from NYC to LA. Such "travel distance" depends on the method of transportation that I decide to take (airplane vs. car vs. train vs. boat vs. ...). It will depend on a plentiful amount of other factors such as the choice of the road to be traveled (if going by car), the atmospheric conditions (if flying), and so on. A typical "travel distance" by car is, for example, about 4,500 km, which is about 12% more than the "air distance." Indeed, we could even design a very inefficient road trip that avoids all highways and will result in a "travel distance" of 8,000 km or even more (200% of the "air distance"). The "travel distance" is a clear example of a path function because it depends on the specific path that I decide to travel to go from NYC to LA. See Figure 1.2.1.



Figure 1.2.1: State Functions vs. Path Functions.

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2: ZEROTH LAW OF THERMODYNAMICS

2.1: What is Thermodynamics?
2.2: The Zeroth Law of Thermodynamics
2.3: Calculation of Heat
2.4: Calculation of Work

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2.1: What is Thermodynamics?

Thermodynamics is the branch of science that deals with heat and work, and their relation to energy. As the definition suggests, thermodynamics is concerned with two types of energy: heat and work. A formal definition of these forms of energy is as follow:

- Work is exchanged if external parameters are changed during the process.
- Heat is exchanged if only internal parameters are changed during the process.

As we saw in chapter 1, heat and work are not "well-behaved" quantities because they are path functions. On the one hand, it might be simple to measure the amount of heat and/or work experimentally, these measured quantities cannot be used to define the state of a system. Since heat and work are path functions, their values depend directly on the methods used to transfer them (their paths). Understanding and quantifying these energy transfers is the reason why thermodynamics was developed in the first place. The origin of thermodynamics dates back to the seventeenth century when people began to use heat and work for technological applications. These early scientists needed a mathematical tool to understand how heat and work were related to each other, and how they were related to the other variables that they were able to measure, such as temperature and volume.

Before we even discuss the definition of energy and how it relates to heat and work, it is crucial to introduce the essential concept of temperature. Temperature is an intuitive concept that has a surprisingly complex definition at the microscopic level. [1] However, for all our purposes, it is not essential to have a microscopic definition of temperature, as long as we have the guarantee that this quantity can be measured unambiguously. In other words, we only need a mathematical definition of temperature that agrees with the physical existence of thermometers.

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1. In fact, we will not even give a rigorous microscopic definition of temperature within this textbook.

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2.2: The Zeroth Law of Thermodynamics

The mathematical definition that guarantees that thermal equilibrium is an equivalence relation is called the zeroth law of thermodynamics. The zeroth law of thermodynamics states that if two thermodynamic systems are each in thermal equilibrium with a third one, then they are in thermal equilibrium with each other. The law might appear trivial and possibly redundant, but it is a fundamental requirement for the mathematical formulation of thermodynamics, so it needs to be stated. The zeroth law can be summarized by the following simple mathematical relation:

Definition: Zeroth Law of Thermodynamics

If $T_A = T_B$, and $T_B = T_C$, then $T_A = T_C$.

Notice that when we state the zeroth law, it appears intuitive. However, this is not necessarily the case. Let's, for example, consider a pot of boiling water at $P = 1 \text{ bar}$. Its temperature, T_{H_2O}, is about 373 K. Let's now submerge in this water a coin made of wood and another coin made of metal. After some sufficient time, the wood coin will be in thermal equilibrium with the water, and its temperature $T_W = T_{H_2O}$. Similarly, the metal coin will also be in thermal equilibrium with the water, hence $T_M = T_{H_2O}$. According to the zeroth law, the temperature of the wood coin and that of the metal coin are precisely the same $T_W = T_M = 373 \text{ K}$, even if they are not in direct contact with each other. Now here's the catch: since wood and metal transmit heat in different manners if I take the coins out of the water and put them immediately in your hands, one of them will be very hot, but the other will burn you. If you had to guess the temperature of the two coins without a thermometer, and without knowing that they were immersed in boiling water, would you suppose that they have the same temperature? Probably not.

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2.3: Calculation of Heat

Heat (Q) is a property that gets transferred between substances. Similarly to work, the amount of heat that flows through a boundary can be measured, but its mathematical treatment is complicated because *heat is a path function*. As you probably recall from general chemistry, the ability of a substance to absorb heat is given by a coefficient called the heat capacity, which is measured in SI in $\frac{\mathrm{J}}{\mathrm{mol\ K}}$. However, since heat is a path function, these coefficients are not unique, and we have different ones depending on how the heat transfer happens.

Processes at constant volume (isochoric)

The heat capacity at constant volume measures the ability of a substance to absorb heat at constant volume. Recasting from general chemistry:

The molar heat capacity at constant volume is the amount of heat required to increase the temperature of 1 mol of a substance by 1 K at constant volume.

This simple definition can be written in mathematical terms as:

$$C_V = \frac{đQ_V}{ndT} \Rightarrow đQ_V = nC_V dT. \tag{2.3.1}$$

Given a known value of C_V, the amount of heat that gets transfered can be easily calculated by measuring the changes in temperature, after integration of Equation \ref{2.3.1:

$$đQ_V = nC_V dT \rightarrow \int đQ_V = n\int_{T_i}^{T_F} C_V dT \rightarrow Q_V = nC_V \int_{T_i}^{T_F} dT, \tag{2.3.2}$$

which, assuming C_V independent of temperature, simply becomes:

$$Q_V \cong nC_V \Delta T. \tag{2.3.3}$$

Processes at constant pressure (isobaric)

Similarly to the previous case, the heat capacity at constant pressure measures the ability of a substance to absorb heat at constant pressure. Recasting again from general chemistry:

The molar heat capacity at constant pressure is the amount of heat required to increase the temperature of 1 mol of a substance by 1 K at constant pressure.

And once again, this mathematical treatment follows:

$$C_P = \frac{đQ_P}{ndT} \Rightarrow đQ_P = nC_P dT \rightarrow \int đQ_P = n\int_{T_i}^{T_F} C_P dT, \tag{2.3.4}$$

which result in the simple formula:

$$Q_P \cong nC_P \Delta T. \tag{2.3.5}$$

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2.4: Calculation of Work

In thermodynamics, work (W) is the ability of a system to transfer energy by exerting a force on its surroundings. Work can be measured simply by evaluating its effects, such as displacing a massive object by some amount of space. The mathematical treatment of work, however, is complicated because *work is a path function*. In the following sections, we will analyze how work is calculated in some prototypical situations commonly encountered in the thermodynamical treatment of systems.

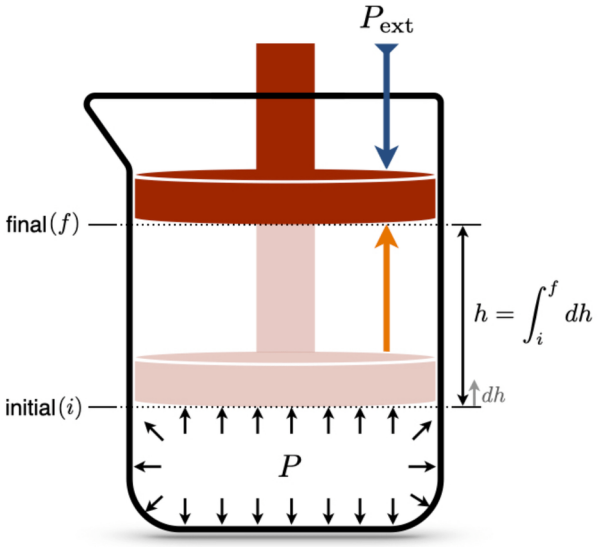


Figure 2.4.1: Isothermal Expansion of an Ideal Gas Against a Constant External Pressure.

Let's consider the situation in Figure 2.4.1, where a special beaker with a piston that is free to move is filled with an ideal gas. The beaker sits on a desk, so the piston is not subject to any external forces other than the external pressure, P_{ext}, and the internal pressure of the gas, P. [1] The piston is initially compressed to a position that is not in equilibrium (i). After the process, the piston reaches a final equilibrium position (f). How do we calculate the work (W) performed by the system?

From basic physics, we recall that the infinitesimal amount of work associated with an object moving in space is given by the force acting on the object (F) multiplied by the infinitesimal amount it gets displaced (dh):

$$đW = -Fdh, \tag{2.4.1}$$

where the negative sign comes from the chemistry sign convention, Definition: System-centric, since the work in Figure 2.4.1 is *performed* by the system (expansion). What kind of force is moving the piston? It is the force due to the pressure of the gas. Relying upon another definition from physics, the pressure is the ratio between the force (F) and the area (A) that such force acts upon:

$$P = F/A. \tag{2.4.2}$$

Obtaining F from Equation 2.4.2 and replacing it in Equation 2.4.1, we obtain:

$$đW = -P\underbrace{Adh}_{dV}, \tag{2.4.3}$$

and considering that Adh (area times infinitesimal height) is the definition of an infinitesimal volume dV, we obtain:

$$đW = -PdV, \tag{2.4.4}$$

If we want to calculate the amount of work performed by a system, W, from Equation 2.4.4, we need to recall that $đW$ is an inexact differential. As such, we cannot integrate it from initial to final as for the (exact) differential of a state function, because:

$$\int_i^f đW \neq W_f - W_i, \tag{2.4.5}$$

but rather:

$$\int_{\text{path}} đW = W, \tag{2.4.6}$$

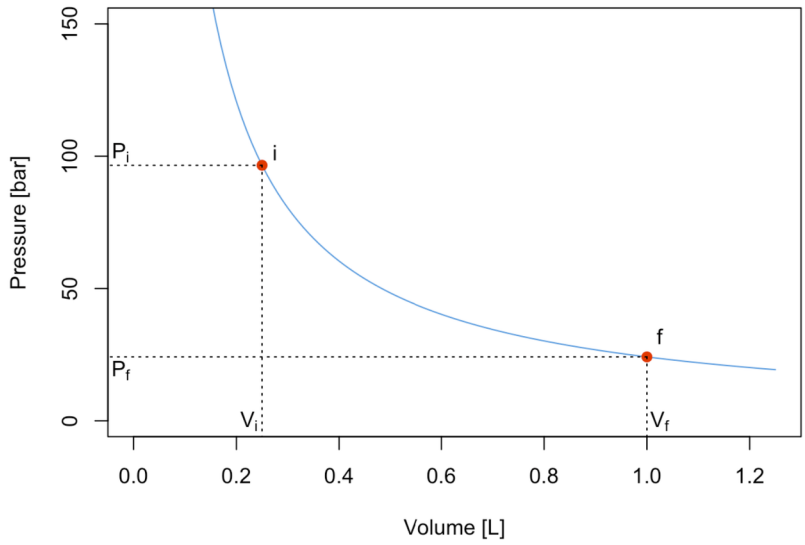
where the integration is performed along the *path*. Using Equation 2.4.6, we can integrate Equation 2.4.4 as:

$$\int đW = W = -\int_i^f PdV, \tag{2.4.7}$$

where the integral on the left-hand side is taken along the path,[2] while the integral on the right-hand side can be taken between the initial and final states, since dV is a state function. How do we solve the integral in Equation 2.4.7? It turns out that there are many different ways to solve this integral (perhaps not surprisingly, since the left-hand side depends on the path), which we will explore in the next section.

$|W_{\text{max}}|$ and $|W_{\text{min}}|$ in processes at constant temperature (isothermal)

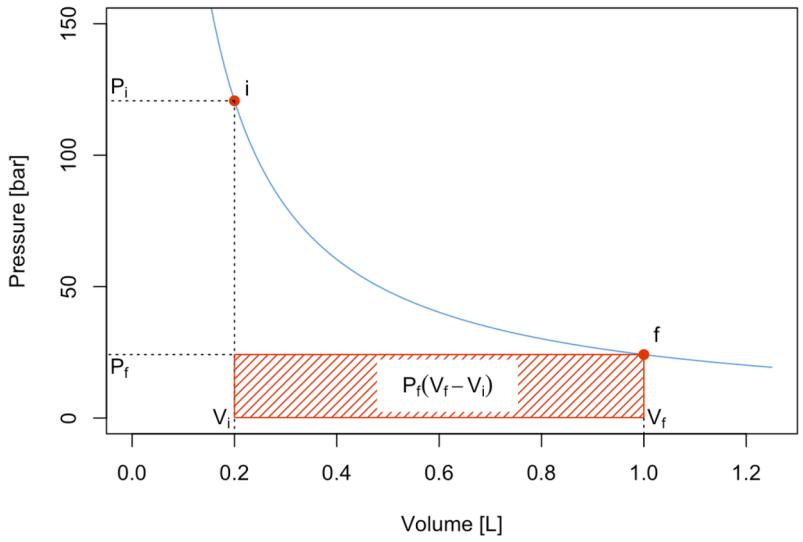
At constant temperature, the piston in Figure 2.4.1 moves along the following PV diagram (this curve is obtained from an ideal gas at constant $T = 298$ K):



An expansion of the gas will happen between P_i and P_f. If the expansion happens in a one-step fast process, for example against external atmospheric pressure, then we can consider such final pressure constant (for example $P_f = P_{\text{ext}} = 1$ bar), and solve the integral as:

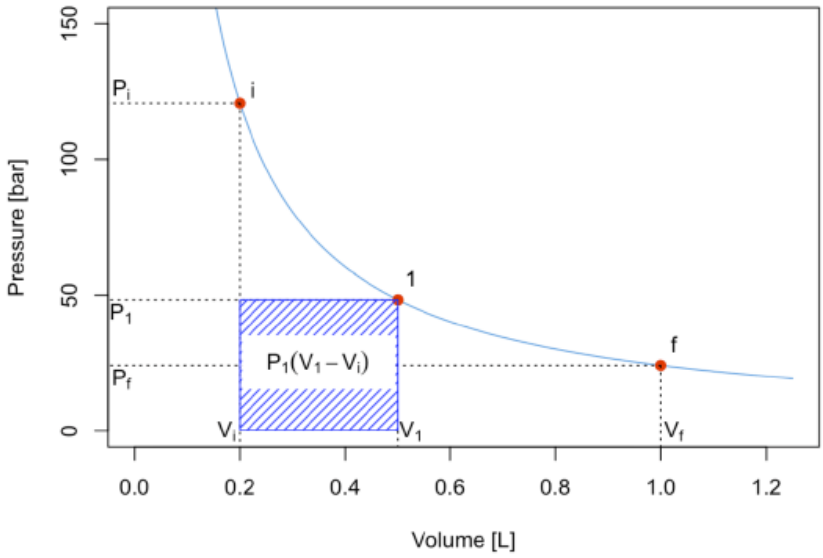
$$W_{\text{1-step}} = -\int_i^f P_{\text{ext}} dV = -P_{\text{ext}} \int_i^f dV = -P_{\text{ext}}(V_f - V_i), \tag{2.4.8}$$

Notice how the work is negative, since during an expansion the work is performed by the system (recall the chemistry sign convention). The absolute value of the work[3] represents the red area of the PV-diagram:



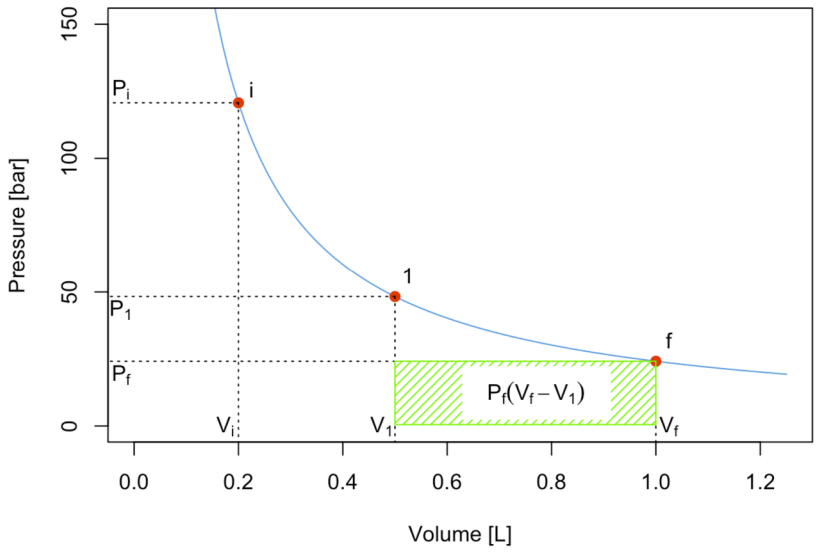
$$|W_{\text{1-step}}| = P_{\text{ext}}(V_f - V_i) \tag{2.4.9}$$

If the process happens in two steps by pausing at an intermediate position (1) until equilibrium is reached, then we should calculate the work by dividing it into two separate processes, A and B, and solve each one as we did in the previous case. The first process is an expansion between P_i and P_1, with P_1 constant. The absolute value of the work, W_A, is represented by the blue area:



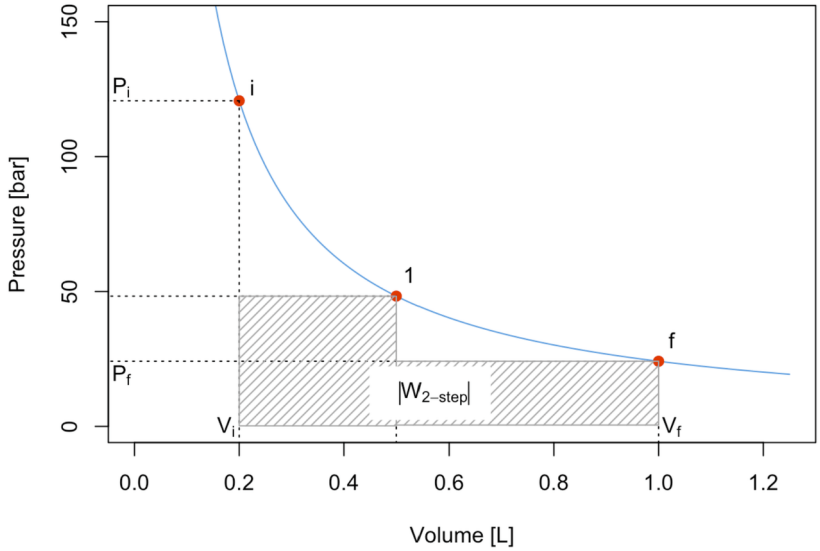
$$|W_A| = P_1(V_1 - V_i) \tag{2.4.10}$$

The second process is an expansion between P_1 and P_f, with $P_f = P_{\text{ext}}$ constant. The absolute value of the work for this second process is represented by the green area:



$$|W_B| = P_f(V_f - V_1) \tag{2.4.11}$$

The total absolute value of the work for the 2-step process is given by the sum of the two areas:

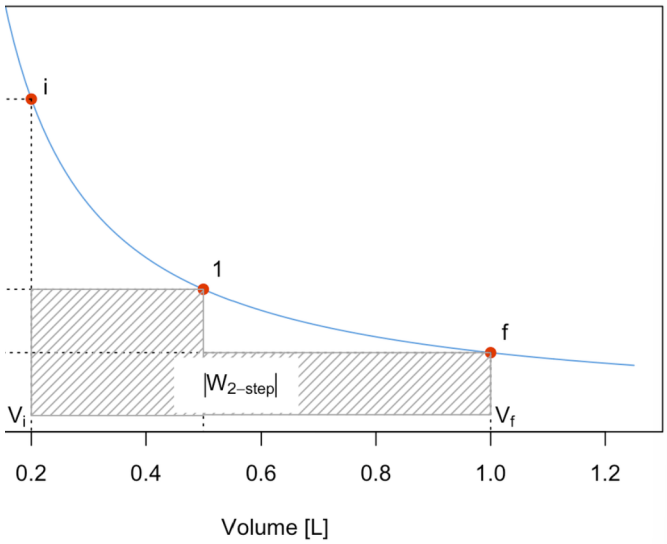


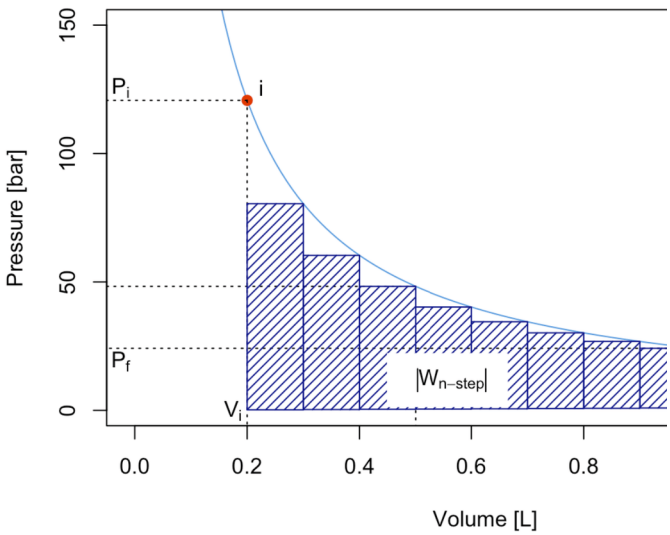
$$|W_{2\text{-step}}| = |W_A| + |W_B| = P_1(V_1 - V_i) + P_f(V_f - V_1). \tag{2.4.12}$$

As can be easily verified by comparing the shaded areas in the plots, $|W_{2\text{-step}}| > |W_{1\text{-step}}|$.

We can easily extend this procedure to consider processes that happens in 3, 4, 5, ..., n steps. What is the limit of this procedure? In other words, what happens when $n \to \infty$? A simple answer is given by the plots in the next Figure, which clearly demonstrates that the maximum value of the area underneath the curve $|W_{\max}|$ is achieved in an ∞-step process, for which the work is calculated as:

$$|W_{\infty\text{-step}}| = |W_{\max}| = \sum_{n}^{\infty} P_n(V_n - V_{n-1}) = \int_i^f P dV. \tag{2.4.13}$$





The integral on the right hand side of Equation 2.4.13 can be solved for an ideal gas by calculating the pressure using the ideal gas law $P = \frac{nRT}{V}$, and solving the integral since n, R, and T are constant:

$$|W_{\max}| = nRT \int_i^f \frac{dV}{V} = nRT \ln \frac{V_f}{V_i}. \tag{2.4.14}$$

This example demonstrates why work is a path function. If we perform a fast 1-step expansion, the system will perform an amount of work that is much smaller than the amount of work it can perform if the expansion between the same points happens slowly in an ∞-step process.

The same considerations that we made up to this point for expansion processes hold specularly for compression ones. The only difference is that the work associated with compressions will have a positive sign since it must be performed onto the system. As such, the amount of work for a transformation that happens in a finite amount of steps will be an upper bound to the minimum amount of work required to compress the system.[4] $|W_{\min}|$ for compressions is calculated as the area underneath the PV curve, exactly as $|W_{\min}|$ for expansions in Equation 2.4.13.

---

1. For this simple thought experiment, we will ignore any external force that is not significant. In other words, we will not consider the friction of the piston on the beaker walls or any other foreign influence.
2. from here on we will replace the notation $\int_{\text{path}}$ with the more convenient $\int$ and we will keep in mind that the integral of an inexact differential must be taken along the path.
3. we use the absolute value to avoid confusions due to the fact that the expansion work is negative according to Definition: System-centric.
4. In contrast to a lower bound for expansion processes.

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3: FIRST LAW OF THERMODYNAMICS

3.1: Calculation of Internal Energy Changes
3.2: The First Law of Thermodynamics
3.3: Reversible and Irreversible Processes

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3.1: Calculation of Internal Energy Changes

The internal energy (U) of a system is a thermodynamic state function defined as:

Definition: Internal Energy

Property of a system that can be either transferred or converted.

In the absence of chemical transformations, heat and work are the only two forms of energy that thermodynamics is concerned with. Keeping in mind Definition: System-Centric, which gives the convention for the signs of heat and work, the internal energy of a system can be written as:

$$U = Q + W, \tag{3.1.1}$$

which we can write in differential form by considering that the internal energy is a state function, as:

$$dU = đQ + đW, \tag{3.1.2}$$

which, using eq. 2.4.4 becomes:

$$dU = đQ - PdV. \tag{3.1.3}$$

Internal energy in isothermal processes

To study the behavior of the internal energy in a process at constant temperature ($dT = 0$), James Prescott Joule (1818–1889) created the apparatus depicted in Figure 3.1.1.

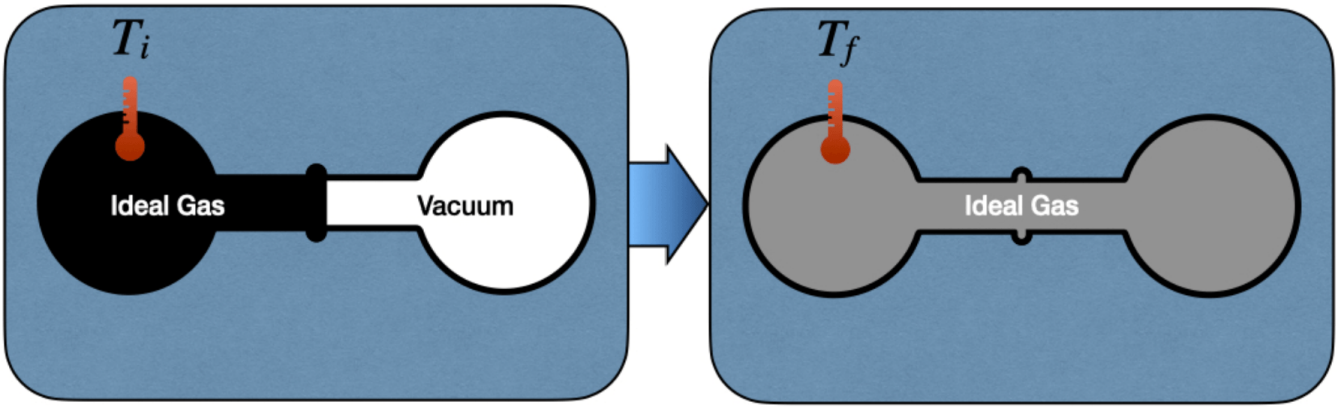


Figure 3.1.1: The Joule Expansion Experiment.

The left side of the Joule apparatus's inner chamber is filled with an ideal gas, while a vacuum is created in the right chamber. Both chambers are immersed in a water bath, to guarantee isolation from the environment. When the communication channel between the chambers is open, the gas expands and equilibrates. The work associated with the transformation is:

$$đW = -P_{\text{ext}}dV = 0, \tag{3.1.4}$$

since the chambers are not in communication with the environment, $P_{\text{ext}} = 0$. Thus, changes in internal energy are associated with the heat transfer of the process, which can be measured by monitoring the temperature of the gas at the beginning, T_i, and at the end of the experiment T_f. Joule noticed experimentally that if he used an ideal gas for this experiment, the temperature would not change $T_i = T_f$. Since the temperature doesn't change, there is no heat transfer, and therefore the internal energy stays constant:

$$dU = đQ = 0. \tag{3.1.5}$$

Note

Notice that Joule's conclusion is valid only for an ideal gas. If we expand a real gas, we do notice a change in temperature associated with the expansion. A typical example of this behavior is when you use a pressurized spray bottle and release its content for an extended time in the air. The container will typically get colder. We will discuss this behavior in chapter 11 when we will study non-ideal gases.

From this simple experiment, we can conclude that the internal energy of an ideal gas depends only on its temperature.

Internal energy in adiabatic processes

An adiabatic process is defined as a process that happens without the exchange of heat. As such, $đQ = 0$, and the work associated with an adiabatic process becomes a state function:

$$dU = đW = -PdV, \tag{3.1.6}$$

which can then be calculated using the formulas that we derived in section 2.4. Notice that isothermal and adiabatic are two very different processes. While an adiabatic process happens without the exchange of heat across the system's boundaries, this does not mean that the system's temperature does not change. Isothermal processes are usually associated with a heat transfer across the boundaries to maintain the temperature of the system constant. For adiabatic processes, it is quite the opposite since they are usually associated with a change in temperature.

Internal energy in isochoric processes

An isochoric process is a process in which the volume does not change. Therefore, $đW = 0$, and $dU = đQ_V$, which using Equation 2.3.1, becomes:

$$dU = đQ_V = nC_V dT. \tag{3.1.7}$$

Since no work is performed at these conditions, the heat becomes a state function. Equation 3.1.7 also gives a mathematical justification of the concept of heat capacity at constant volume. C_V can now be interpreted as the partial derivative (a coefficient) of a state function (the internal energy):

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{V,n=1}, \tag{3.1.8}$$

where we have replaced the total derivative d with a partial one ∂, and we have specified that the derivation happens at constant volume and number of moles. Equation 3.1.8 equation brings a rigorous definition of heat capacity at constant volume for 1 mol of substance:

Definition: Heat Capacity

The heat capacity of a substance, C_V, represents its ability to absorb energy at constant volume.

Internal energy in isobaric processes

In an isobaric process, the pressure does not change, hence $dP = 0$. Unfortunately, Equation 3.1.2 for this case does not simplify further, as happened in the two previous cases. However, in section 2.3, we have introduced the useful concept of heat capacity at constant P. C_P was used in an adiabatic process in the same manner as C_V was used in the isochoric case. That is, as a coefficient to measure the amount of heat absorbed at constant pressure. Equation 3.1.8 gave a mathematical definition of C_V as the partial derivative of a state function (the internal energy). But if heat capacities are coefficients, and coefficients are partial derivatives of state functions, how do we explain C_P? In order to do so, we can introduce a new state function, called the enthalpy

(H), as:

$$H = U + PV, \tag{3.1.9}$$

and its differential, calculated as:

$$dH = dU + d(PV) = dU + PdV + \overbrace{VdP}^{0}, \tag{3.1.10}$$

which can be rearranged as:

$$dU = dH - PdV, \tag{3.1.11}$$

Replacing Equation 3.1.11 into Equation 3.1.3:

$$dH - PdV = đQ_P - PdV, \tag{3.1.12}$$

which simplifies to:

$$dH = đQ_P. \tag{3.1.13}$$

Equation 3.1.13 establishes that the heat exchanged at constant pressure is equal to a new state function called the enthalpy, defined by Equation 3.1.9. It also establishes a mathematical justification of the concept of heat capacity at constant pressure. Similarly to C_V, C_P can now be interpreted as the partial derivative (a coefficient) of the new state function (the enthalpy):

$$C_P = \left(\frac{\partial H}{\partial T}\right)_{P,n=1}, \tag{3.1.14}$$

Equation 3.1.14 brings also a rigorous definition of heat capacity at constant pressure for 1 mol of substance:

Definition: Heat Capacity

The heat capacity of a substance, C_P, represents its ability to absorb enthalpy at constant pressure.

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3.2: The First Law of Thermodynamics

We finally come to a working definition of the first law. If we take an isolated system—i.e., a system that does not exchange heat nor mass with its surroundings—its internal energy is conserved. If the internal energy is conserved, $dU = 0$. Therefore, for an isolated system:

$$đQ = -đW,$$

and heat and work can be easily calculated using any of the appropriate formulas introduced in either section 2.4 or 2.3.

The first law is a conservation law. It is intuitive since it comes directly from Lavoisier's principle of "nothing is lost, nothing is created, everything is transformed." Considering that the only system that is truly isolated is the universe, we can condense the first law in one simple sentence:

Definition: First Law of Thermodynamics

First Law of Thermodynamics: The energy of the universe is conserved.

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3.3: Reversible and Irreversible Processes

Let's now consider the cycle in Figure 3.3.1. The process in this case starts from state 1 (system at P_1V_1), expands to state 2 (system at P_2V_2), and compresses back to state 1 (system back to P_1V_1).

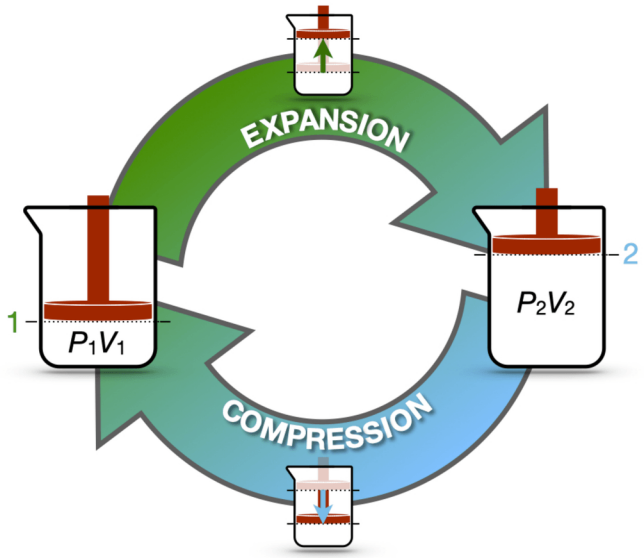


Figure 3.3.1: Expansion/Compression Cycle of an Ideal Gas.

Since the process starts and finishes at the same state, the value of the internal energy at the end of the process will be the same as its value at the beginning, regardless of the path:[1]

$$\oint dU = 0, \tag{3.3.1}$$

where the symbol $\oint$ indicates an integral around a cycle. Considering the work associated with the cycle, however, the situation is radically different because it depends on the path that the system is taking, and in general

$$\oint_{\text{path}} đW \neq 0. \tag{3.3.2}$$

For instance, if we perform the expansion in one step, the work associated with it will be (using Equation 3.3.8):[2]

$$W_{\text{1-step}}^{\text{expansion}} = -P_2(\underbrace{V_2 - V_1}_{>0}) < 0, \tag{3.3.3}$$

and if we also perform the compression in 1-step: [3]

$$W_{\text{1-step}}^{\text{compression}} = -P_1(\underbrace{V_1 - V_2}_{<0}) > 0. \tag{3.3.4}$$

With a little bit of math, it is easy to prove that the total work for the entire cycle is:

$$\begin{aligned} W_{\text{1-step}}^{\text{cycle}} &= W_{\text{1-step}}^{\text{expansion}} + W_{\text{1-step}}^{\text{compression}} \\ &= -P_2(V_2 - V_1) - P_1(V_1 - V_2) \\ &= -P_2(V_2 - V_1) + P_1(V_2 - V_1) \\ &= (\underbrace{V_2 - V_1}_{>0})(\underbrace{P_1 - P_2}_{>0}) > 0, \end{aligned} \tag{3.3.5}$$

or, in other words, net work is destroyed.

Note

In practice, if we want to manually perform this cycle by pushing on the piston by hand, we will notice that it requires more energy to push down than the amount it gives back when we release it, and it moves back up.

In contrast, if both the expansion and the compression happen in a slow ∞-step manner, the work associated with them will be W_{max} and W_{min}, respectively, which are calculated using Equation 3.3.14. The total work related with the cycle will be in this case:

$$\begin{aligned} W_{\infty\text{-step}}^{\text{cycle}} &= W_{\text{max}}^{\text{expansion}} + W_{\text{min}}^{\text{compression}} \\ &= -nRT \ln \frac{V_f}{V_i} - nRT \ln \frac{V_i}{V_f} \\ &= -nRT \underbrace{\left(\ln \frac{V_f}{V_i} - \ln \frac{V_f}{V_i} \right)}_{=0} = 0, \end{aligned} \tag{3.3.6}$$

which means that, in this case, work is not destroyed nor created.

Note

In practice, if we were able to perform this cycle manually by pushing on the piston down by hand, we will notice that it requires the same amount of energy to push down than the amount it gives back when it moves up.

This process can happen both ways without losses, and is called *reversible*:

Definition: Reversible Process

Reversible Process: a process whose direction can be returned to its original position by inducing infinitesimal changes to some property of the system via its surroundings.[4]

Reversible processes are ideal processes that are hard to realize in practice since they require transformations that happen in an infinite amount of steps (infinitely slowly).

---

1. recall that the internal energy is a state function, so its value depends exclusively from the conditions at the beginning and at the end. In a cycle, we're going back to the same point, so the conditions at the beginning and at the end are equal by definition.
2. notice that the work for the expansion is negative, as it should be.
3. notice that the work for the compression is positive, as it should be.
4. Definition from: Sears, F.W. and Salinger, G.L. (1986), Thermodynamics, Kinetic Theory, and Statistical Thermodynamics, 3rd edition (Addison-Wesley.)

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4: THERMOCHEMISTRY

4.1: Reaction Enthalpies

4.2: Standard Enthalpies of Formation

4.3: Hess's Law

4.4: Calculations of Enthalpies of Reaction at T ≠ 298 K

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4.1: Reaction Enthalpies

In chapter 3, we have discussed thermodynamical changes in energy in the absence of chemical reactions. When a chemical reaction takes place, some bonds break and/or some new one form. This process either absorbs or releases the energy contained in these bonds. For a proper thermodynamic treatment of the system, this extra energy must be included in the net balance.

In this chapter, we will consider the heat associated with chemical reactions. Since most chemical reactions happen at constant atmospheric pressure (isobaric conditions) in the lab, we can use eq. 3.1.13 to replace the inexact differential of the heat with the exact differential of the state function called enthalpy. The advantage of this transformation is that it allows us to study the heat associated with chemical reactions at constant pressure independently of their path. If we call the molecules at the beginning of the reaction "reactants" and the molecules at the end of the reaction "products," the heat associated with the reaction (rxn) is defined as:

$$\Delta_{\text{rxn}}H = H_{\text{products}} - H_{\text{reactants}} \ .$$

For example, if we take a simple reaction of the form:

$$\text{A} + \text{B} \rightarrow \text{C} + \text{D},$$

the heat at constant pressure is equal to the enthalpy of reaction, which is calculated as:

$$Q_P = \Delta_{\text{rxn}}H = \underbrace{(H_{\text{C}} + H_{\text{D}})}_{\text{products}} - \underbrace{(H_{\text{A}} + H_{\text{B}})}_{\text{reactants}} . \tag{4.1.1}$$

Using the chemistry sign convention, Definition: System-centric, reactions are classified in terms of the sign of their reaction enthalpies as follows:

Definition: Signs of Reaction Enthalpies

$\Delta_{\text{rxn}}H > 0 \Rightarrow$ Endothermic reaction (heat is gained by the system).
$\Delta_{\text{rxn}}H < 0 \Rightarrow$ Exothermic reaction (heat is lost by the system).

If we expand the sample reaction to account for its stoichiometry:

$$a\text{A} + b\text{B} \rightarrow c\text{C} + d\text{D} \ ,$$

where a, b, c, d are the stoichiometric coefficients of species $\text{A}, \text{B}, \text{C}, \text{D}$. Equation 4.1.1 can be rewritten as:

$$Q_P = \Delta_{\text{rxn}}H = \underbrace{(cH_{\text{C}} + dH_{\text{D}})}_{\text{products}} - \underbrace{(aH_{\text{A}} + bH_{\text{B}})}_{\text{reactants}}, \tag{4.1.2}$$

while for the most general case we can write it:

$$\Delta_{\text{rxn}}H = \sum_i \nu_i H_i,$$

where ν_i is the stoichiometric coefficient of species i with its own sign. The signs of the stoichiometric are defined according to Equation 4.1.2 as:

Definition: Signs of the stoichiometric coefficients

ν_i is positive if i is a product.
ν_i is negative if i is a reactant.

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4.2: Standard Enthalpies of Formation

In principle, we could use eq. 4.1.3 to calculate the reaction enthalpy associated with any reaction. However, to do so, the absolute enthalpies H_i of reactants and products would be required. Unfortunately, absolute enthalpies are not known—and theoretically unknowable, since this would require an absolute zero for the enthalpy scale, which does not exist.[1] To prevent this problem, enthalpies relative to a defined reference state must be used. This reference state is defined at the constituent elements in their standard state, and the enthalpies of 1 mol of substance in this reference state are called **standard enthalpies of formation**.

Definition: Standard Enthalpy of Formation

The standard enthalpy of formation of compound i, $\Delta_\mathrm{f}H_i^\ominus$, is the change of enthalpy during the formation of 1 mol of i from its constituent elements, with all substances in their standard states.

The standard pressure is defined at $P^\ominus = 100\ \mathrm{kPa} = 1\ \mathrm{bar}$.[2] There is no standard temperature, but standard enthalpies of formation are usually reported at room temperature, $T = 298.15\ \mathrm{K}$. Standard states are indicated with the symbol $^\ominus$ and they are defined for elements as the form in which such element is most stable at standard pressure (for example, for hydrogen, carbon, and oxygen the standard states are $\mathrm{H}_{2(g)}, \mathrm{C}_{(s,\mathrm{graphite})}, \mathrm{and}\ \mathrm{O}_{2(g)}$, respectively).[3]

For example, the standard enthalpies of formation of some common compounds at $T = 298.15\ \mathrm{K}$ are calculated from the following reactions:

$$\begin{aligned} \mathrm{C}_{(s,\mathrm{graphite})} + \mathrm{O}_{2(g)} &\rightarrow \mathrm{CO}_{2(g)} \qquad & \Delta_\mathrm{f}H^\ominus_{\mathrm{CO}_{2(g)}} &= -394\ \mathrm{kJ/mol} \\ \mathrm{C}_{(s,\mathrm{graphite})} + 2\mathrm{H}_{2(g)} &\rightarrow \mathrm{CH}_{4(g)} \qquad & \Delta_\mathrm{f}H^\ominus_{\mathrm{CH}_{4(g)}} &= -75\ \mathrm{kJ/mol} \\ \mathrm{H}_{2(g)} + \frac{1}{2}\mathrm{O}_{2(g)} &\rightarrow \mathrm{H_2O}_{(l)} \qquad & \Delta_\mathrm{f}H^\ominus_{\mathrm{H_2O}_{(l)}} &= -286\ \mathrm{kJ/mol} \end{aligned} \tag{4.2.1}$$

A comprehensive list of standard enthalpies of formation of inorganic and organic compounds is also reported in appendix 16.

---

1. An example of a known absolute zero for a scale is the zero of the temperature scale, a temperature that can be approached only as a limit from above. No such thing exists for the enthalpy.
2. prior to 1982 the value of $P^\ominus = 1.0\mathrm{atm}$ was used. The two values of $P^\ominus$ are within 1% of each other, since 1 atm = 101.325 kPa.
3. There are some exception, such as phosphorus, for which the most stable form at 1 bar is black phosphorus, but white phosphorus is chosen as the standard reference state for zero enthalpy of formation. For the purposes of this course, however, we can safely ignore them.

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4.3: Hess's Law

The calculation of a standard reaction enthalpy can be performed using the following cycle:

$$\begin{array}{ccc} \text{reactants} & \xrightarrow{\Delta_{\text{rxn}}H^{\ominus}} & \text{products} \\ -\Delta_{\text{f}}H^{\ominus}_{\text{reactants}} \downarrow & & \uparrow \Delta_{\text{f}}H^{\ominus}_{\text{products}} \\ \text{"elements in their standard reference state"} & & \end{array} \tag{4.3.1}$$

This process is summarized by the simple formula:

$$\Delta_{\text{rxn}}H^{\ominus} = \Delta_{\text{f}}H^{\ominus}_{\text{products}} - \Delta_{\text{f}}H^{\ominus}_{\text{reactants}}. \tag{4.3.2}$$

Notice how there is a negative sign in front of the enthalpy of formation of the reactants because they are normally defined for the reactions that go from the elements to the reactants and not vice-versa. To close the cycle in Equation ???, however, we should go from the reactants to the elements, and therefore we must invert the sign in front of the formation enthalpies of the reactants. Equation 4.3.2 can be generalized using the same technique used to derive eq. 4.1.4, resulting in:

$$\Delta_{\text{rxn}}H^{\ominus} = \sum_i \nu_i \Delta_{\text{f}}H_i{}^{\ominus}, \tag{4.3.3}$$

which is a mathematical expression of the law that is known as **Hess's Law**. Hess's law is valid at constant pressure because, at those conditions, the heat of reaction—a path function—is equal to the enthalpy of reaction—a state function. Therefore, the enthalpy of a reaction depends exclusively on the initial and final state, and it can be obtained via the pathway that passes through the elements in their standard state (the formation pathway).

Exercise 4.3.1

Calculate the standard enthalpy of formation at 298 K for the combustion of 1 mol of methane, using the data in eq. 4.2.1.

Answer available at the end of this section.

Answers

Exercise 4.3.1

The reaction that is under consideration is:

$$\text{CH}_{4(g)} + 2\text{O}_{2(g)} \rightarrow \text{CO}_{2(g)} + 2\text{H}_2\text{O}_{(l)} \qquad \Delta_{\text{f}}H^{\ominus}_{\text{CH}_{4(g)}} = ?$$

Using Hess's Law, Equation 4.3.3, the enthalpy of formation for methane is:

$$\Delta_{\text{rxn}}H^{\ominus} = \Delta_{\text{f}}H^{\ominus}_{\text{CO}_{2(g)}} + 2\Delta_{\text{f}}H^{\ominus}_{\text{H}_2\text{O}_{(l)}} - \Delta_{\text{f}}H^{\ominus}_{\text{CH}_{4(g)}} - 2\underbrace{\Delta_{\text{f}}H^{\ominus}_{\text{O}_{2(g)}}}_{=0}$$

whose values are reported in eq. 4.2.1. Notice that the formation enthalpy of $O_{2(g)}$ is zero, since it is an element in its standard state. The final result is:

$$\Delta_{\text{rxn}}H^{\ominus} = \overbrace{-394}^{\Delta_{\text{f}}H^{\ominus}_{\text{CO}_{2(g)}}} + 2\overbrace{(-286)}^{\Delta_{\text{f}}H^{\ominus}_{\text{H}_2\text{O}_{(l)}}} - \overbrace{(-75)}^{\Delta_{\text{f}}H^{\ominus}_{\text{CH}_{4(g)}}} = -891\text{kJ/mol}.$$

where the negative sign indicates that the reaction is exothermic (see eq. 4.1.1), as we should expect. The cycle that we used to solve this exercise can be summarized with :

$$\begin{array}{ccc} \text{CH}_{4(g)} + 2\text{O}_{2(g)} & \xrightarrow{\Delta_{\text{rxn}}H^{\ominus}} & \text{CO}_{2(g)} + 2\text{H}_2\text{O}_{(l)} \\ -\Delta_{\text{f}}H^{\ominus}_{\text{CH}_{4(g)},\text{O}_{2(g)}} \searrow & & \nearrow \Delta_{\text{f}}H^{\ominus}_{\text{CO}_{2(g)},\text{H}_{2(g)}} \\ & \text{H}_{2(g)}, \text{C}_{(s,\text{graphite})}, \text{O}_{2(g)} & \end{array}$$

Notice that at standard pressure and $T = 298\ \text{K}$ water is in liquid form. However, when we burn methane, the heat associated with the exothermic reaction immediately vaporize the water. Substances in different states of matter have different formation enthalpies, and $\Delta_{\text{f}}H^{\ominus}_{\text{H}_2\text{O}_{(l)}} = -242\ \text{kJ/mol}$. The difference between the formation enthalpies of the same substance in different states represents the latent heat that separates them. For example, for water:

$$\begin{aligned} \Delta_{\text{vap}}H^{\ominus}_{\text{H}_2\text{O}} &= \Delta_{\text{f}}H^{\ominus}_{\text{H}_2\text{O}_{(g)}} - \Delta_{\text{f}}H^{\ominus}_{\text{H}_2\text{O}_{(l)}} \\ &= (-242) - (-286) = +44\ \text{kJ/mol} \end{aligned}$$

which is the latent heat of vaporization for water, $\Delta_{\text{vap}}H^{\ominus}_{\text{H}_2\text{O}}$. The latent heat is positive to indicate that the system absorbs energy in going from the liquid to the gaseous state (and it will release energy when going the opposite direction from gas to liquid).

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4.4: Calculations of Enthalpies of Reaction at T ≠ 298 K

Standard enthalpies of formation are usually reported at room temperature (T = 298 K), but enthalpies of formation at any temperature T' can be calculated from the values at 298 K using eqs. (2.4) and (3.13):

$$\begin{aligned} dH = C_P dT \rightarrow \int_{H^{\ominus}_{T=298}}^{H_{T'}} dH &= \int_{T=298}^{T'} C_P dT \\ H^{\ominus}_{T'} - H^{\ominus}_{T=298} &= \int_{T=298}^{T'} C_P dT \\ H^{\ominus}_{T'} &= H^{\ominus}_{T=298} + \int_{T=298}^{T'} C_P dT, \end{aligned} \tag{4.9}$$

which, in conjunction with Hess's Law (Equation ???), results in:

$$\Delta_{\text{rxn}} H^{\ominus}_{T'} = \Delta_{\text{rxn}} H^{\ominus}_{T=298} + \int_{T=298}^{T'} \Delta C_P dT, \tag{4.10}$$

with $\Delta C_P = \sum_i \nu_i C_{P,i}$.

Exercise 4.4.2

Calculate $\Delta_{\text{rxn}} H$ of the following reaction at 398 K, knowing that $\Delta_{\text{rxn}} H^{\ominus}$ at 298 K is -283.0 kJ/mol, and the following C_P values: $\text{CO}_{(g)}$ = 29 J/(mol K), $\text{O}_{2(g)}$ = 30 J/(mol K), $\text{CO}_{2(g)}$ = 38 J/(mol K):

$$\text{CO}_{(g)} + \frac{1}{2}\text{O}_{2(g)} \rightarrow \text{CO}_{2(g)},$$

Answer available at the end of this section.

Answers

Exercise 4.4.2

Using Equation 4.10 we obtain:

$$\Delta_{\text{rxn}} H^{398} = \overbrace{-283.0}^{\Delta_{\text{rxn}} H^{\ominus}} + \int_{298}^{398} (\overbrace{38}^{C_P^{\text{CO}_2}} - \overbrace{29}^{C_P^{\text{CO}}} - \frac{1}{2}\overbrace{30}^{C_P^{\text{O}_2}}) \times 10^{-3} dT,$$

which, assuming that the heat capacities does not depend on the temperature, becomes:

$$\begin{aligned} \Delta_{\text{rxn}} H^{398} &= -283.0 + \left(38 - 29 - \frac{1}{2}30\right) \times 10^{-3}(398 - 298) \\ &= -283.6 \text{ kJ/mol}. \end{aligned}$$

As we notice from this result, a difference in temperature of 100 K translates into a change in $\Delta_{\text{rxn}} H^{\ominus}$ of this reaction of only 0.6 kJ/mol. This is a trend that is often observed, and values of $\Delta_{\text{rxn}} H$ are very weakly dependent on changes in temperature for most chemical reactions. This numerical result can also be compared with the amount that is experimentally measured for $\Delta_{\text{rxn}} H^{398}$ of this reaction, which is –283.67 kJ/mol. This comparison strongly supports the assumption that we used to solve the integral in Equation 4.10, confirming that the heat capacities are mostly independent of temperature.

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5: THERMODYNAMIC CYCLES

The first law of thermodynamics places no restrictions on the conversion of energy from one form to another. For example, let's consider once again the Joule experiment (Figure 3.1.1). If we design a cycle that goes from the gas on the left chamber only to the gas equilibrated in both chambers and backward, as in Figure 5.1, there are no restrictions imposed on this hypothetical cycle by the first law.

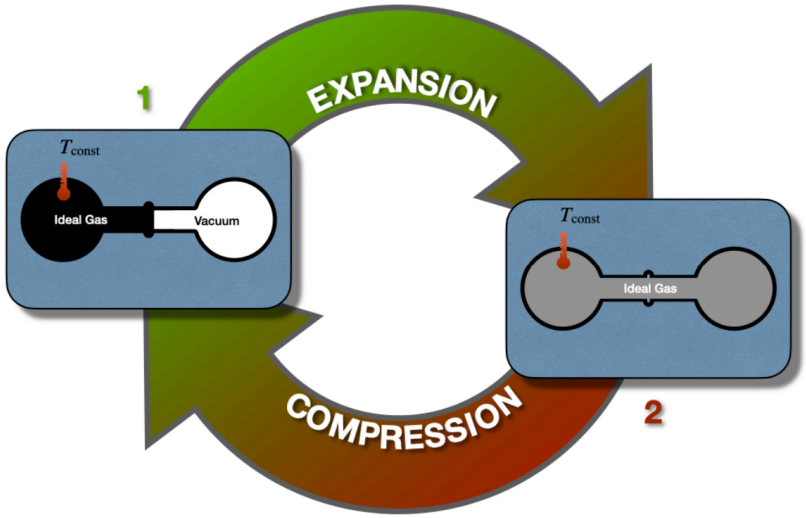


Figure 5.1: Closing the Cycle in The Joule Expansion Experiment.

As we saw in section 3.1.1, states 1 and 2 have exactly the same energy at constant temperature. Restricting the analysis to the information contained in the first law, the ideal gas could hypothetically go from state 1 (all gas in the left chamber) to state 2 (gas in both chambers), as well as spontaneously close the cycle back from state 2 to state 1, without external intervention. While the transformation from $1 \rightarrow 2$ is intuitively spontaneous (it's the same transformation that we considered in section 3.1.1), the backward transformation from $2 \rightarrow 1$ is clearly not as intuitive. In this case, the gas should spontaneously compress back to the left side, leaving a vacuum on the right chambers, without interventions from the outside. This transformation is clearly never observed. A gas just does not spontaneously concentrate on one side of a room, leaving a vacuum on the other side. In fact, when we need to create a vacuum, a lot of energy must be spent. Suppose we use exclusively information contained in the first law. In this case, there is nothing that might suggest a system's preference to perform the transformation $1 \rightarrow 2$, while restricting the $2 \rightarrow 1$ from happening spontaneously. Both states have the same energy, and

$$\oint dU = 0,$$

James Joule himself was indeed convinced that this must be the case and that we don't observe the backward transformation in practice only because we cannot build ideal machines.[1] Another scientist of that era was not convinced. William Thomson, the 1st Baron Kelvin (1824–1907), was unsure about this idea, and invested substantial resources to try to prove Joule's wrong.[2]

A few years later, the controversy between Joule and Kelvin was redeemed in favor of the latter, thanks to the experiments of French military engineer Nicolas Léonard Sadi Carnot (1796–1832). The work of Carnot began in France several years before Joule and Kelvin's time.[3] At that time, the importance of steam engines was growing for industrial applications, but a theoretical perspective was lacking. Carnot was convinced that a scientific understanding of heat engines was necessary to improve their efficiency.

---

1. Either because we don't really have ideal gases, or because we are unable to construct mechanical devices without loss, or in general because of other experimental factors
2. Interestingly enough, both Joule and Lord Kelvin are now recognized as key figures in the development of thermodynamics

and science in general. So much so, that the energy unit and the temperature unit in the SI system are named after them.
3. Carnot's lone book, the *Réflexions sur la Puissance Motrice du Feu* ("Reflections on the Motive Power of Fire") was published in France in 1824, the same year Kelvin was born and just 6 years after Joule's birth.

5.1: Carnot Cycle

5.2: Energy, Heat, and Work in the Carnot Cycle

5.3: Efficiency of a Carnot Cycle

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5.1: Carnot Cycle

The main contribution of Carnot to thermodynamics is his abstraction of the steam engine's essential features into a more general and idealized heat engine. The definition of Carnot's idealized cycle is as follows:

Definition: Carnot Cycle

A Carnot cycle is an idealized process composed of two isothermal and two adiabatic transformations. Each transformation is either an expansion or a compression of an ideal gas. All transformations are assumed to be reversible, and no energy is lost to mechanical friction.

A Carnot cycle connects two "heat reservoirs" at temperatures T_h (hot) and T_l (low), respectively. The reservoirs have a large thermal capacity so that their temperatures are unaffected by the cycle. The system is composed exclusively by the ideal gas, which is the only substance that changes temperature throughout the cycle. If we report the four transformations of a Carnot cycle on a PV diagram, we obtain the following plot:

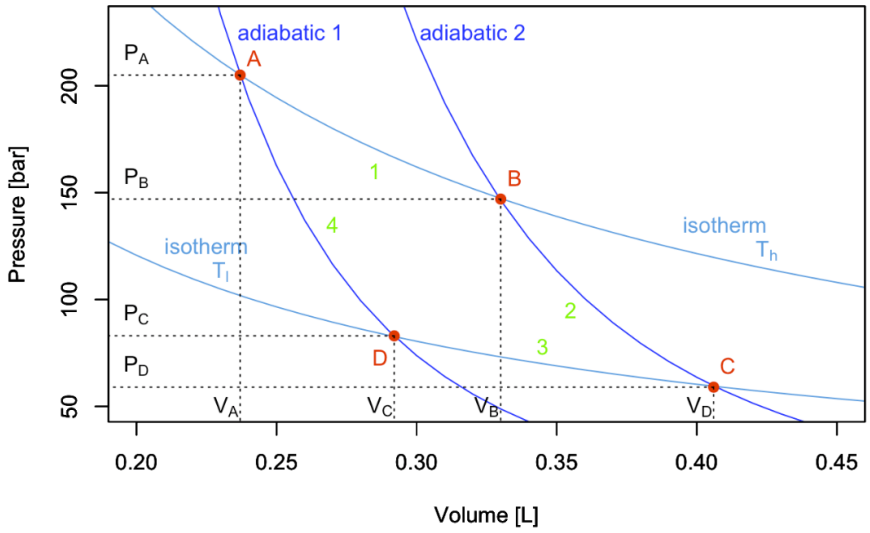


Figure 5.1.1: PV-Diagram of a Carnot Cycle.

Stage 1: isothermal expansion $A \rightarrow B$

At this stage heat is released from the hot reservoir and is absorbed by the ideal gas particles within the system. Thus, the temperature of the system rises. The high temperature causes the gas particles to expand; pushing the piston upwards and doing work on the surroundings.

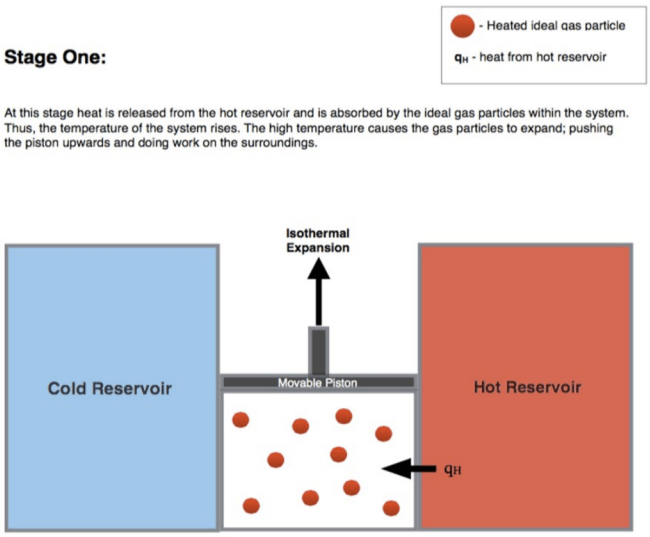


Figure 5.1.2

Starting the analysis of the cycle from point A in Figure 5.1.1,[1] the first transformation we encounter is an isothermal expansion at T_h. Since the transformation is isothermal:

$$\Delta U_1 = \overbrace{W_1}^{<0} + \overbrace{Q_1}^{>0} = 0 \Rightarrow Q_1 = -W_1,$$

and heat and work can be calculated for this stage using Equation 2.4.14:

$$\begin{aligned} Q_1 = |Q_h| &= nRT_h \overbrace{\ln \frac{V_B}{V_A}}^{>0 \text{ since } V_B > V_A} > 0, \\ W_1 &= -Q_1 = -nRT_h \ln \frac{V_B}{V_A} < 0, \end{aligned} \tag{5.1.1}$$

where we denoted $|Q_h|$ the absolute value of the heat that gets **into** the system from the hot reservoir.

Stage 2: adiabatic expansion $B \to C$

At this stage expansion continues, however there is no heat exchange between system and surroundings. Thus, the system is undergoing adiabatic expansion. The expansion allows the ideal gas particles to cool, decreasing the temperature of the system.

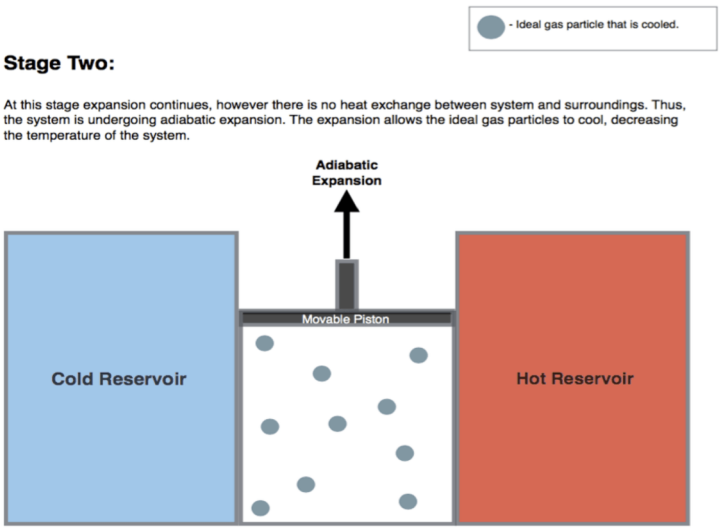


Figure 5.1.3

The second transformation is an adiabatic expansion between T_h and T_l. Since we are at adiabatic conditions:

$$Q_2 = 0 \Rightarrow \Delta U_2 = W_2,$$

and the negative energy (expansion work) can be calculated using:

$$\Delta U_2 = W_2 = n \underbrace{\int_{T_h}^{T_l} C_V dT}_{<0 \text{ since } T_l<T_h} < 0.$$

Stage 3: isothermal compression $C \to D$

At this stage the surroundings do work on the system which causes heat to be released (qc). The temperature within the system remains the same. Thus, isothermal compression occurs.

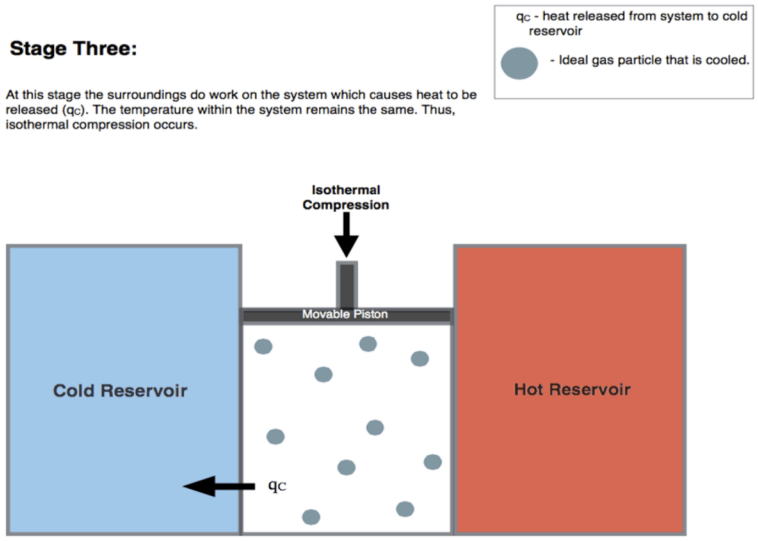


Figure 5.1.4

The third transformation is an isothermal compression at T_l. The formulas are the same as those used for stage 1, but they will

results in heat and work with reversed signs (since this is a compression):

$$\Delta U_3 = \overbrace{W_3}^{>0} + \overbrace{Q_3}^{<0} = 0 \Rightarrow Q_3 = -W_3,$$

and:

$$\begin{aligned} Q_3 = |Q_l| &= nRT_l \overbrace{\ln \frac{V_D}{V_C}}^{<0 \text{ since } V_D<V_C} < 0, \\ W_3 = -Q_3 &= -nRT_l \ln \frac{V_D}{V_C} > 0, \end{aligned} \tag{5.1.2}$$

where $|Q_l|$ is the absolute value of the heat that gets **out of** the system to the cold reservoir ($|Q_l|$ being the heat entering the system).

Stage 4: adiabatic compression $D \to A$

No heat exchange occurs at this stage, however, the surroundings continue to do work on the system. Adiabatic compression occurs which raises the temperature of the system as well as the location of the piston back to its original state (prior to stage one).

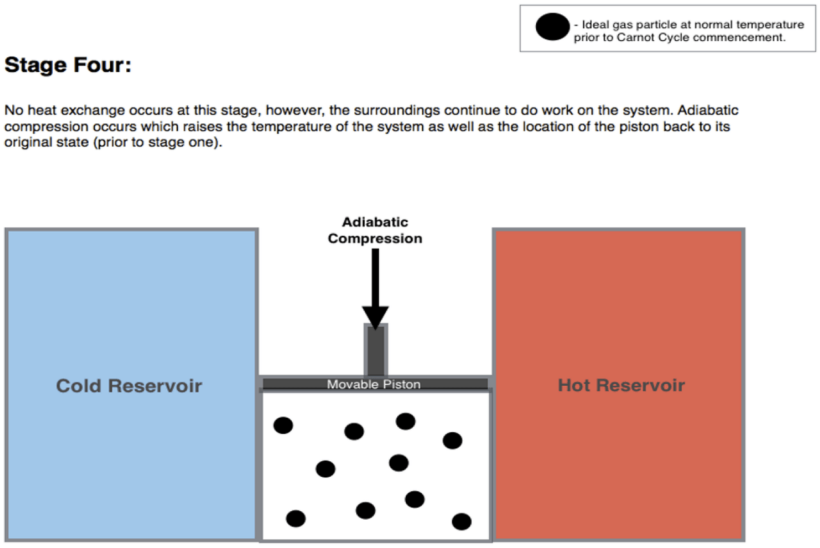


Figure 5.1.5

The fourth and final transformation is an adiabatic comprssion that restores the system to point A, bringing it from T_l to T_h. Similarly to stage 3:

$$Q_4 = 0 \Rightarrow \Delta U_4 = W_4,$$

Since we are at adiabatic conditions. The energy associated with this process is now positive (compression work), and can be calculated using:

$$\Delta U_4 = W_4 = n \underbrace{\int_{T_l}^{T_h} C_V dT}_{>0 \text{ since } T_h>T_l} > 0.$$

Notice how $\Delta U_4 = -\Delta U_2$ because $\int_x^y = -\int_y^x$.

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1. ♢The stages of a Carnot depicted at the beginning of each of this section and the following three ones are genetaken from

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5.2: Energy, Heat, and Work in the Carnot Cycle

Summarizing the results of the previous sections, the total amount of energy for a Carnot cycle is:

$$\begin{aligned}\Delta U_{\mathrm{TOT}} &= \Delta U_1 + \Delta U_2 + \Delta U_3 + \Delta U_4 \\ &= 0 + n\int_{T_h}^{T_l} C_V dT + 0 + n\int_{T_l}^{T_h} C_V dT \\ &= n\int_{T_h}^{T_l} C_V dT - n\int_{T_h}^{T_l} C_V dT = 0\end{aligned} \tag{5.2.1}$$

which is obviously zero, since $\oint dU = 0$. The amounts of work and heat, however, are not zero, since Q and W are path functions. Therefore:

$$\begin{aligned}W_{\mathrm{TOT}} &= W_1 + W_2 + W_3 + W_4 \\ &= -nRT_h \ln\frac{V_B}{V_A} + n\int_{T_h}^{T_l} C_V dT - nRT_l \ln\frac{V_D}{V_C} + n\int_{T_l}^{T_h} C_V dT \\ &= -nRT_h \ln\frac{V_B}{V_A} - nRT_l \ln\frac{V_D}{V_C},\end{aligned} \tag{5.2.2}$$

which, considering that $V_C/V_D = V_B/V_A$, reduces to:

$$W_{\mathrm{TOT}} = -nR\left(T_h - T_l\right)\ln\frac{V_B}{V_A} < 0,$$

which is negative, because $T_h > T_l$ and $V_B > V_A$. Negative work means that the work is done by the system. In other words, the system is performing PV-work by transferring heat from a hot reservoir to a cold one via a Carnot cycle. On the other hand, for the heat:

$$\begin{aligned}Q_{\mathrm{TOT}} &= Q_1 + Q_2 + Q_3 + Q_4 \\ &= Q_h + 0 + Q_l + 0 \\ &= nRT_h \ln\frac{V_B}{V_A} + nRT_l \ln\frac{V_D}{V_C} \\ &= nR\left(T_h - T_l\right)\ln\frac{V_B}{V_A} = -W_{\mathrm{TOT}},\end{aligned} \tag{5.2.3}$$

which, simplifies to:

$$W_{\mathrm{TOT}} = -(Q_1 + Q_3),$$

and, replacing Q_1 and Q_3 with the absolute values of the heats drawn from the hot and cold reservoirs, $|Q_h|$, and $|Q_l|$ respectively:

$$|W_{\mathrm{TOT}}| = |Q_h| - |Q_l|\,,$$

or, in other words, more heat is extracted from the hot reservoir than it is put into the cold one. The difference between the absolute value of these amounts of heat gives the total work of the cycle. This process is depicted in Figure 5.2.1.

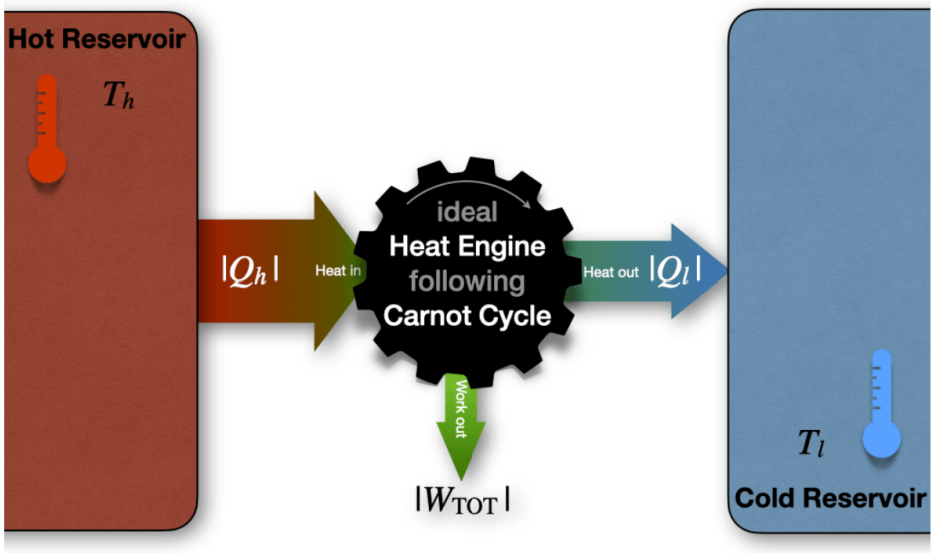


Figure 5.2.1: Carnot Cycle Diagram.

Exercise 5.2.1

Up to this point, we have discussed Carnot cycles working in the hot → cold direction ($A \to B \to C \to D \to A$), since this is the primary mode of operation of heat engines that produce work. However, a heat engine could also—in principle—work in the reversed cold $rightarrow$ hot direction ($A \to D \to C \to B \to A$). Write the equations for heat, work, and energy of each stage of a Carnot cycle going the opposite direction than the one discussed in sections 5.1 and 5.2.

Answer available at the end of this section.

Answers

Exercise 5.2.1

When the heat engine works in reverse order, the formulas remain the same, but all the signs in front of Q, W, and U will be reversed. In this case, the total work would get into the systems, and heat would be transferred from the cold reservoir to the hot one. Figure 5.2.1 would be modified as:
This reversed mode of operation is the basic principle behind refrigerators and air conditioning.

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5.3: Efficiency of a Carnot Cycle

The efficiency (ε) of a cycle is defined as the ratio between the absolute value of the work extracted from the cycle ($|W_{\mathrm{TOT}}|$) and the heat that gets into the system ($|Q_h|$):

$$\varepsilon = \frac{|W_{\mathrm{TOT}}|}{|Q_h|} = \frac{-W_{\mathrm{TOT}}}{Q_1} \tag{5.3.1}$$

where the minus sign in front of the work is necessary because the efficiency is defined as a positive number. Replacing Equation 5.2.5 into eq. 5.3.1, we obtain:

$$\varepsilon = \frac{Q_3 + Q_1}{Q_1} = 1 + \frac{Q_3}{Q_1}.$$

If we go back to Equation 5.3.1 and we replace Equation 5.2.3 for W_{TOT} and Equation 5.1.3 for Q_1, we obtain:

$$\varepsilon = \frac{nR\,(T_h - T_l)\ln V_B/V_A}{nRT_h \ln V_B/V_A} = \frac{T_h - T_l}{T_h} = 1 - \frac{T_l}{T_h} < 1, \tag{5.3.2}$$

which proves that the efficiency of a Carnot cycle is strictly smaller than 1.[1] In other words, no cycle can convert 100% of the heat into work it extracts from a hot reservoir. This finding had remarkable consequences on the entire thermodynamics field and set the foundation for the introduction of entropy. We will use eqs. 5.3.1 and 5.3.2 for this purpose in the next chapter, but we conclude the discussion on Carnot cycles by returning back to Lord Kelvin. In 1851 he used this finding to state his statement "It is impossible for a self-acting machine, unaided by any external agency, to convey heat from one body to another at a higher temperature. It is impossible, by means of inanimate material agency, to derive mechanical effect from any portion of matter by cooling it below the temperature of the coldest of the surrounding objects."[2] This statement conclusively disproved Joule's original theories and demonstrated that there is some fundamental principle to govern the flow of heat beyond the first law of thermodynamics.

---

1. Equation 5.3.2 can be equal to 1 only if $T_l = 0\ \mathrm{K}$ or $T_h = \infty$, two conditions that are both equally impossible.
2. Thomson W. Transactions of the Royal Society of Edinburgh. 1851 XX 261–268, 289–298..

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6: SECOND LAW OF THERMODYNAMICS

In chapter 5, we have discussed heat engines as a means of understanding how some processes are spontaneous while others are not. Carnot's findings did not just simply inspire Lord Kelvin on this subject, but they also motivated Rudolf Clausius (1822–1888) to introduce the concept of entropy.

6.1: Entropy

6.2: Irreversible Cycles

6.3: The Second Law of Thermodynamics

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6.1: Entropy

Let's return to the definition of efficiency of a Carnot cycle and bring together eqs. 5.3.2 and 5.3.3:

$$\varepsilon = 1 + \frac{Q_3}{Q_1} = 1 - \frac{T_l}{T_h}.$$

Simplifying this equality, we obtain:

$$\frac{Q_3}{T_l} = -\frac{Q_1}{T_h}, \tag{6.1.1}$$

or alternatively:

$$\frac{Q_3}{T_l} + \frac{Q_1}{T_h} = 0. \tag{6.1.2}$$

The left hand side of Equation 6.1.2 contains the sum of two quantities around the Carnot cycle, each calculated as $\frac{Q_{\text{REV}}}{T}$, with Q_{REV} being the heat exchanged at reversible conditions (recall that according to Definition: Carnot Cycle each transformation in a Carnot cycle is reversible). Equation 6.1.1 can be generalized to a sequence of connected Carnot cycles joining more than two isotherms by taking the summation across different temperatures:

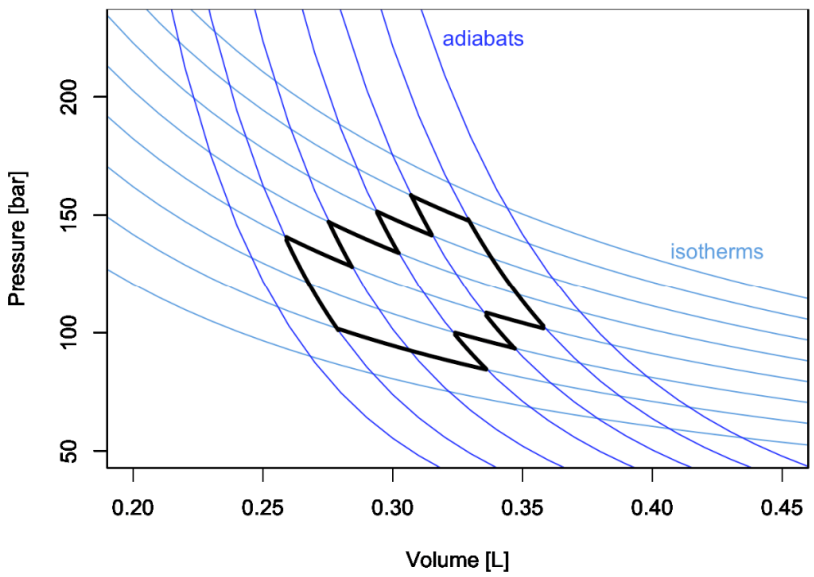


Figure 6.1.1

$$\sum_i \frac{Q_{\text{REV}}}{T_i} = 0, \tag{6.1.3}$$

where the summation happens across a sequence of Carnot cycles that connects different temperatures. Eqs. \label{6.1.3} and 6.1.3 show that for a Carnot cycle—or a series of connected Carnot cycles—there exists a conserved quantity obtained by dividing the heat associated with each reversible stage and the temperature at which such heat is exchanged. If a quantity is conserved around a cycle, it must be independent on the path, and therefore it is a state function. Looking at similar equations, Clausius introduced in 1865 a new state function in thermodynamics, which he decided to call entropy and indicate with the letter S:

Definition: Entropy

$$S = \frac{Q_{\text{REV}}}{T}.$$

We can use the new state function to generalize Equation 6.1.3 to any reversible cycle in a PV-diagram by using the rules of calculus. First, we will slice S into an infinitesimal quantity:

$$dS = \frac{đQ_{\text{REV}}}{T},$$

then we can extend the summation across temperatures of Equation 6.1.3 to a sum over infinitesimal quantities—that is the integral—around the cycle:

$$\oint dS = \oint \frac{đQ_{\text{REV}}}{T} = 0.$$

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6.2: Irreversible Cycles

Up to this point, we have discussed *reversible* cycles only. Notice that the heat that enters the definition of entropy (Definition: Entropy) is the heat exchanged at reversible conditions since it is only at those conditions that the right-hand side of Equation 6.1.5 becomes a state function. What happens when we face an irreversible cycle? The efficiency of a Carnot cycle in Equation 5.3.3 is the maximum efficiency that an idealized thermodynamic cycle can reach. As such, any irreversible cycle will incontrovertibly have an efficiency smaller than the maximum efficiency of the idealized Carnot cycle. Therefore, Equation 6.1.1 for an *irreversible* cycle will not hold anymore and must be rewritten as:

$$\overbrace{1+\frac{Q_3}{Q_1}}^{\varepsilon_{\text{IRR}}} < \overbrace{1-\frac{T_l}{T_h}}^{\varepsilon_{\text{REV}}}, \tag{6.2.1}$$

and, following the same procedure used in section 6.1, we can rewrite Equation 6.2.1 as:

$$\frac{Q_3^{\text{IRR}}}{Q_1^{\text{IRR}}} < -\frac{T_l}{T_h} \longrightarrow \frac{Q_3^{\text{IRR}}}{T_l} + \frac{Q_1^{\text{IRR}}}{T_h} < 0 \longrightarrow \sum_i \frac{Q_{\text{IRR}}}{T_i} < 0,$$

which can be generalized using calculus to:

$$\oint \frac{đQ_{\text{IRR}}}{T} < 0. \tag{6.2.2}$$

Putting eqs. 6.1.6 and 6.2.2 together, we obtain:

$$\oint \frac{đQ}{T} \leq 0, \tag{6.2.3}$$

where the equal sign holds for reversible transformations exclusively, while the inequality sign holds for irreversible ones. Equation 6.2.3 is known as **Clausius inequality.**

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6.3: The Second Law of Thermodynamics

Now we can consider an isolated system undergoing a cycle composed of an irreversible forward transformation ($1 \rightarrow 2$) and a reversible backward transformation ($2 \rightarrow 1$), as in Figure 6.3.1.

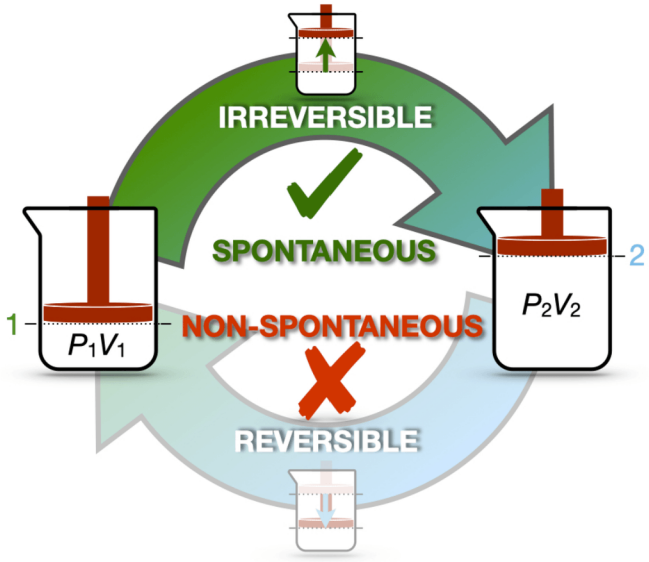


Figure 6.3.1: Spontaneous and Non-Spontaneous Transformations in a Cycle.

This cycle is similar to the cycle depicted in Figure 6.3.1 for the Joule's expansion experiment. In this case, we have an intuitive understanding of the spontaneity of the irreversible expansion process, while the non-spontaneity of the backward compression. Since the cycle has at least one irreversible step, it is overall irreversible, and we can calculate:

$$\oint \frac{đQ_{\text{IRR}}}{T} = \int_1^2 \frac{đQ_{\text{IRR}}}{T} + \int_2^1 \frac{đQ_{\text{REV}}}{T}.$$

We can then use Clausius inequality (Equation 6.2.4) to write:

$$\int_1^2 \frac{đQ_{\text{IRR}}}{T} + \int_2^1 \frac{đQ_{\text{REV}}}{T} < 0, \tag{6.3.1}$$

which can be rearranged as:

$$\underbrace{\int_1^2 \frac{đQ_{\text{REV}}}{T}}_{\int_1^2 dS = \Delta S} > \underbrace{\int_1^2 \frac{đQ_{\text{IRR}}}{T}}_{=0}, \tag{6.3.2}$$

where we have used the fact that, for an isolated system (the universe), $đQ_{\text{IRR}} = 0$. Equation 6.3.2 can be rewritten as:

$$\Delta S > 0, \tag{6.3.3}$$

which proves that for any irreversible process in an isolated system, the entropy is increasing. Using Equation 6.3.3 and considering that the only system that is truly isolated is the universe, we can write a concise statement for a new fundamental law of thermodynamics:

Definition: Second Law of Thermodynamics

For any spontaneous process, the entropy of the universe is increasing.

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7: CALCULATION OF ENTROPY AND THE THIRD LAW OF THERMODYNAMICS

The Second Law can be used to infer the spontaneity of a process, as long as the entropy of the universe is considered. To do so, we need to remind ourselves that the universe can be divided into a system and its surroundings (environment). When we calculate the entropy of the universe as an indicator of the spontaneity of a process, we need to *always* consider changes in entropy in *both* the system (sys) and its surroundings (surr):

$$\Delta S^{\text{universe}} = \Delta S^{\text{sys}} + \Delta S^{\text{surr}},$$

or, in differential form:

$$dS^{\text{universe}} = dS^{\text{sys}} + dS^{\text{surr}},$$

7.1: Calculation of ΔSsys

7.2: Calculation of ΔSsurr

7.3: Clausius Theorem

7.4: The Third Law of Thermodynamics

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7.1: Calculation of ΔSsys

In general ΔS^{sys} can be calculated using either its Definition: Entropy, or its differential formula, Equation 6.1.5. In practice, it is always convenient to keep in mind that entropy is a state function, and as such it does not depend on the path. For this reason, we can break every transformation into elementary steps, and calculate the entropy on any path that goes from the initial state to the final state, such as, for example:

$$\begin{array}{ccc} P_i, T_i & \xrightarrow{\Delta_{\text{TOT}} S_{\text{sys}}} & P_f, T_f \\ {\scriptstyle \Delta_1 S^{\text{sys}}} \searrow & & \nearrow {\scriptstyle \Delta_2 S^{\text{sys}}} \\ & P_i, T_f & \end{array} \tag{7.1.1}$$

$$\Delta_{\text{TOT}} S^{\text{sys}} = \Delta_1 S^{\text{sys}} + \Delta_2 S^{\text{sys}},$$

with $\Delta_1 S^{\text{sys}}$ calculated at constant P, and $\Delta_2 S^{\text{sys}}$ at constant T. The most important elementary steps from which we can calculate the entropy resemble the prototypical processes for which we calculated the energy in section 3.1.

Entropy in isothermal processes

- For an ideal gas at constant temperature $\Delta U = 0$, and $Q_{\text{REV}} = -W_{\text{REV}}$. Using the formula for W_{REV} in either Equation (??) or Equation (??), we obtain:

$$\Delta S^{\text{sys}} = \int_i^f \frac{đQ_{\text{REV}}}{T} = \frac{-W_{\text{REV}}}{T} = \frac{nRT \ln \dfrac{V_f}{V_i}}{T} = nR \ln \frac{V_f}{V_i},$$

  or, similarly:

$$\Delta S^{\text{sys}} = nR \ln \frac{P_i}{P_f}.$$

- A phase change is a particular case of an isothermal process that does not follow the formulas introduced above since an ideal gas never liquefies. The entropy associated with a phase change at constant pressure can be calculated from its definition, remembering that $Q_{\text{rev}} = \Delta H$. For example for vaporizations:

$$\Delta_{\text{vap}} S = \frac{\Delta_{\text{vap}} H}{T_B},$$

with $\Delta_{\text{vap}} H$ being the enthalpy of vaporization of a substance, and T_B its boiling temperature.

It is experimentally observed that the entropies of vaporization of many liquids have almost the same value of:

$$\Delta_{\text{vap}} S \approx 10.5R, \tag{7.1.2}$$

which corresponds in SI to the range of about 85–88 J/(mol K). This simple rule is named **Trouton's rule**, after the French scientist that discovered it, Frederick Thomas Trouton (1863-1922).

Exercise 7.1.1

Calculate the standard entropy of vaporization of water knowing $\Delta_{\text{vap}} H^{\ominus}_{\text{H}_2\text{O}} = 44 \text{ kJ/mol}$, as calculated in Exercise 4.3.1.

Answer available at the end of this section.

Entropy in adiabatic processes

Since adiabatic processes happen without the exchange of heat, $đQ = 0$, it would be tempting to think that $\Delta S^{\text{sys}} = 0$ for every one of them. A transformation at constant entropy (isentropic) is always, in fact, a reversible adiabatic process. However, the opposite

case is not always true, and an irreversible adiabatic transformation is usually associated with a change in entropy. To explain this fact, we need to recall that the definition of entropy includes the heat exchanged at reversible conditions only. Therefore, for irreversible adiabatic processes $\Delta S^{\text{sys}} \neq 0$. The calculation of the entropy change for an irreversible adiabatic transformation requires a substantial effort, and we will not cover it at this stage. The situation for adiabatic processes can be summarized as follows:

$$\begin{aligned} &\text{reversible:} && \frac{đQ_{\text{REV}}}{T} = 0 \longrightarrow \Delta S^{\text{sys}} = 0 \quad \text{(isentropic)}, \\ &\text{irreversible:} && \frac{đQ_{\text{IRR}}}{T} = 0 \longrightarrow \Delta S^{\text{sys}} \neq 0. \end{aligned} \tag{7.1.3}$$

Entropy in isochoric processes

We can calculate the heat exchanged in a process that happens at constant volume, Q_V, using Equation 2.3.2. Since the heat exchanged at those conditions equals the energy (Equation 3.1.7), and the energy is a state function, we can use Q_V regardless of the path (reversible or irreversible). The entropy associated with the process will then be:

$$\Delta S^{\text{sys}} = \int_i^f \frac{đQ_{\text{REV}}}{T} = \int_i^f nC_V \frac{dT}{T},$$

which, assuming C_V independent of temperature and solving the integral on the right-hand side, becomes:

$$\Delta S^{\text{sys}} \approx nC_V \ln \frac{T_f}{T_i}.$$

Entropy in isobaric processes

Similarly to the constant volume case, we can calculate the heat exchanged in a process that happens at constant pressure, Q_P, using Equation 2.3.4. Again, similarly to the previous case, Q_P equals a state function (the enthalpy), and we can use it regardless of the path to calculate the entropy as:

$$\Delta S^{\text{sys}} = \int_i^f \frac{đQ_{\text{REV}}}{T} = \int_i^f nC_P \frac{dT}{T},$$

which, assuming C_P independent of temperature and solving the integral on the right-hand side, becomes:

$$\Delta S^{\text{sys}} \approx nC_P \ln \frac{T_f}{T_i}.$$

◈

Answers

Exercise 7.1.1

Using Equation 7.1.2—and knowing that at standard conditions of $P^{\ominus} = 1\ \text{bar}$ the boiling temperature of water is 373 K—we calculate:

$$\Delta_{\text{vap}} S^{\ominus}_{\text{H}_2\text{O}} = \frac{44 \times 10^3 \text{J/mol}}{373\ \text{K}} = 118\ \text{J/(mol K)}.$$

The entropy of vaporization of water is far from Trouton's rule range of 85–88 J/(mol K) because of the hydrogen bond interactions between its molecules. Other similar exceptions are ethanol, formic acid, and hydrogen fluoride.

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7.2: Calculation of ΔSsurr

While the entropy of the system can be broken down into simple cases and calculated using the formulas introduced above, the entropy of the surroundings does not require such a complicated treatment, and it can always be calculated as:

$$\Delta S^{\text{surr}} = \frac{Q_{\text{surr}}}{T_{\text{surr}}} = \frac{-Q_{\text{sys}}}{T_{\text{surr}}},$$

or, in differential form:

$$dS^{\text{surr}} = \frac{đQ_{\text{surr}}}{T_{\text{surr}}} = \frac{-đQ_{\text{sys}}}{T_{\text{surr}}},$$

where the substitution $Q_{\text{surr}} = -Q_{\text{sys}}$ can be performed regardless of whether the transformation is reversible or not. In other words, the surroundings always absorb heat reversibly. To justify this statement, we need to restrict the analysis of the interaction between the system and the surroundings to just the vicinity of the system itself. Outside of a generally restricted region, the rest of the universe is so vast that it remains untouched by anything happening inside the system.[1] To facilitate our comprehension, we might consider a system composed of a beaker on a workbench. We can then consider the room that the beaker is in as the immediate surroundings. To all effects, the beaker+room combination behaves as a system isolated from the rest of the universe. The room is obviously much larger than the beaker itself, and therefore every energy production that happens in the system will have minimal effect on the parameters of the room. For example, an exothermal chemical reaction occurring in the beaker will not affect the overall temperature of the room substantially. When we study our reaction, T_{surr} will be constant, and the transfer of heat from the reaction to the surroundings will happen at reversible conditions.

Exercise 7.2.1

Calculate the changes in entropy of the universe for the process of 1 mol of supercooled water, freezing at –10°C, knowing the following data: $\Delta_{\text{fus}}H = 6\ \text{kJ/mol}$, $C_P^{\text{H}_2\text{O}_{(l)}} = 76\ \text{J/(mol K)}$, $C_P^{\text{H}_2\text{O}_{(s)}} = 38\ \text{J/(mol K)}$, and assuming both C_P to be independent on temperature.

Answer available at the end of this section.

1. Even if we think at the most energetic event that we could imagine happening here on earth—such as the explosion of an atomic bomb or the hit of a meteorite from outer space—such an event will not modify the average temperature of the universe by the slightest degree.

Answers

Exercise 7.2.1

ΔS^{sys} for the process under consideration can be calculated using the following cycle:

$$\begin{array}{ccc} \text{H}_2\text{O}_{(l)} & \xrightarrow{\Delta S_{\text{sys}}} & \text{H}_2\text{O}_{(s)} \qquad T = 263\ K \\ {\scriptstyle \Delta S_1}\downarrow & & \uparrow{\scriptstyle \Delta S_3} \\ \text{H}_2\text{O}_{(l)} & \xrightarrow{\Delta S_2} & \text{H}_2\text{O}_{(s)} \qquad T = 273\ K \end{array} \tag{7.2.1}$$

$$\Delta S^{\text{sys}} = \Delta S_1 + \Delta S_2 + \Delta S_3$$

ΔS_1 and ΔS_3 are the isobaric heating and cooling processes of liquid and solid water, respectively, and can be calculated filling the given data into Equation 7.1.12. ΔS_2 is a phase change (isothermal process) and can be calculated translating Equation 7.1.6 to the freezing transformation. Overall:

$$\begin{aligned} \Delta S^{\text{sys}} &= \int_{263}^{273} \frac{C_P^{\text{H}_2\text{O}_{(l)}}}{T} dT + \frac{-\Delta_{\text{fus}}H}{273} + \int_{273}^{263} \frac{C_P^{\text{H}_2\text{O}_{(s)}}}{T} dT \\ &= 76 \ln \frac{273}{263} - \frac{6 \times 10^3}{273} + 38 \ln \frac{263}{273} = -20.6\ \text{J/K}. \end{aligned} \tag{7.2.2}$$

Don't be confused by the fact that ΔS^{sys} is negative. This is not the entropy of the universe! Hence it tells nothing about spontaneity! We can now calculate ΔS^{surr} from Q_{sys}, noting that we can calculate the enthalpy around the same cycle in Equation ???. To do that, we already have $\Delta_{\text{fus}}H$ from the given data, and we can calculate ΔH_1 and ΔH_3 using Equation 2.3.4.

$$
\begin{aligned}
Q^{\text{sys}} = \Delta H &= \int_{263}^{273} C_P^{\text{H}_2\text{O}_{(l)}} dT + (-\Delta_{\text{fus}} H) + \int_{273}^{263} C_P^{\text{H}_2\text{O}_{(s)}} dT \\
&= 76 \times 10^{-3}(273 - 263) - 6 + 38 \times 10^{-3}(263 - 273) \\
&= -5.6 \text{ kJ}.
\end{aligned} \tag{7.2.3}
$$

$$
\Delta S^{\text{surr}} = \frac{-Q_{\text{sys}}}{T} = \frac{5.6 \times 10^3}{263} = +21.3 \text{ J/K}.
$$

Bringing ??? and ??? results together, we obtain:

$$
\Delta S^{\text{universe}} = \Delta S^{\text{sys}} + \Delta S^{\text{surr}} = -20.6 + 21.3 = +0.7 \text{ J/K}.
$$

Since the entropy changes in the universe are positive, the process is spontaneous, as expected.

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7.3: Clausius Theorem

By replacing Equation 7.2.2 into 7.2 we can write the differential change in the entropy of the system as:

$$dS^{\text{sys}} = dS^{\text{universe}} - dS^{\text{surr}} = dS^{\text{universe}} + \frac{đQ_{\text{sys}}}{T}.$$

According to the second law, for any spontaneous process $dS^{\text{universe}} \geq 0$, and therefore, replacing it into Equation $7.3.1$:

$$dS^{\text{sys}} \geq \frac{đQ}{T},$$

which is the mathematical expression of the so-called **Clausius theorem**. Eq. $7.3.2$ distinguishes between three conditions:

$$\begin{aligned} dS^{\text{sys}} &> \frac{đQ}{T} && \text{spontaneous, irreversible transformation} \\ dS^{\text{sys}} &= \frac{đQ}{T} && \text{reversible transformation} \\ dS^{\text{sys}} &< \frac{đQ}{T} && \text{non-spontaneous, irreversible transformation,} \end{aligned}$$

Clausius theorem provides a useful criterion to infer the spontaneity of a process, especially in cases where it's hard to calculate $\Delta S^{\text{universe}}$. Eq. $7.3.2$ requires knowledge of quantities that are dependent on the system exclusively, such as the difference in entropy, the amount of heat that crosses the boundaries, and the temperature at which the process happens.[1] If a process produces more entropy than the amount of heat that crosses the boundaries divided by the absolute temperature, it will be spontaneous. Vice versa, if the entropy produced is smaller than the amount of heat crossing the boundaries divided by the absolute temperature, the process will be non-spontaneous. The equality holds for systems in equilibrium with their surroundings, or for reversible processes since they happen through a series of equilibrium states. Measuring or calculating these quantities might not always be the simplest of calculations. We will return to the Clausius theorem in the next chapter when we seek more convenient indicators of spontaneity.

---

1. In cases where the temperature of the system changes throughout the process, T is just the (constant) temperature of its immediate surroundings, T_{surr}, as explained in section 7.2.

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7.4: The Third Law of Thermodynamics

In chapter 4, we have discussed how to calculate reaction enthalpies for any reaction, given the formation enthalpies of reactants and products. In this section, we will try to do the same for reaction entropies. In this case, however, our task is simplified by a fundamental law of thermodynamics, introduced by Walther Hermann Nernst (1864–1941) in 1906.[1] The statement that was initially known as Nernst's Theorem is now officially recognized as the third fundamental law of thermodynamics, and it has the following definition:

Definition: Third Law of Thermodynamics

The entropy of a perfectly ordered, pure, crystalline substance is zero at $T = 0\ \mathrm{K}$.

This law sets an unambiguous zero of the entropy scale, similar to what happens with absolute zero in the temperature scale. The absolute value of the entropy of every substance can then be calculated in reference to this unambiguous zero. As such, absolute entropies are always positive. This is in stark contrast to what happened for the enthalpy. An unambiguous zero of the enthalpy scale is lacking, and standard formation enthalpies (which might be negative) must be agreed upon to calculate relative differences.

In simpler terms, given a substance i, we are not able to measure absolute values of its enthalpy H_i (and we must resort to known enthalpy differences, such as $\Delta_\mathrm{f}H^\ominus$ at standard pressure). At the same time, for entropy, we can measure S_i thanks to the third law, and we usually report them as $S_i^\ominus$. A comprehensive list of standard entropies of inorganic and organic compounds is reported in appendix 16. Reaction entropies can be calculated from the tabulated standard entropies as differences between products and reactants, using:

$$\Delta_\mathrm{rxn}S^\ominus = \sum_i \nu_i S_i^\ominus,$$

with ν_i being the usual stoichiometric coefficients with their signs given in Definition: Signs of the Stoichiometric Coefficients.

The careful wording in the definition of the third law Definition: Third Law of Thermodynamics allows for the fact that some crystal might form with defects (i.e., not as a perfectly ordered crystal). In this case, a residual entropy will be present even at $T = 0\ \mathrm{K}$. However, this residual entropy can be removed, at least in theory, by forcing the substance into a perfectly ordered crystal.[2]

An interesting corollary to the third law states that it is impossible to find a procedure that reduces the temperature of a substance to $T = 0\ \mathrm{K}$ in a finite number of steps.

---

1. Walther Nernst was awarded the 1920 Nobel Prize in Chemistry for his work in thermochemistry.
2. A procedure that—in practice—might be extremely difficult to achieve.

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8: THERMODYNAMIC POTENTIALS

8.1: Fundamental Equation of Thermodynamics
8.2: Thermodynamic Potentials
8.3: Free Energies
8.4: Maxwell Relations

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8.1: Fundamental Equation of Thermodynamics

Let's summarize some of the results from the first and second law of thermodynamics that we have seen so far. For reversible processes in closed systems:

$$\begin{aligned} \text{From } 1^{\text{st}} \text{ Law:} \qquad & dU = đQ_{\text{REV}} - PdV \\ \text{From The Definition of Entropy:} \qquad & dS = \frac{đQ_{\text{REV}}}{T} \rightarrow đQ_{\text{REV}} = TdS \\ \Rightarrow \quad & dU = TdS - PdV. \end{aligned} \tag{8.1.1}$$

Equation ??? is called the **fundamental equation of thermodynamics** since it combines the first and the second laws. Even though we started the derivation above by restricting to reversible transformations only, if we look carefully at Equation ??? , we notice that it exclusively involves state functions. As such, it applies to both reversible and irreversible processes. The fundamental equation, however, remains constrained to closed systems. This fact restricts its utility for chemistry, since when a chemical reaction happens, the mass in the system will change, and the system is no longer closed.

At the end of the 19th century, Josiah Willard Gibbs (1839–1903) proposed an important addition to the fundamental equation to account for chemical reactions. Gibbs was able to do so by introducing a new quantity that he called the chemical potential:

Definition: Chemical Potential

The chemical potential is the amount of energy absorbed or released due to a change of the particle number of a given chemical species.

The chemical potential of species i is usually abbreviated as μ_i, and it enters the fundamental equation of thermodynamics as:

$$dU = TdS - PdV + \sum_i \mu_i dn_i,$$

where dn_i is the differential change in the number of moles of substance i, and the summation extends over all chemical species in the system.

According to the fundamental equation, the internal energy of a system is a function of the three variables entropy, S, volume, V, and the numbers of moles $\{n_i\}$.[1] Because of their importance in determining the internal energy, these three variables are crucial in thermodynamics. Under several circumstances, however, they might not be the most convenient variables to use.[2] To emphasize the important connections given by the fundamental equation, we can use the notation $U(S, V, \{n_i\})$ and we can term S, V, and $\{n_i\}$ **natural variables** of the energy.

---

1. In the case of the numbers of moles we include them in curly brackets to indicate that there might be more than one, depending on how many species undergo chemical reactions.
2. For example, we don't always have a simple way to calculate or to measure the entropy.

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8.2: Thermodynamic Potentials

Starting from the fundamental equation, we can define new thermodynamic state functions that are more convenient to use under certain specific conditions. The new functions are determined by using a mathematical procedure called the Legendre transformation. A Legendre transformation is a linear change in variables that brings from an initial mathematical function to a new function obtained by subtracting one or more products of conjugate variables.[1]

Taking the internal energy as defined in Equation 8.1.1, we can perform such procedure by subtracting products of the following conjugate variables pairs: $T \text{ and } S$ or $-P \text{ and } V$. This procedure aims to define new state functions that depend on more convenient natural variables.[2] The new functions are called "thermodynamic potential energies," or simply **thermodynamic potentials**.[3] An example of this procedure is given by the definition of enthalpy that we have already seen in section 3.1.4. If we take the internal energy and subtract the product of two conjugate variables ($-P$ and V), we obtain a new state function called **enthalpy**, as we did in Equation 3.1.9). Taking the differential of this definition, we obtain:

$$dH = dU + VdP + PdV, \tag{8.2.1}$$

and using the fundamental equation, Equation 8.1.2, to replace dU, we obtain:

$$\begin{aligned} dH &= TdS - PdV + \sum_i \mu_i dn_i + VdP + PdV \\ &= TdS + VdP + \sum_i \mu_i dn_i. \end{aligned} \tag{8.2.2}$$

which is the fundamental equation for enthalpy. The natural variables of the enthalpy are S, P, and $\{n_i\}$. The Legendre transformation has allowed us to go from $U(S, V, \{n_i\})$ to $H(S, P, \{n_i\})$ by replacing the dependence on the extensive variable, V , with an intensive one, P.

Following the same procedure, we can perform another Legendre transformation to replace the entropy with a more convenient intensive variable such as the temperature. This can be done by defining a new function called the **Helmholtz free energy**, A, as:

$$A = U - TS \tag{8.2.3}$$

which, taking the differential and using the fundamental equation (Equation 8.2.2) becomes:

$$\begin{aligned} dA = dU - SdT - TdS &= TdS - PdV + \sum_i \mu_i dn_i - SdT - TdS \\ &= -SdT - PdV + \sum_i \mu_i dn_i. \end{aligned} \tag{8.2.4}$$

The Helmholtz free energy is named after Hermann Ludwig Ferdinand von Helmholtz (1821—1894), and its natural variables are temperature, volume, and the number of moles.

Finally, suppose we perform a Legendre transformation on the internal energy to replace both the entropy and the volume with intensive variables. In that case, we can define a new function called the **Gibbs free energy**, G, as:

$$G = U - TS + PV \tag{8.2.5}$$

which, taking again the differential and using Equation ??? becomes:

$$\begin{aligned} dG &= dU - SdT - TdS + VdP + PdV \\ &= TdS - PdV + \sum_i \mu_i dn_i - SdT - TdS + VdP + PdV \\ &= VdP - SdT + \sum_i \mu_i dn_i. \end{aligned} \tag{8.2.6}$$

The Gibbs free energy is named after Willard Gibbs himself, and its natural variables are temperature, pressure, and number of moles.

A summary of the four thermodynamic potentials is given in the following table.

Table 8.2.1

Name	Symbol	Fundamental Equation	Natural Variables
Energy	U	$dU = TdS - PdV + \sum_i \mu_i dn_i$	$S, V, \{n_i\}$
Enthalpy	H	$dH = TdS + VdP + \sum_i \mu_i dn_i$	$S, P, \{n_i\}$
Helmholtz Free Energy	A	$dA = -SdT - PdV + \sum_i \mu_i dn_i$	$T, V, \{n_i\}$
Gibbs Free Energy	G	$dG = VdP - SdT + \sum_i \mu_i dn_i$	$T, P, \{n_i\}$

The thermodynamic potentials are the analog of the potential energy in classical mechanics. Since the potential energy is interpreted as the capacity to do work, the thermodynamic potentials assume the following interpretations:

- Internal energy (U) is the capacity to do work plus the capacity to release heat.
- Enthalpy (H) is the capacity to do non-mechanical work plus the capacity to release heat.
- Gibbs free energy (G) is the capacity to do non-mechanical work.
- Helmholtz free energy (A) is the capacity to do mechanical plus non-mechanical work.[4]

Where non-mechanical work is defined as any type of work that is not expansion or compression (PV–work). A typical example of non-mechanical work is electrical work.

---

1. The mathematical condition that is fulfilled when performing a Legendre transformation is that the first derivatives of the original function and its transformation are inverse functions of each other.
2. The rigorous mathematical definition of conjugate variables is unimportant at this stage. However, we can relate the variables in a pair with basic physics by noticing how the first variable in a pair is always intensive (T and $-P$), while the second one is always extensive (S and V). The intensive variables represent thermodynamic driving forces (as compared with mechanical forces in classical mechanics), while the extensive ones are the thermodynamic displacements (as compared with spatial displacements in classical mechanics). Similarly to classical mechanics, the product of two conjugate variables in a pair yields an energy. The minus sign in front of P is explained by the fact that an increase in the force should always correspond to an increase in the displacement (while P and V are inversely related).
3. Even if we introduced both concepts in the same chapter, it is important to never confuse the *thermodynamic potentials*—which are potential energy functions—with the *chemical potential*—which have been introduced by Gibbs to study heat in chemical reactions.
4. For the mathematically inclined, an entertaining method to summarize the same thermodynamic potentials is the thermodynamic square.

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8.3: Free Energies

The Legendre transformation procedure translates all information contained in the original function to the new one. Therefore, $H(S,P,\{n_i\})$, $A(T,V,\{n_i\})$, and $G(T,P,\{n_i\})$ all contain the same information that is in $U(S,V,\{n_i\})$. However, the new functions depend on different natural variables, and they are useful at different conditions. For example, when we want to study chemical changes, we are interested in studying the term $\sum_i \mu_i dn_i$ that appears in each thermodynamic potential. To do so, we need to isolate the chemical term by keeping all other natural variables constant. For example, changes in the chemical term will correspond to changes in the internal energy at constant S and constant V:

$$dU(S,V,\{n_i\}) = \sum_i \mu_i dn_i \quad \text{if} \quad dS = dV = 0. \tag{8.3.1}$$

Similarly:

$$\begin{aligned} dH(S,P,\{n_i\}) &= \sum_i \mu_i dn_i \quad \text{if} \quad dS = dP = 0, \\ dA(T,V,\{n_i\}) &= \sum_i \mu_i dn_i \quad \text{if} \quad dT = dV = 0, \\ dG(T,P,\{n_i\}) &= \sum_i \mu_i dn_i \quad \text{if} \quad dT = dP = 0. \end{aligned} \tag{8.3.2}$$

The latter two cases are particularly interesting since most of chemistry happens at either constant volume,[1] or constant pressure.[2] Since $dS = 0$ is not a requirement for both free energies to describe chemical changes, we can apply either of them to study non-isentropic processes. If a process is not isentropic, it either increases the entropy of the universe, or it decreases it. Therefore—according to the second law—it is either spontaneous or not. Using this concept in conjunction with Clausius theorem, we can devise new criteria for inferring the spontaneity of a process that depends exclusively on the free energies.

Recalling Clausius theorem:

$$dS^{\text{sys}} \geq \frac{đQ}{T_{\text{surr}}} \quad \longrightarrow \quad TdS \geq đQ, \tag{8.3.3}$$

we can consider the two cases: constant V ($đQ_V = dU$, left), and constant P ($đQ_P = dH$, right):

$$\begin{array}{ll} \text{constant } V: & \text{constant } P: \\ TdS \geq dU & TdS \geq dH \\ TdS - dU \geq 0 & TdS - dH \geq 0 \end{array} \tag{8.3.4}$$

we can then simplify the definition of free energies, eqs. 8.2.4 and 8.2.6:

$$\begin{array}{ll} \text{constant } T,V: & \text{constant } T,P: \\ (dA)_{T,V} = dU - TdS & (dG)_{T,P} = dH - TdS \\ dU = (dA)_{T,V} + TdS & dH = (dG)_{T,P} + TdS \end{array} \tag{8.3.5}$$

and by merging dU and dH from eqs. ??? into Clausius theorem expressed using eqs. ???, we obtain:

$$\begin{array}{ll} TdS - (dA)_{T,V} - TdS \geq 0 & TdS - (dG)_{T,P} - TdS \geq 0 \\ (dA)_{T,V} \leq 0 & (dG)_{T,P} \leq 0. \end{array} \tag{8.3.6}$$

These equations represent the conditions on dA and dG for inferring the spontaneity of a process, and can be summarized as follows:

Definition: Spontaneous Process

During a spontaneous process at constant temperature and volume, the Helmholtz free energy will decrease $(dA < 0)$, until it reaches a stationary point at which the system will be at equilibrium $(dA = 0)$.
During a spontaneous process at constant temperature and pressure, the Gibbs free energy will decrease $(dG < 0)$, until it reaches a stationary point at which the system will be at equilibrium $(dG = 0)$.

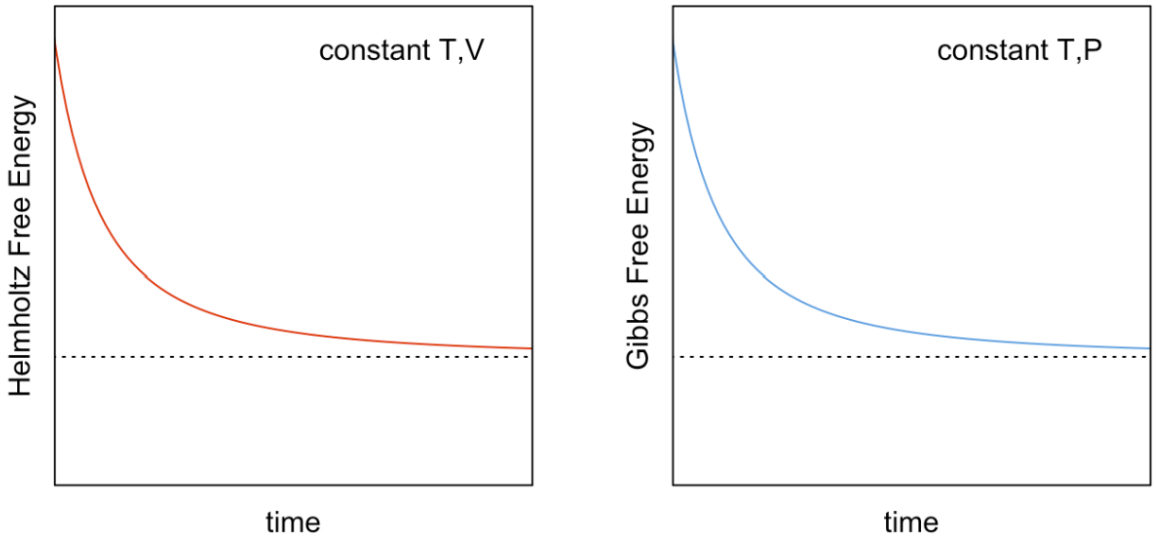


Figure 8.3.1: Behavior of Helmholtz (red) and Gibbs (blue) Free Energies for Spontaneous Processes at Constant T, V (left) and Constant T, P (right).

1. for example, several industrial processes in chemical plants.
2. for example, most processes in a chemistry lab.

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8.4: Maxwell Relations

Let's consider the fundamental equations for the thermodynamic potentials that we have derived in section 8.1:

$$\begin{aligned} dU(S,V,\{n_i\}) &= \ TdS - PdV + \sum_i \mu_i dn_i \\ dH(S,P,\{n_i\}) &= \ TdS + VdP + \sum_i \mu_i dn_i \\ dA(T,V,\{n_i\}) &= -SdT - PdV + \sum_i \mu_i dn_i \\ dG(T,P,\{n_i\}) &= -SdT + VdP + \sum_i \mu_i dn_i \ . \end{aligned} \tag{8.4.1}$$

From the knowledge of the natural variable of each potential, we could reconstruct these formulas by using the total differential formula:

$$\begin{aligned} dU &= \underbrace{\left(\frac{\partial U}{\partial S}\right)_{V,\{n_i\}}}_{T} dS + \underbrace{\left(\frac{\partial U}{\partial V}\right)_{S,\{n_i\}}}_{-P} dV + \sum_i \underbrace{\left(\frac{\partial U}{\partial n_i}\right)_{S,V,\{n_{j\neq i}\}}}_{\mu_i} dn_i \\ dH &= \underbrace{\left(\frac{\partial H}{\partial S}\right)_{P,\{n_i\}}}_{T} dS + \underbrace{\left(\frac{\partial H}{\partial P}\right)_{S,\{n_i\}}}_{V} dP + \sum_i \underbrace{\left(\frac{\partial H}{\partial n_i}\right)_{S,P,\{n_{j\neq i}\}}}_{\mu_i} dn_i \\ dA &= \underbrace{\left(\frac{\partial A}{\partial T}\right)_{V,\{n_i\}}}_{-S} dT + \underbrace{\left(\frac{\partial A}{\partial V}\right)_{T,\{n_i\}}}_{-P} dV + \sum_i \underbrace{\left(\frac{\partial A}{\partial n_i}\right)_{T,V,\{n_{j\neq i}\}}}_{\mu_i} dn_i \\ dG &= \underbrace{\left(\frac{\partial G}{\partial T}\right)_{V,\{n_i\}}}_{-S} dT + \underbrace{\left(\frac{\partial G}{\partial P}\right)_{T,\{n_i\}}}_{V} dP + \sum_i \underbrace{\left(\frac{\partial G}{\partial n_i}\right)_{T,P,\{n_{j\neq i}\}}}_{\mu_i} dn_i \ , \end{aligned} \tag{8.4.2}$$

we can derive the following new definitions:

$$\begin{aligned} T &= \left(\frac{\partial U}{\partial S}\right)_{V,\{n_i\}} = \left(\frac{\partial H}{\partial S}\right)_{P,\{n_i\}} \\ -P &= \left(\frac{\partial U}{\partial V}\right)_{S,\{n_i\}} = \left(\frac{\partial A}{\partial V}\right)_{T,\{n_i\}} \\ V &= \left(\frac{\partial H}{\partial P}\right)_{S,\{n_i\}} = \left(\frac{\partial G}{\partial P}\right)_{T,\{n_i\}} \\ -S &= \left(\frac{\partial A}{\partial T}\right)_{V,\{n_i\}} = \left(\frac{\partial G}{\partial T}\right)_{V,\{n_i\}} \\ &\text{and:} \\ \mu_i &= \left(\frac{\partial U}{\partial n_i}\right)_{S,V,\{n_{j\neq i}\}} = \left(\frac{\partial H}{\partial n_i}\right)_{S,P,\{n_{j\neq i}\}} \\ &= \left(\frac{\partial A}{\partial n_i}\right)_{T,V,\{n_{j\neq i}\}} = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,\{n_{j\neq i}\}} \ . \end{aligned} \tag{8.4.3}$$

Since T, P, V, and S are now defined as partial first derivatives of a thermodynamic potential, we can now take a second partial derivation with respect to a separate variable, and rely on Schwartz's theorem to derive the following relations:

$$\begin{aligned}
\frac{\partial^2 U}{\partial S \partial V} &= +\left(\frac{\partial T}{\partial V}\right)_{S,\{n_{j\neq i}\}} = -\left(\frac{\partial P}{\partial S}\right)_{V,\{n_{j\neq i}\}} \\
\frac{\partial^2 H}{\partial S \partial P} &= +\left(\frac{\partial T}{\partial P}\right)_{S,\{n_{j\neq i}\}} = +\left(\frac{\partial V}{\partial S}\right)_{P,\{n_{j\neq i}\}} \\
-\frac{\partial^2 A}{\partial T \partial V} &= +\left(\frac{\partial S}{\partial V}\right)_{T,\{n_{j\neq i}\}} = +\left(\frac{\partial P}{\partial T}\right)_{V,\{n_{j\neq i}\}} \\
\frac{\partial^2 G}{\partial T \partial P} &= -\left(\frac{\partial S}{\partial P}\right)_{T,\{n_{j\neq i}\}} = +\left(\frac{\partial V}{\partial T}\right)_{P,\{n_{j\neq i}\}}
\end{aligned} \tag{8.4.4}$$

The relations in ??? are called **Maxwell relations**,[1] and are useful in experimental settings to relate quantities that are hard to measure with others that are more intuitive.

Exercise 8.4.1

Derive the last Maxwell relation in Equation ???.

Answer available at the end of this section.

1. Maxwell relations should not be confused with the Maxwell equations of electromagnetism.

Answers

Exercise 8.4.1

We can start our derivation from the definition of V and S as a partial derivative of G:

$$V = \left(\frac{\partial G}{\partial P}\right)_{T,\{n_i\}} \qquad \text{and:} \qquad -S = \left(\frac{\partial G}{\partial T}\right)_{V,\{n_i\}},$$

and then take a second partial derivative of each quantity with respect to the second variable:

$$\begin{aligned}
\left(\frac{\partial V}{\partial T}\right)_{P,\{n_i\}} &= \frac{\partial}{\partial T}\left[\left(\frac{\partial G}{\partial P}\right)_{T,\{n_i\}}\right]_{P,\{n_i\}} \\
-\left(\frac{\partial S}{\partial P}\right)_{T,\{n_i\}} &= \frac{\partial}{\partial P}\left[\left(\frac{\partial G}{\partial T}\right)_{P,\{n_i\}}\right]_{T,\{n_i\}}.
\end{aligned} \tag{8.4.5}$$

These two derivatives are mixed partial second derivatives of G with respect to T and P, and therefore, according to Schwartz's theorem, they are equal to each other:

$$\frac{\partial}{\partial T}\left[\left(\frac{\partial G}{\partial P}\right)_{T,\{n_i\}}\right]_{P,\{n_i\}} = \frac{\partial}{\partial P}\left[\left(\frac{\partial G}{\partial T}\right)_{P,\{n_i\}}\right]_{T,\{n_i\}},$$

$$\text{hence:} \tag{8.4.6}$$

$$\left(\frac{\partial V}{\partial T}\right)_{P,\{n_i\}} = -\left(\frac{\partial S}{\partial P}\right)_{T,\{n_i\}},$$

which is the last of Maxwell relations, as defined in Equation ???. This relation is particularly useful because it connects the quantity $\left(\frac{\partial S}{\partial P}\right)_{T,\{n_i\}}$—which is impossible to measure in a lab—with the quantity $\left(\frac{\partial V}{\partial T}\right)_{P,\{n_i\}}$—which is easier to measure from an experiment that determines isobaric volumetric thermal expansion coefficients.

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9: GIBBS FREE ENERGY

In this chapter, we will concentrate on chemical processes that happen at constant T and constant P.[1] As such, we will focus our attention on the Gibbs free energy.

---

1. The majority of chemical reactions in a lab happens at those conditions, and all biological functions happen at those conditions as well.

9.1: Gibbs Equation

9.2: Temperature Dependence of ΔG

9.3: Pressure Dependence of ΔG

9.4: Composition Dependence of ΔG

9.5: Chemical Equilibrium

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9.1: Gibbs Equation

Recalling from chapter 8, the definition of G is:

$$G = U - TS + PV = H - TS,$$

which, taking the differential at constant T and P, becomes:

$$dG = dH \overbrace{-SdT}^{=0} - TdS = dH - TdS.$$

Integrating Equation ??? between the initial and final states of a process results in:

$$\begin{aligned} \int_i^f dG &= \int_i^f dH - T\int_i^f dS \\ \Delta G &= \Delta H - T\Delta S \end{aligned} \tag{9.1.1}$$

which is the famous **Gibbs equation** for ΔG. Using Definition: Spontaneous Process, we can use ΔG to infer the spontaneity of a chemical process that happens at constant T and P using $\Delta G \leq 0$. If we set ourselves at standard conditions, we can calculate the standard Gibbs free energy of formation, $\Delta_{\text{rxn}}G^{\ominus}$, for any reaction as:

$$\begin{aligned} \Delta_{\text{rxn}}G^{\ominus} &= \Delta_{\text{rxn}}H^{\ominus} - T\Delta_{\text{rxn}}S^{\ominus} \\ &= \sum_i \nu_i \Delta_{\text{f}}H_i^{\ominus} + T\sum_i \nu_i S_i^{\ominus}, \end{aligned} \tag{9.1.2}$$

where $\Delta_{\text{f}}H_i^{\ominus}$ are the standard enthalpies of formation, $S_i^{\ominus}$ are the standard entropies, and ν_i are the stoichiometric coefficients for every species i involved in the reaction. All these quantities are commonly available, and we have already discussed their usage in chapters 4 and 7, respectively.[1]

The following four options are possible for $\Delta G^{\ominus}$ of a chemical reaction:

$\Delta G^{\ominus}$		$\Delta H^{\ominus}$	$\Delta S^{\ominus}$	**Spontaneous?**
–	*if*	–	+	*Always*
+	*if*	+	–	*Never*
–/+	*if*	–	–	*Depends on T:* spontaneous at low T
+/–	*if*	+	+	*Depends on T:* spontaneous at high T

Or, in other words:

- Exothermic reactions that increase the entropy are always spontaneous.
- Endothermic reactions that reduce the entropy are always non-spontaneous.
- For the other two cases, the spontaneity of the reaction depends on the temperature:
  - Exothermic reactions that reduce the entropy are spontaneous at low T.
  - Endothermic reactions that increase the entropy are spontaneous at high T.

A simple criterion to evaluate the entropic contribution of a reaction is to look at the total number of moles of the reactants and the products (as the sum of the stoichiometric coefficients). If the reaction is producing more molecules than it destroys $\left(\left|\sum_{\text{products}} \nu_i\right| > \left|\sum_{\text{reactants}} \nu_i\right|\right)$, it will increase the entropy. Vice versa, if the total number of moles in a reaction is reducing $\left(\left|\sum_{\text{products}} \nu_i\right| < \left|\sum_{\text{reactants}} \nu_i\right|\right)$, the entropy will also reduce.

As we saw in section 8.2, the natural variables of the Gibbs free energy are the temperature, T, the pressure, P, and chemical

composition, as the number of moles $\{n_i\}$. The Gibbs free energy can therefore be expressed using the total differential as (see also, last formula in Equation 8.4.2):

$$dG(T,P,\{n_i\}) = \underbrace{\left(\frac{\partial G}{\partial T}\right)_{P,\{n_i\}} dT}_{\text{temperature dependence}} + \underbrace{\left(\frac{\partial G}{\partial P}\right)_{T,\{n_i\}} dP}_{\text{pressure dependence}} + \sum_i \underbrace{\left(\frac{\partial G}{\partial n_i}\right)_{T,P,\{n_{j\neq i}\}} dn_i}_{\text{composition dependence}}. \tag{9.1.3}$$

If we know the behavior of G as we vary each of the three natural variables independently of the other two, we can reconstruct the total differential dG. Each of these terms represents a coefficient in Equation 9.1.3, which are given in Equation 8.4.3.

---

1. ⚠It is not uncommon to see values of $\Delta_f G^\ominus$ tabulated alongside $\Delta_f H^\ominus$ and $S_i^\ominus$, which simplifies even further the calculation. In fact, a comprehensive list of standard Gibbs free energy of formation of inorganic and organic compounds is reported in the appendix of this book 16. For cases where $\Delta_f G^\ominus$ are not reported, they can always be calculated by their constituents.

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9.2: Temperature Dependence of ΔG

$$\left(\frac{\partial G}{\partial T}\right)_{P,\{n_i\}} = -S$$

Let's analyze the first coefficient that gives the dependence of the Gibbs energy on temperature. Since this coefficient is equal to $-S$ and the entropy is always positive, G must decrease when T increases at constant P and $\{n_i\}$, and vice versa.

If we replace this coefficient for $-S$ in the Gibbs equation, Equation 9.1.3, we obtain:

$$\Delta G = \Delta H + T\left(\frac{\partial \Delta G}{\partial T}\right)_{P,\{n_i\}}, \tag{9.2.1}$$

and since Equation 9.2.1 includes both ΔG and its partial derivative with respect to temperature $\left(\frac{\partial \Delta G}{\partial T}\right)_{P,\{n_i\}}$ we need to rearrange it to include the temperature derivative only. To do so, we can start by evaluating the partial derivative of $\left(\frac{\Delta G}{T}\right)$ using the chain rule:

$$\left[\frac{\partial\left(\frac{\Delta G}{T}\right)}{\partial T}\right]_{P,\{n_i\}} = \frac{1}{T}\left(\frac{\partial \Delta G}{\partial T}\right)_{P,\{n_i\}} - \frac{1}{T^2}\Delta G, \tag{9.2.2}$$

which, replacing ΔG from Equation 9.2.1 into Equation 9.2.2, becomes:

$$\begin{aligned}\left[\frac{\partial\left(\frac{\Delta G}{T}\right)}{\partial T}\right]_{P,\{n_i\}} &= \frac{1}{T}\left(\frac{\partial \Delta G}{\partial T}\right)_{P,\{n_i\}} - \frac{1}{T^2}\left[\Delta H + T\left(\frac{\partial \Delta G}{\partial T}\right)_{P,\{n_i\}}\right] \\ &= \frac{1}{T}\left(\frac{\partial \Delta G}{\partial T}\right)_{P,\{n_i\}} - \frac{\Delta H}{T^2} - \frac{1}{T}\left(\frac{\partial \Delta G}{\partial T}\right)_{P,\{n_i\}},\end{aligned} \tag{9.2.3}$$

which simplifies to:

$$\left[\frac{\partial\left(\frac{\Delta G}{T}\right)}{\partial T}\right]_{P,\{n_i\}} = -\frac{\Delta H}{T^2}. \tag{9.2.4}$$

Equation ??? is known as the **Gibbs–Helmholtz equation**, and is useful in its integrated form to calculate the Gibbs free energy for a chemical reaction at any temperature T by knowing just the standard Gibbs free energy of formation and the standard enthalpy of formation for the individual species, which are usually reported at $T = 298\ \text{K}$. The integration is performed as follows:

$$\begin{aligned}\int_{T_i=298\ \text{K}}^{T_f=T} \frac{\partial\left(\frac{\Delta_{\text{rxn}} G}{T}\right)}{\partial T} &= -\int_{T_i=298\ \text{K}}^{T_f=T} \frac{\Delta_{\text{rxn}} H}{T^2} \\ \frac{\Delta_{\text{rxn}} G^{\ominus}(T)}{T} &= \frac{\Delta_{\text{rxn}} G^{\ominus}}{298\ \text{K}} + \Delta_{\text{rxn}} H^{\ominus}\left(\frac{1}{T^2} - \frac{1}{(298\ \text{K})^2}\right),\end{aligned} \tag{9.2.5}$$

giving the integrated Gibbs–Helmholtz equation:

$$\frac{\Delta_{\text{rxn}} G^{\ominus}(T)}{T} = \frac{\sum_i \nu_i \Delta_{\text{f}} G_i^{\ominus}}{298\ \text{K}} + \sum_i \nu_i \Delta_{\text{f}} H_i^{\ominus}\left(\frac{1}{T^2} - \frac{1}{(298\ \text{K})^2}\right) \tag{9.2.6}$$

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9.3: Pressure Dependence of ΔG

$$\left(\frac{\partial G}{\partial P}\right)_{T,\{n_i\}} = V$$

We can now turn the attention to the second coefficient that gives how the Gibbs free energy changes when the pressure change. To do this, we put the system at constant T and $\{n_i\}$, and then we consider infinitesimal variations of G. From Equation 8.2.6:

$$dG = VdP - SdT + \sum_i \mu_i dn_i \quad \xrightarrow{\text{constant } T,\{n_i\}} \quad dG = VdP, \tag{9.3.1}$$

which is the differential equation that we were looking for. To study changes of G for macroscopic changes in P, we can integrate Equation 9.3.1 between initial and final pressures, and considering an ideal gas, we obtain:

$$\begin{aligned} \int_i^f dG &= \int_i^f VdP \\ \Delta G &= nRT \int_i^f \frac{dP}{P} = nRT \ln \frac{P_f}{P_i}. \end{aligned} \tag{9.3.2}$$

If we take $P_i = P^{\ominus} = 1 \text{ bar}$, we can rewrite Equation ??? as:

$$G = G^{\ominus} + nRT \ln \frac{P_f}{P^{\ominus}}, \tag{9.3.3}$$

which is useful to convert standard Gibbs free energies of formation at pressures different than standard pressure, using:

$$\Delta_f G = \Delta_f G^{\ominus} + nRT \ln \frac{P_f}{\underbrace{P^{\ominus}}_{=1 \text{ bar}}} = \Delta_f G^{\ominus} + nRT \ln P_f \tag{9.3.4}$$

For liquids and solids, V is essentially independent of P (liquids and solids are incompressible), and Equation 9.3.1 can be integrated as:

$$\Delta G = \int_i^f VdP = V \int_i^f dP = V\Delta P. \tag{9.3.5}$$

The plots in Figure 9.3.1 show the remarkable difference in the behaviors of $\Delta_f G$ for a gas and for a liquid, as obtained from eqs. ??? and 9.3.5.

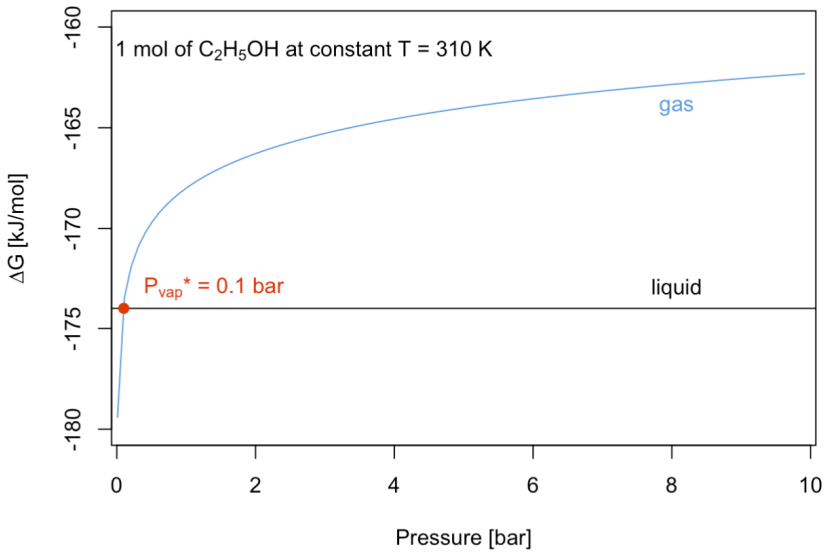


Figure 9.3.1: Dependence of the Gibbs Free Energy of Formation of Liquid and Gaseous Ethanol at T = 310 K. The Curves Cross at the Vapor Pressure of Liquid Ethanol at this Temperature, which is 0.1 bar.

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9.4: Composition Dependence of ΔG

$$\left(\frac{\partial G}{\partial n_i}\right)_{T,P} = \mu_i$$

The third and final coefficient gives the chemical potential as the dependence of G on the chemical composition at constant T and P. Similarly to the previous cases, we can take the definition of the coefficient and integrate it directly between the initial and final stages of a reaction. If we consider a reaction product, pure substance i, at the beginning of the reaction there will be no moles of it $n_i = 0$, and consequently $G = 0$.[1] We can then integrate the left-hand side between zero and the number of moles of product at the end of the reaction, n, and the right-hand side between zero and the Gibbs free energy of the product, G. The integral will become:

$$\int_0^G dG = \int_0^n \mu^* dn, \tag{9.4.1}$$

where μ^* indicates the chemical potential of a pure substance, which is independent on the number of moles by definition. As such, Equation 9.4.1 becomes:

$$\int_0^G dG = \mu^* \int_0^n dn \quad \rightarrow \quad G = \mu^* n \quad \rightarrow \quad \mu^* = \frac{G}{n}, \tag{9.4.2}$$

which gives a straightforward interpretation of the chemical potential of a pure substance as the molar Gibbs free energy.

We can start from Equation 9.3.3 and write for a pure substance that is brought from $P_i = P^\ominus$ to $P_f = P$ at constant T:

$$G - G^\ominus = nRT \ln \frac{P}{P^\ominus}, \tag{9.4.3}$$

dividing both sides by n, we obtain:

$$\frac{G}{n} - \frac{G^\ominus}{n} = RT \ln \frac{P}{P^\ominus}, \tag{9.4.4}$$

which, for a pure substance at $P^\ominus = 1 \text{ bar}$, becomes:

$$\mu^* - \mu^\ominus = RT \ln P. \tag{9.4.5}$$

Notice that, while we use the pressure of the gas inside the logarithm in Equation 9.4.5, the quantity is formally divided by the standard pressure $P^\ominus = 1 \text{ bar}$, and therefore it is a dimensionless quantity, as it should be. For simplicity of notation, however, we will omit the division by $P^\ominus$ in the remaining of this textbook, especially wherever it does not create confusion. Let's now consider a mixture of ideal gases, and let's try to find out whether the chemical potential of a pure gas inside the mixture, μ_i^{mixture}, is the same as its chemical potential outside the mixture, μ^*. To do so, we can use Equation 9.4.5 and replace the pressure P with the partial pressure P_i:

$$\mu_i^{\text{mixture}} = \mu_i^\ominus + RT \ln P_i, \tag{9.4.6}$$

where the partial pressure P_i can be obtained from the simple relation that is known as **Dalton's Law**:

$$P_i = y_i P, \tag{9.4.7}$$

with y_i being the concentration of gas i measured as a mole fraction in the gas phase $y_i = \dfrac{n_i}{n_{\text{TOT}}} < 1$. Replacing Equation 9.4.7 into Equation 9.4.6, we obtain:

$$\begin{aligned} \mu_i^{\text{mixture}} &= \mu_i^\ominus + RT \ln(y_i P) \\ &= \underbrace{\mu_i^\ominus + RT \ln P}_{\mu_i^*} + RT \ln y_i, \end{aligned} \tag{9.4.8}$$

which then reduces to the following equation:

$$\mu_i^{\text{mixture}} = \mu_i^* + RT \ln y_i. \tag{9.4.9}$$

Analyzing Equation 9.4.9, we can immediately see that, since $y_i < 1$:

$$\mu_i^{\text{mixture}} < \mu_i^*, \tag{9.4.10}$$

or, in other words, the chemical potential of a substance in the mixture is always lower than the chemical potential of the pure substance. If we consider a process where we start from two separate pure ideal gases and finish with a mixture of the two, we can calculate the change in Gibbs free energy due to the mixing process with:

$$\Delta_{\text{mixing}} G = \sum n_i \left(\mu_i^{\text{mixture}} - \mu_i^*\right) < 0, \tag{9.4.11}$$

or, in other words, the process is spontaneous under all circumstances, and pure ideal gases will always mix.

---

1. For reactants, the same situation usually applies but in reverse. More complicated cases where the reaction does not consume all reactants are possible, but insignificant for the following treatment.

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9.5: Chemical Equilibrium

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10: CHEMICAL EQUILIBRIUM

10.1: Reaction Quotient and Equilibrium Constant
10.2: Temperature Dependence of Keq
10.3: Pressure and Composition Dependence of Keq

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10.1: Reaction Quotient and Equilibrium Constant

Let's consider a prototypical reaction at constant T, P:

$$a\mathrm{A} + b\mathrm{B} \rightarrow c\mathrm{C} + d\mathrm{D} \tag{10.1.1}$$

The Gibbs free energy of the reaction is defined as:

$$\Delta_{\mathrm{rxn}}G = G_{\mathrm{products}} - G_{\mathrm{reactants}} = G^{\mathrm{C}} + G^{\mathrm{D}} - G^{\mathrm{A}} - G^{\mathrm{B}}, \tag{10.1.2}$$

and replacing the absolute Gibbs free energies with the chemical potentials μ_i, we obtain:

$$\Delta_{\mathrm{rxn}}G = c\mu_{\mathrm{C}} + d\mu_{\mathrm{D}} - a\mu_{\mathrm{A}} - b\mu_{\mathrm{B}}. \tag{10.1.3}$$

Assuming the reaction is happening in the gas phase, we can then use Equation 9.4.6 to replace the chemical potentials with their value in the reaction mixture, as:

$$\begin{aligned}\Delta_{\mathrm{rxn}}G &= c(\mu_{\mathrm{C}}^{\ominus} + RT\ln P_{\mathrm{C}}) + d(\mu_{\mathrm{D}}^{\ominus} + RT\ln P_{\mathrm{D}}) - a(\mu_{\mathrm{A}}^{\ominus} + RT\ln P_{\mathrm{A}}) - b(\mu_{\mathrm{B}}^{\ominus} + RT\ln P_{\mathrm{B}}) \\ &= \underbrace{c\mu_{\mathrm{C}}^{\ominus} + d\mu_{\mathrm{D}}^{\ominus} - a\mu_{\mathrm{A}}^{\ominus} - b\mu_{\mathrm{B}}^{\ominus}}_{\Delta_{\mathrm{rxn}}G^{\ominus}} + RT\ln\frac{P_{\mathrm{C}}^{c}\cdot P_{\mathrm{D}}^{d}}{P_{\mathrm{A}}^{a}\cdot P_{\mathrm{B}}^{b}}.\end{aligned} \tag{10.1.4}$$

We can define a new quantity called the *reaction quotient* as a function of the partial pressures of each substance:[1])

$$Q_P = \frac{P_{\mathrm{C}}^{c}\cdot P_{\mathrm{D}}^{d}}{P_{\mathrm{A}}^{a}\cdot P_{\mathrm{B}}^{b}}, \tag{10.1.5}$$

and we can then simply rewrite Equation ??? using Equation 10.1.5 as:

$$\Delta_{\mathrm{rxn}}G = \Delta_{\mathrm{rxn}}G^{\ominus} + RT\ln Q_P. \tag{10.1.6}$$

This equation tells us that the sign of $\Delta_{\mathrm{rxn}}G$ is influenced by the reaction quotient Q_P. For a spontaneous reaction at the beginning, the partial pressures of the reactants are much higher than the partial pressures of the products, therefore $Q_P \ll 1$ and $\Delta_{\mathrm{rxn}}G < 0$, as we expect. As the reaction proceeds, the partial pressures of the products will increase, while the partial pressures of the reactants will decrease. Consequently, both Q_P and $\Delta_{\mathrm{rxn}}G$ will increase. The reaction will completely stop when $\Delta_{\mathrm{rxn}}G = 0$, which is the chemical equilibrium point. At the reaction equilibrium:

$$\Delta_{\mathrm{rxn}}G = 0 = \Delta_{\mathrm{rxn}}G^{\ominus} + RT\ln K_P, \tag{10.1.7}$$

where we have defined a new quantity called **equilibrium constant**, as the value the reaction quotient assumes when the reaction reaches equilibrium, and we have denoted it with the symbol K_P.[2] From Equation 10.1.7 we can derive the following fundamental equation on the standard Gibbs free energy of reaction:

$$\Delta_{\mathrm{rxn}}G^{\ominus} = -RT\ln K_P. \tag{10.1.8}$$

To extend the concept of K_P beyond the four species in the prototypical reaction (10.1), we can use the product of a series symbol ($\prod_i$), and write:

$$K_P = \prod_i P_{i,\mathrm{eq}}^{\nu_i}, \tag{10.1.9}$$

where $P_{i,\mathrm{eq}}$ are the partial pressure of each species at equilibrium. Eq. (10.1.9) is in principle valid for ideal gases only. However, reaction involving ideal gases are pretty rare. As such, we can further extend the concept of equilibrium constant and write:

$$K_{\mathrm{eq}} = \prod_i a_{i,\mathrm{eq}}^{\nu_i}, \tag{10.1.10}$$

where we have replaced the partial pressure at equilibrium, $P_{i,\mathrm{eq}}$, with a new concept introduced initially by Gilbert Newton Lewis (1875–1946),[3] that he termed **activity**, and represented by the letter a. For ideal gases, it is clear that $a_i = P_i/P^{\ominus}$. For non-ideal

gases, the activity is equal to the fugacity $a_i = f_i/P^{\ominus}$, a concept that we will investigate in the next chapter. For pure liquids and solids, the activity is simply $a_i = 1$. For diluted solutions, the activity is equal to a measured concentration (such as, for example, the mole fraction x_i in the liquid phase, and y_i in the gas phase, or the molar concentration $[i]/[i]^{\ominus}$ with $[i]^{\ominus} = 1\ [mol/L]$). Finally for concentrated solutions, the activity is related to the measured concentration via an activity coefficient. We will return to the concept of activity in chapter 14, when we will specifically deal with solutions. For now, it is interesting to use the activity to write the definition of the following two constants:

$$K_y = \prod_i (y_{i,\text{eq}})^{\nu_i} \qquad K_C = \left(\prod_i [i]_{\text{eq}}/[i]^{\ominus} \right)^{\nu_i}, \tag{10.1.11}$$

which can then be related with K_P for a mixture of ideal gases using:

$$P_i = y_i P \qquad P_i = \frac{n_i}{V} RT = [i]RT, \tag{10.1.12}$$

which then results in:

$$K_P = K_y \cdot \left(\frac{P}{P^{\ominus}} \right)^{\Delta\nu} \qquad K_P = K_C \left(\frac{[i]^{\ominus} RT}{P^{\ominus}} \right)^{\Delta\nu}, \tag{10.1.13}$$

with $\Delta\nu = \sum_i \nu_i$.

Using the general equilibrium constant, K_{eq}, we can also rewrite the fundamental equation on $\Delta_{\text{rxn}}G^{\ominus}$ that we derived in Equation 10.1.8 to be applicable at most conditions, as:

$$\Delta_{\text{rxn}}G^{\ominus} = -RT \ln K_{\text{eq}}, \tag{10.1.14}$$

and since $\Delta_{\text{rxn}}G^{\ominus}$ depends on T, P and $\{n_i\}$, it is useful to explore how K_{eq} depends on those variables as well.

---

1. Notice that since we used Equation 9.4.5 to derive the reaction quotient, the partial pressures inside it are always dimensionless since they are divided by $P^{\ominus}$.
2. The subscript P refers to the fact that the equilibrium constant is measured in terms of partial pressures.
3. Gilber Lewis is the same scientist that invented the concept of Lewis Structures.

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10.2: Temperature Dependence of Keq

To study the temperature dependence of K_{eq} we can use Equation 10.1.14 for the general equilibrium constant and write:

$$\ln K_{\text{eq}} = -\frac{\Delta G^{\ominus}}{RT}, \tag{10.2.1}$$

which we can then differentiate with respect to temperature at constant $P, \{n_i\}$ on both sides:

$$\left(\frac{\partial \ln K_{\text{eq}}}{\partial T}\right)_{P,\{n_i\}} = -\frac{1}{R}\left[\frac{\partial\left(\frac{\Delta G^{\ominus}}{T}\right)}{\partial T}\right]_{P,\{n_i\}}, \tag{10.2.2}$$

and, using Gibbs-Helmholtz equation (Equation ???) to simplify the left hand side, becomes:

$$\left(\frac{\partial \ln K_{\text{eq}}}{\partial T}\right)_{P,\{n_i\}} = -\frac{1}{R}\left(-\frac{\Delta H^{\ominus}}{T^2}\right) = \frac{\Delta H^{\ominus}}{RT^2}, \tag{10.2.3}$$

which gives the dependence of $\ln K_{\text{eq}}$ on T that we were looking for. Equation 10.2.3 is also called **van 't Hoff equation,**[1] and it is the mathematical expression of Le Chatelier's principle. The simplest interpretation is as follows:

- For an exothermic reaction ($\Delta H^{\ominus} < 0$): K_{eq} will decrease as the temperature increases.
- For an endothermic reaction ($\Delta H^{\ominus} > 0$): K_{eq} will increase as the temperature increases.

If we integrate the van 't Hoff equation between two arbitrary points at constant P, and assuming constant $\Delta H^{\ominus}$, we obtain the following:

$$\int_1^2 d\ln K_{\text{eq}} = \frac{\Delta H^{\ominus}}{R}\int_1^2 \frac{dT}{T^2}, \tag{10.2.4}$$

which leads to the linear equation:

$$\ln K_{\text{eq}}(2) = \ln K_{\text{eq}}(1) - \frac{\Delta H^{\ominus}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right). \tag{10.2.5}$$

which is the equation that produces the so-called **van 't Hoff plots**, from which $\Delta H^{\ominus}$ can be experimentally determined:

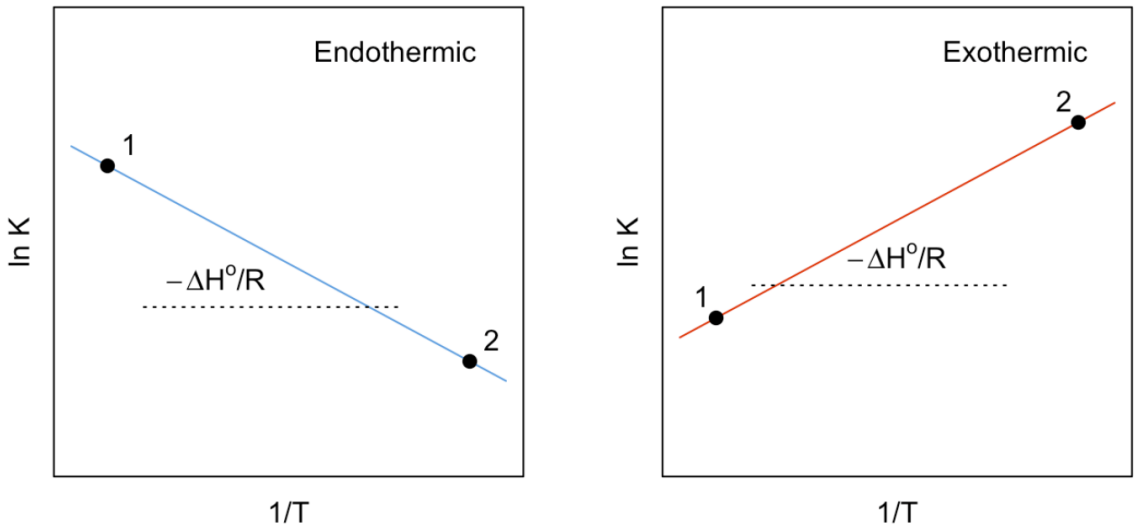


Figure 10.2.1: Van 't Hoff Plots for an Endothermic (Left, Blue) and an Exothermic (Right, Red) Reactions at Constant P.

1. named after Jacobus Henricus "Henry" van 't Hoff Jr. (1852–1911).

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10.3: Pressure and Composition Dependence of Keq

While K_P is independent of both temperature and number of moles for an ideal gas, the same is not necessarily true for the other equilibrium constants.

$$\left(\frac{\partial K_P}{\partial P}\right)_{T,\{n_i\}} = 0 \qquad \left(\frac{\partial K_P}{\partial n_i}\right)_{T,P} = 0. \tag{10.3.1}$$

For example, it is easy to look at Equation 10.1.13 and determine that K_y usually depends on P.[1] Using Dalton's Law, Equation 9.4.7, we can also notice that the equilibrium partial pressures of the reactants and products in a gas-phase reaction can be expressed in terms of their equilibrium mole fractions y_i and the total pressure P. As such, we can use K_y to demonstrate that the equilibrium mole fractions will change when P changes,[2] as it is demonstrated by the following exercise.

Exercise 10.3.1

Calculate the mole fraction change for the dissociation of $\mathrm{Cl}_{2(g)}$ when the pressure is increased from $P^\ominus$ to $P_f = 2.5\ \text{bar}$ at constant $T = 2\ 298\ \text{K}$, knowing that $\Delta_\text{f}G^\ominus_{\mathrm{Cl}_{(g)}} = 105.3\ \text{kJ/mol}$ and $\Delta_\text{f}H^\ominus_{\mathrm{Cl}_{(g)}} = 121.3\ \text{kJ/mol}$, and remembering that both of these values are tabulated at $T = 298\ \text{K}$.

Answer available at the end of this section.

The dependence of K_eq on P highlighted above is another mathematical expression of Le Chatelier's principle, on this occasion, for changes in pressure. The interpretation For a reaction happening in the gas phase is as follows:

- If the total pressure increases, the equilibrium will shift towards the side of the chemical equation that contains the smallest total amount of moles (the equilibrium in exercise 10.3.1 shifts toward the reactant).

---

1. K_y becomes independent of P in the particular case where $\Delta\nu = 0$, i.e., for reactions where the total number of moles of reactants is the same as the total number of moles of the products.
2. Keep in mind that K_P will *not* change.
3. Notice how a positive $\Delta_\text{rxn}G^\ominus$ indicates that the dissociation of $\mathrm{CL}_{2(g)}$ is non-spontaneous at $T = 298\ \text{K}$ and $P = 1\ \text{bar}$. As such, we should expect a very small value for K_P.
4. The results corresponds to $K_P = 1.2 \times 10^{-37}$, an incredible miniscule number, as we should expect given the data of $\Delta_\text{rxn}G^\ominus$.
5. Concentration cannot be negative.

Answers

Exercise 10.3.1

Let's consider the reaction:

$$\mathrm{Cl}_{2(g)} \rightleftarrows 2\mathrm{Cl}_{(g)}$$

We can divide the exercise into two parts. In the first one, we will deal with calculating the equilibrium constant at $T = 2\ 298\ \text{K}$ from the data at $T = 298\ \text{K}$. In the second one, we will calculate the change in mole fraction when the pressure is increased from $P^\ominus = 1\ \text{bar}$ to $P_f = 2.5\ \text{bar}$.

Let's begin the first part by calculating $\Delta_\text{rxn}G^\ominus$ and $\Delta_\text{rxn}H^\ominus$ from:

$$\Delta_\text{rxn}G^\ominus = 2\Delta_\text{f}G^\ominus_{\mathrm{Cl}_{(g)}} - \Delta_\text{f}G^\ominus_{\mathrm{Cl}_{2(g)}}$$
$$\Delta_\text{rxn}H^\ominus = 2\Delta_\text{f}H^\ominus_{\mathrm{Cl}_{(g)}} - \Delta_\text{f}H^\ominus_{\mathrm{Cl}_{2(g)}},$$

and since $\mathrm{Cl}_{2(g)}$ is an element in its most stable form at $T = 298\ \text{K}$, its standard enthalpy and Gibbs free energy of formation are $\Delta_\text{f}H^\ominus_{\mathrm{Cl}_{2(g)}} = \Delta_\text{f}G^\ominus_{\mathrm{Cl}_{2(g)}} = 0$. Therefore:[3]

$$\Delta_\text{rxn}G^\ominus = 2 \cdot 105.3 - 0 = 210.6\ \text{kJ/mol}$$
$$\Delta_\text{rxn}H^\ominus = 2 \cdot 121.3 - 0 = 242.6\ \text{kJ/mol}.$$

Using Equation 10.1.8 to calculate $K_P(P^\ominus, 298\ \text{K})$, we obtain:[4]

$$\ln[K_P(P^\ominus, 298\ \text{K})] = \frac{-\Delta_\text{rxn}G^\ominus}{RT} = \frac{-210.6 \times 10^3}{8.31 \cdot 298} = -85.0.$$

We can now use the integrated van 't Hoff equation, Equation 10.2.5, to calculate K_P at $T = 2\ 298\ \text{K}$:

$$\ln[K_P(P^\ominus, 2\,298\ \text{K})] = \ln[K_P(P^\ominus, 298\ \text{K})] + \\ - \frac{\Delta_{\text{rxn}} H^\ominus}{R} \left(\frac{1}{2\,298} - \frac{1}{298} \right),$$

which becomes:

$$\ln[K_P(P^\ominus, 2\,298\ \text{K})] = -85.0 + \\ - \frac{242.6 \times 10^3}{8.31} \left(\frac{1}{2\,298} - \frac{1}{298} \right) = 0.262\ ,$$

which corresponds to:

$$K_P(P^\ominus, 2\,298\ \text{K}) = \exp(0.262) = 1.30.$$

Let's now move to the second part of the exercise, where we increase the pressure from $1\ \text{bar}$ to $2.5\ \text{bar}$ at constant $T = 2\ 298\ \text{K}$. We start by writing the definition of K_P and K_y:

$$K_P = \frac{P^2_{\text{Cl}_{(g)}}}{P_{\text{Cl}_{2(g)}}} \qquad K_y = \frac{y^2_{\text{Cl}_{(g)}}}{y_{\text{Cl}_{2(g)}}},$$

and using Equation 10.1.13:

$$\Delta\nu = 2 - 1 = 1$$
$$K_P = K_y \cdot \frac{P}{P^\ominus} \quad \longrightarrow K_y = K_P \left(\frac{P}{P^\ominus} \right)^{-1},$$

we can calculate the initial K_y at $P_i = P^\ominus$, using:

$$K_y(P^\ominus, 2\,298\ \text{K}) = 1.30 = \frac{1.30}{1}.$$

and calculate the initial concentration of $\text{Cl}_{(g)}$ and $\text{Cl}_{(g)}$ at $P^\ominus$, recalling that $y_{\text{Cl}_{2(g)}} = 1 - y_{\text{Cl}_{(g)}}$:

$$K_y(P_i, 2\,298\ \text{K}) = \frac{\left(y^i_{\text{Cl}_{(g)}}\right)^2}{y^i_{\text{Cl}_{(g)}}} = 1.30.$$

Solving the quadratic equation, we obtain one negative answer—which is unphysical—,[5] and:

$$y^i_{\text{Cl}_{(g)}} = 0.662 \quad \longrightarrow y^i_{\text{Cl}_{2(g)}} = 1 - 0.662 = 0.338.$$

At the end of the process, $P_f = 2.5\ \text{bar}$, and we obtain:

$$K_y(P_f, 2\,298\ \text{K}) = 0.520 = K_P \frac{P^\ominus}{P_f} = \frac{1.30}{2.5},$$

and, using the same technique used before to solve the quadratic equation:

$$K_y(P_f, 2\,298\ \text{K}) = \frac{\left(y^f_{\text{Cl}_{(g)}}\right)^2}{y^f_{\text{Cl}_{(g)}}} = 0.520,$$

gives:

$$y^f_{\text{Cl}_{(g)}} = 0.507 \quad \longrightarrow y^i_{\text{Cl}_{2(g)}} = 1 - 0.507 = 0.493.$$

To summarize, when we increase the pressure from $1\ \text{bar}$ to $2.5\ \text{bar}$ at $T = 2\ 298\ \text{K}$, the equilibrium constant in terms of the mole fraction decreases from $K_y(P^\ominus, 2\ 298\ \text{K}) = 1.30$ to $K_y(P_f = 2.5\ \text{bar}, 2\ 298\ \text{K}) = 0.520$. This reduction is causing a shift of the equilibrium towards the reactants, with the concentration of $\text{Cl}_{2(g)}$ increasing from $y^i_{\text{Cl}_{2(g)}} = 0.338$ to $y^f_{\text{Cl}_{2(g)}} = 0.493$ and the concentration of $\text{Cl}_{(g)}$ decreasing from $y^i_{\text{Cl}_{2(g)}} = 0.662$ to $y^f_{\text{Cl}_{(g)}} = 0.507$.

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11: IDEAL AND NON-IDEAL GASES

11.1: The Ideal Gas Equation
11.2: Behaviors of Non-Ideal Gases
11.3: Critical Phenomena
11.4: Fugacity

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11.1: The Ideal Gas Equation

The concept of an ideal gas is a theoretical construct that allows for straightforward treatment and interpretation of gases' behavior. As such, the ideal gas is a simplified *model* that we use to understand nature, and it does not correspond to any real system. The following two assumptions define the ideal gas model:

Definition: Ideal Gas

- The particles that compose an ideal gas do not occupy any volume.
- The particles that compose an ideal gas do not interact with each other.

Because of its simplicity, the ideal gas model has been the historical foundation of thermodynamics and of science in general. The first studies of the ideal gas behavior date back to the seventeenth century, and the scientists that performed them are among the founders of modern science.

Boyle's Law

In 1662 Robert Boyle (1627–1691) found that the pressure and the volume of an ideal gas are inversely related at constant temperature. Boyle's Law has the following mathematical description:

$$P \propto \frac{1}{V} \quad \text{at const. } T, \tag{11.1.1}$$

or, in other terms:

$$PV = k_1 \quad \text{at const. } T, \tag{11.1.2}$$

which results in the familiar PV plots of Figure 11.1.1. As we already discussed in chapter 2, each of the curves in Figure 11.1.1 is obtained at constant temperature, and it is therefore called *"isotherm."*

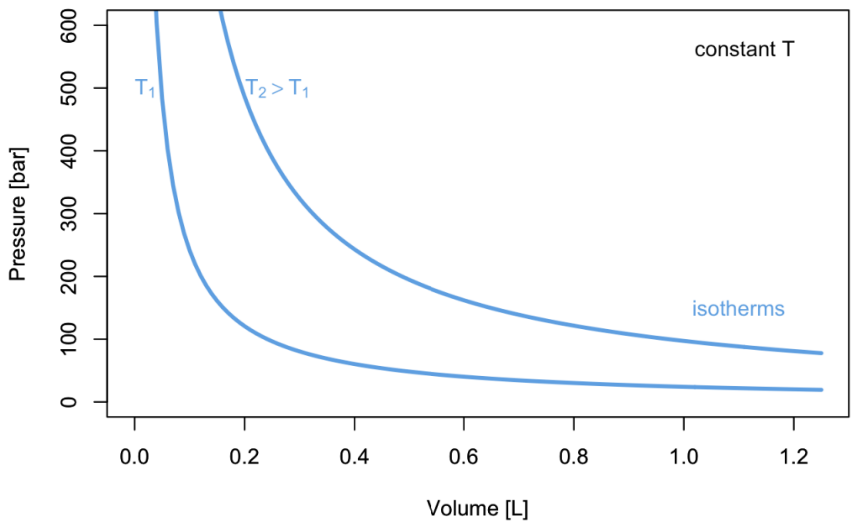


Figure 11.1.1: PV-Diagram of an ideal Gas.

Charles's and Gay-Lussac's Laws

It took scientists more than a century to expand Boyle's work and study the relationship between volume and temperature. In 1787 Jacques Alexandre César Charles (1746–1823) wrote the relationship known as Charles's Law:

$$V \propto T \quad \text{at const. } P, \tag{11.1.3}$$

or, in other terms:

$$V = k_2 T \quad \text{at const. } P, \tag{11.1.4}$$

which results in the plots of Figure 11.1.2. Each of the curves is obtained at constant pressure, and it is termed *"isobar."*

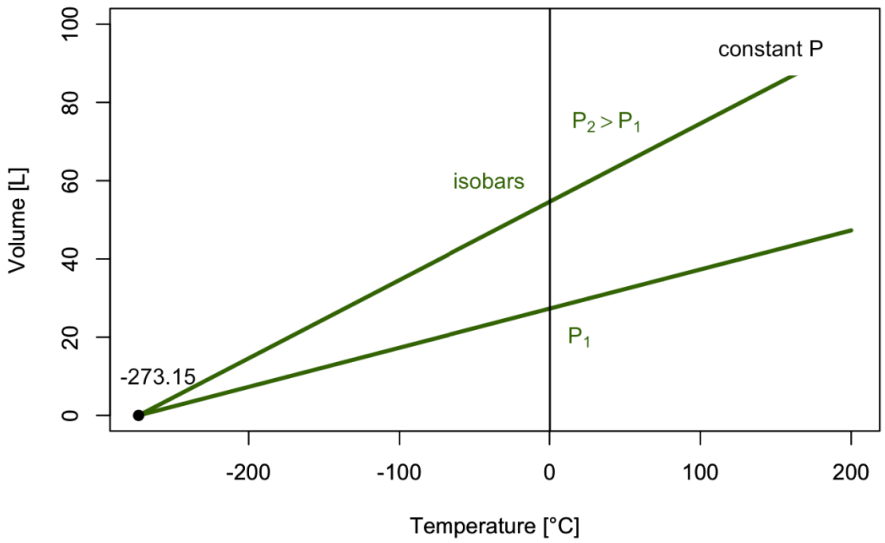


Figure 11.1.2: VT-Diagram of an ideal Gas.

The interesting thing about isobars is that each line seems to converge to a specific point along the temperature line when we extrapolate them to $V \to 0$. This led to the introduction of the absolute temperature scale, suggesting that the temperature will never get smaller than $-273.15^{\circ}\mathrm{C}$.

It took an additional 21 years to write a formal relationship between pressure and temperature. The following relationships were proposed by Joseph Louis Gay-Lussac (1778–1850) in 1808:

$$P \propto T \quad \text{at const. } V, \tag{11.1.5}$$

or, in other terms:

$$P = k_3 T \quad \text{at const. } V, \tag{11.1.6}$$

which results in the plots of Figure 11.1.3. Each of the curves is obtained at constant volume, and it is termed *"isochor."*

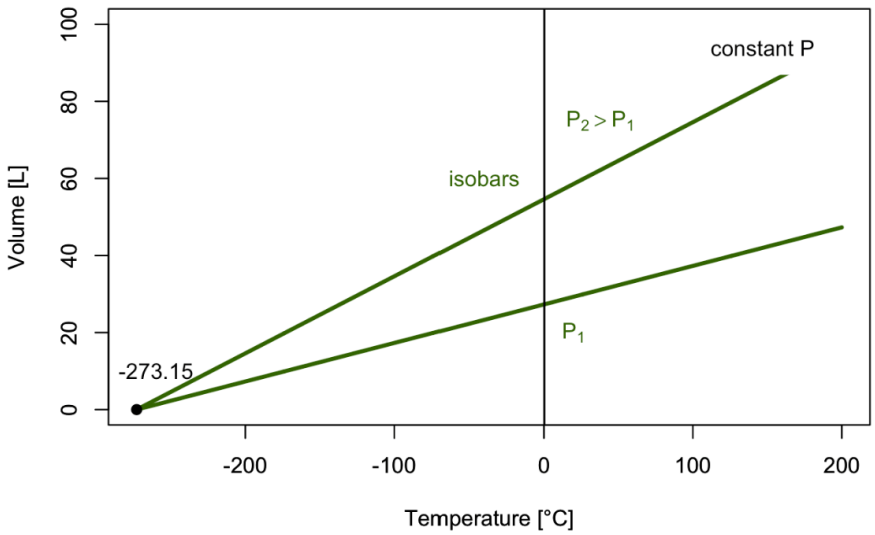


Figure 11.1.3: PT-Diagram of an ideal Gas.

Avogadro's Law

Ten years later, Amedeo Avogadro (1776–1856) discovered a seemingly unrelated principle by studying the composition of matter. His Avogadro's Law encodes the relationship between the number of moles in an ideal gas and its volume as:

$$V \propto n \quad \text{at const. } P, T, \tag{11.1.7}$$

or in other terms:

$$V = k_4 n \quad \text{at const. } P, T, \tag{11.1.8}$$

The ideal gas Law

Despite all of the ingredients being available for more than 20 years, it's only in 1834 that Benoît Paul Émile Clapeyron (1799–1864) was finally able to combine them into what is now known as the **ideal gas Law**. Using the same formulas obtained above, we can write:

$$PV = \underbrace{k_3 T}_{\text{from Gay-Lussac's}} \cdot \underbrace{k_4 n,}_{\text{from Avogadro's}} \tag{11.1.9}$$

which by renaming the product of the two constants k_3 and k_4 as R, becomes:

$$PV = nRT \tag{11.1.10}$$

The value of the constant R can be determined experimentally by measuring the volume that 1 mol of an ideal gas occupies at a constant temperature (e.g., at $T = 0^\circ\text{C}$) and a constant pressure (e.g., atmospheric pressure $P = 1 \text{ atm}$). At those conditions, the volume is measured at 22.4 L, resulting in the following value of R:

$$R = \frac{VP}{nT} = \frac{22.4 \cdot 1}{1 \cdot 273} = 0.082 \ \frac{\text{L atm}}{\text{mol K}}, \tag{11.1.11}$$

which a simple conversion to SI units transforms into:

$$R = 8.31 \ \frac{\text{J}}{\text{mol K}}. \tag{11.1.12}$$

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11.2: Behaviors of Non-Ideal Gases

Non-ideal gases (sometimes also referred to as “real gases”), do not behave as ideal gases because at least one of the assumptions in Definition: Ideal Gas is violated. What characterizes non-ideal gases is that there is no unique equation that we can use to describe their behavior. For this reason, we have a plethora of several experimental models, none of which is superior to the other. The van der Waals (vdW) equation is the only model that we will analyze in detail because of its simple interpretation. However, it is far from universal, and for several non-ideal gases, it is severely inaccurate. Other popular non-ideal gases equations are the Clausius equation, the virial equation, the Redlich–Kwong equation and several others.[1]

The van der Waals equation

One of the simplest empirical equation that describes non-ideal gases was obtained in 1873 by Johannes Diderik van der Waals (1837–1923). The vdW equation includes two empirical parameters (a and b) with different values for different non-ideal gases. Each of the parameters corresponds to a correction for the breaking of one of the two conditions that define the ideal gas behavior (Definition: Ideal Gas). The vdW equation is obtained from the ideal gas equation performing the following simple substitutions:

$$\begin{aligned} P &\rightarrow \left(P+\frac{a}{\overline{V}^2}\right) \\ \overline{V} &\rightarrow \left(\overline{V}-b\right), \end{aligned} \tag{11.2.1}$$

which results in:

$$\begin{aligned} P\overline{V}=RT \;&\rightarrow\; \left(P+\frac{a}{\overline{V}^2}\right)\left(\overline{V}-b\right)=RT \\ P&=\frac{RT}{\overline{V}-b}-\frac{a}{\overline{V}^2}. \end{aligned} \tag{11.2.2}$$

The parameter a accounts for the presence of intermolecular interactions, while the parameter b accounts for the non-negligible volume of the gas molecules. Despite the parameters having simple interpretations, their values for each gas must be determined experimentally. Values for these parameters for some significant non-ideal gas are reported below:

	$a\left[\frac{\mathrm{L}^2\mathrm{bar}}{\mathrm{mol}^2}\right]$	$b\left[\frac{\mathrm{L}}{\mathrm{mol}}\right]$
Ammonia	4.225	0.0371
Argon	1.355	0.03201
Carbon dioxide	3.640	0.04267
Carbon monoxide	1.505	0.03985
Chlorine	6.579	0.05622
Freon	10.78	0.0998
Helium	0.0346	0.0238
Hydrogen	0.2476	0.02661
Mercury	8.200	0.01696
Methane	2.283	0.04278
Neon	0.2135	0.01709

	$a\left[\frac{\mathrm{L}^2\mathrm{bar}}{\mathrm{mol}^2}\right]$	$b\left[\frac{\mathrm{L}}{\mathrm{mol}}\right]$
Nitrogen	1.370	0.0387
Oxygen	1.382	0.03186
Radon	6.601	0.06239
Xenon	4.250	0.05105

Joule–Thomson effect

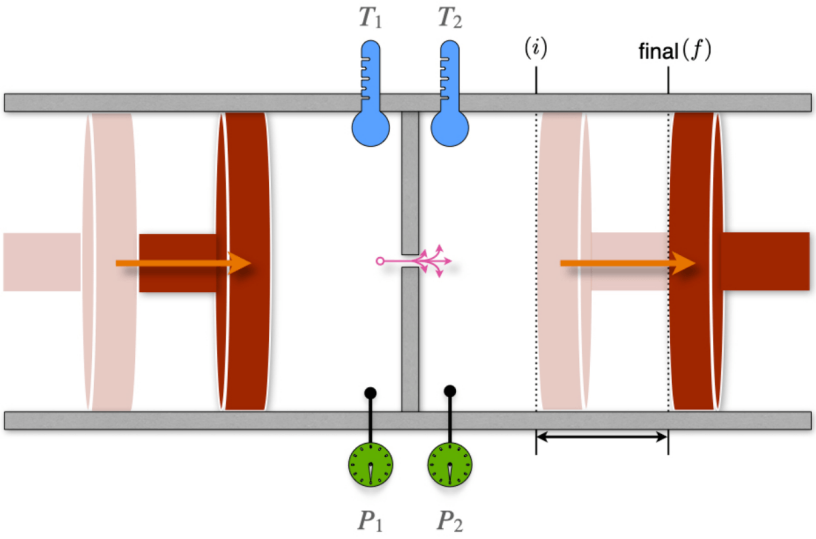


Figure 11.2.1: The Joule–Thomson Experiment.

We have already met William Thomson, also known as Lord Kelvin, and his seminal work on the second law of thermodynamics. In conjunction with that work, Thomson is famous for developing a sensitive method for measuring the temperature changes related to the expansion of a gas. These experiments improved on the earlier work by James Joule, and Lord Kelvin's improved instrument depicted in Figure 11.2.4 is named the Joule–Thomson apparatus. The apparatus is composed of two chambers, each with its own mobile piston. The chambers are connected via a valve or a porous plug. The entire equipment is also thermally isolated from the surroundings. This instrument is a more sensitive version of the Joule expansion apparatus that we already described in section 3 (compare with Figure 3.1.1).

Thomson realized that a gas flowing through an obstruction experience a drop in pressure. If the entire apparatus is insulated, it will not exchange heat with its surroundings ($Q = 0$), and each transformation will happen at adiabatic conditions. Let's consider an initial condition with 1 mol of gas in the left chamber, occupying a volume V_l, and a completely closed right chamber, for which $V_r^i = 0$. After the process completes, the volume of the right chamber will reduce to $V_l{}^f = 0$, while the volume of the right chamber will be V_r. Using the first law of thermodynamics, we can write:

$$\Delta U = U_r - U_l = \underbrace{Q}_{=0} + W = W_l + W_r, \tag{11.2.3}$$

with:

$$\begin{aligned} W_l &= -\int_{V_l}^{0} P_l dV = P_l V_l \\ W_r &= -\int_{0}^{V_r} P_r dV = -P_r V_r. \end{aligned} \tag{11.2.4}$$

Replacing 11.2.4 into Equation 11.2.3, results in:

$$\begin{aligned} U_r - U_l &= P_l V_l - P_r V_r \\ \underbrace{U_r + P_r V_r}_{H_r} &= \underbrace{U_l + P_l V_l}_{H_l}, \end{aligned} \tag{11.2.5}$$

which, replacing the definition of enthalpy $H = U + PV$, we obtain:

$$\begin{aligned} H_r &= H_l \\ \Delta H &= 0, \end{aligned} \tag{11.2.6}$$

or, in other words, the process is **isenthalpic**. Using the total differential of H:

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP = C_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP, \tag{11.2.7}$$

we obtain:

$$\Delta H = \int dH = \int C_P dT + \int \left(\frac{\partial H}{\partial P}\right)_T dP = 0, \tag{11.2.8}$$

or, in purely differential form:

$$dH = C_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP = 0, \tag{11.2.9}$$

From Equation 11.2.9 we can define a new coefficient, called the *Joule–Thomson coefficient*, μ_{JT}, that measures the rate of change of temperature of a gas with respect to pressure in the Joule–Thomson process:

$$\mu_{\text{JT}} = \left(\frac{\partial T}{\partial P}\right)_H = -\frac{1}{C_P}\left(\frac{\partial H}{\partial T}\right)_P \tag{11.2.10}$$

The value of μ_{JT} depends on the type of gas, the temperature and pressure before expansion, and the heat capacity at constant pressure of the gas. The temperature at which μ_{JT} changes sign is called the "Joule–Thomson inversion temperature." Since the pressure decreases during an expansion, ∂P is negative by definition, and the following possibilities are available for μ_{JT}:

Gas temperature:	∂P	μ_{JT}	∂T	**The gas will:**
Below the inversion temperature	–	+	–	cool
Above the inversion temperature	–	–	+	warm

For example, helium has a very low Joule–Thomson inversion temperature at standard pressure ($T = 45\ \text{K}$), and it warms when expanded at constant enthalpy at typical room temperatures. The only other gases that have standard inversion temperature lower than room temperature are hydrogen and neon. On the other hand, nitrogen and oxygen have high inversion temperatures ($T = 621\ \text{K}$ and $T = 764\ \text{K}$, respectively), and they both cool when expanded at room temperature. Therefore, it is possible to use the Joule–Thomson effect in refrigeration processes such as air conditioning.[2] As we already discussed in chapter 3, the temperature of an ideal gases stays constant in an adiabatic expansion, therefore its Joule–Thomson coefficient is always equal to zero.

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1. For more information on empirical equations for non-ideal gases see this Wikipedia page.
2. Nitrogen and oxygen are the two most abundant gases in the air. A sequence of Joule–Thomson expansions are also used for the industrial liquefaction of air.

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11.3: Critical Phenomena

Compressibility factors

The compressibility factor is a correction coefficient that describes the deviation of a real gas from ideal gas behaviour. It is usually represented with the symbol z, and is calculated as:

$$z = \frac{\overline{V}}{\overline{V}_{\text{ideal}}} = \frac{P\overline{V}}{RT}. \tag{11.3.1}$$

It is evident from Equation 11.3.1 that the compressibility factor is dependent on the pressure, and for an ideal gas $z = 1$ always. For a non-ideal gas at any given pressure, z can be higher or lower than one, separating the behavior of non-ideal gases into two possibilities. The dependence of the compressibility factor against pressure is represented for $\mathrm{H_2}$ and $\mathrm{CO_2}$ in Figure 11.3.5.

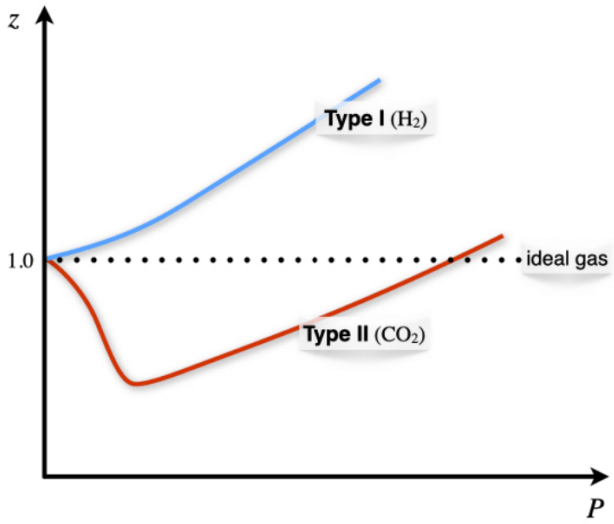


Figure 11.3.1: Non-Ideal Gases Behaviors.

The two types of possible behaviors are differentiated based on the compressibility factor at $P \to 0$. To analyze these situations we can use the vdW equation to calculate the compressibility factor as:

$$z = \frac{\overline{V}}{RT}\left(\frac{RT}{\overline{V} - b} - \frac{a}{\overline{V}^2}\right). \tag{11.3.2}$$

and then we can differentiate this equation at constant temperature with respect to changes in the pressure near $P = 0$, to obtain:

$$\left(\frac{\partial z}{\partial P}\right)_T\Big|_{P=0} = \frac{1}{RT}\left(b - \frac{a}{RT}\right). \tag{11.3.3}$$

which is then interpreted as follows:

- **Type I gases**: $b > \dfrac{a}{RT} \;\Rightarrow\; \dfrac{\partial z}{\partial P} > 0$ *molecular size* dominates ($\mathrm{H_2}$ −like behavior).
- **Type II gases**: $b < \dfrac{a}{RT} \;\Rightarrow\; \dfrac{\partial z}{\partial P} < 0$ *attractive forces* dominates ($\mathrm{CO_2}$ −like behavior).

The dependence of the compressibility factor as a function of temperature (Figure 11.3.6) results in different plots for each of the two types of behavior.

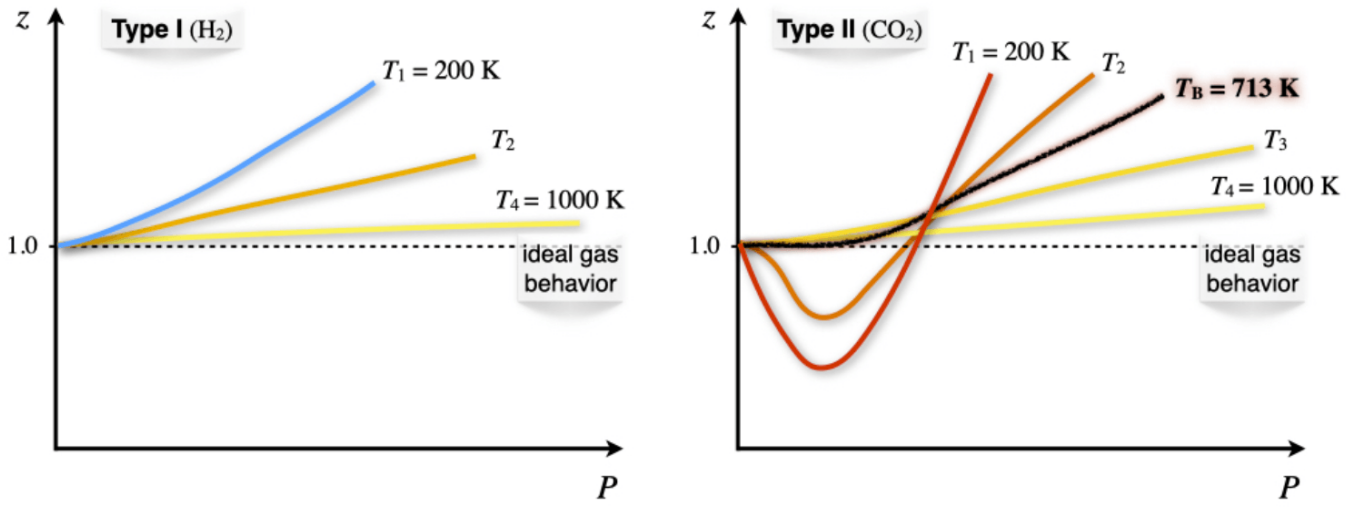


Figure 11.3.2: Temperature Dependence of the Compressibility Factor.

Both type I and type II non-ideal gases will approach the ideal gas behavior as $T \to \infty$, because $\frac{1}{RT} \to 0$ as $T \to \infty$. For type II gases, there are three interesting situations:

- At low T: $b < \frac{a}{RT} \;\Rightarrow\; \frac{\partial z}{\partial P} < 0$, which is the behavior described above.
- At high T: $b > \frac{a}{RT} \;\Rightarrow\; \frac{\partial z}{\partial P} > 0$, which is the same behavior of type I gases.
- At a very specific temperature, inversion will occur (i.e., at $T = 713\ \text{K}$ for CO_2). This temperature is called the **Boyle temperature**, T_B, and is the temperature at which the attractive and repulsive forces balance out. It can be calculated from the vdW equation, since $b - \frac{a}{RT_\text{B}} = 0 \;\Rightarrow\; T_\text{B} = \frac{a}{bR}$. At the Boyle's temperature a type II gas shows ideal gas behavior over a large range of pressure.

Phase diagram of a non-ideal gas

Let's now turn our attention to the PV phase diagram of a non-ideal gas, reported in Figure 11.3.7.

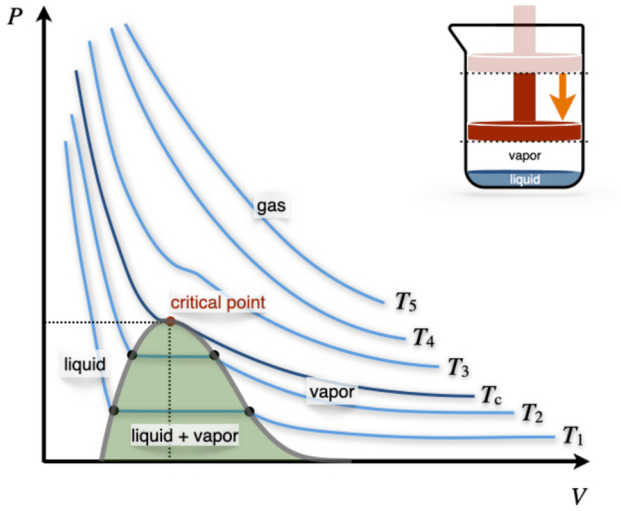


Figure 11.3.3: The Pressure–Volume Diagram of a Non-Ideal Gas.

We can start the analysis from an isotherm at a high temperature. Since every gas will behave as an ideal gas at those conditions,

the corresponding isotherms will look similar to those of an ideal gas (T_5 and T_4 in Figure 11.3.3). Lowering the temperature, we start to see the deviation from ideality getting more prominent (T_3 in Figure 11.3.3) until we reach a particular temperature called the critical temperature, T_c.

Definition: Critical Temperature

The temperature above which no appearance of a second phase is observed, regardless of how high the pressure becomes.

At the critical temperature and below, the gas liquefies when the pressure is increased. For this reason, the liquefaction of a gas is called a *critical phenomenon*.

The critical temperature is the coordinate of a unique point, called the **critical point**, that can be visualized in the three-dimensional T, P, V diagram of each gas (Figure 11.3.4)[1].

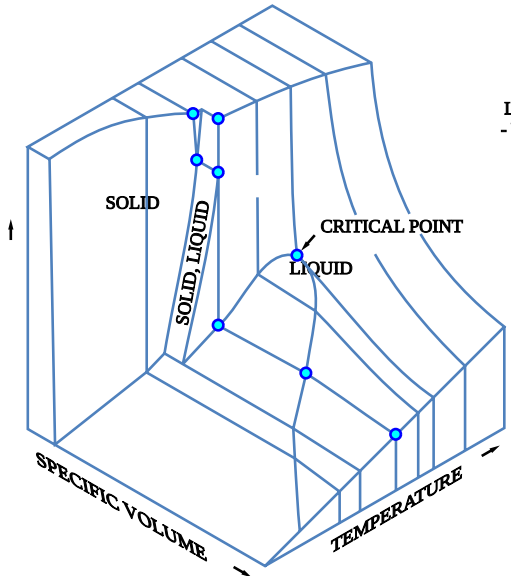


Figure 11.3.4: The three-dimensional diagram. (CC By-SA 3.0 unported; Donald L. Smith via Wikipedia)

The critical point has coordinates $T_c, P_c, \overline{V}_c$. These critical coordinates can be determined from the vdW equation at T_c, as:

$$T_c = \frac{8a}{27Rb} \qquad P_c = \frac{a}{27b^2} \qquad \overline{V}_c = 3b, \tag{11.3.4}$$

These relations are used, in practice, to determine the vdW constants a, b from the experimentally measured critical isotherms.

The critical compressibility factor, z_c, is predicted from the vdW equation at:

$$z_c = \frac{P_c \overline{V}_c}{RT_c} = \left(\frac{a}{27b^2}\right)\left(\frac{3b}{R}\right)\left(\frac{27Rb}{8a}\right) = \frac{3}{8} = 0.375, \tag{11.3.5}$$

a value that is independent of the gas. Experimentally measured values of z_c for different non-ideal gases are in the range of 0.2–0.3. These values can be used to infer the accuracy of the vdW equation for each non-ideal gas. Since the experimental z_c is usually lower than the one calculated from the vdW equation, we can deduce that the vdW equation overestimates the critical molar volume.

Notice how slicing the $PT\overline{V}$ diagram at constant T results in the PV diagram that we reported in Figure 11.3.4. On the other hand, slicing the $PT\overline{V}$ diagram at constant P results in the PT diagram that we will examine in detail in the next chapter.

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11.4: Fugacity

The chemical potential of a pure ideal gas can be calculated using Equation 9.4.5. Since we are not interested in mixture, we can drop the asterisk in μ^*, and rewrite Equation 9.4.5 as:

$$\mu_{\text{ideal}} = \mu^{\ominus} + RT \ln \frac{P}{P^{\ominus}}. \tag{11.4.1}$$

For a non-ideal gas, the pressure cannot be used in Equation 11.4.1 because each gas response to changes in pressure is not universal. We can, however, define a new variable to replace the pressure in Equation 11.4.1 and call it fugacity (f).

Definition: Fugacity

The effective pressure of a non-ideal gas that corresponds to the pressure of an ideal gas with the same temperature and chemical potential of the non-ideal one.

Equation 11.4.1 then becomes:

$$\mu_{\text{non-ideal}} = \mu^{\ominus} + RT \ln \frac{f}{P^{\ominus}}. \tag{11.4.2}$$

Since the chemical potential of a gas μ is equal to the standard chemical potential $\mu^{\ominus}$ when $P = P^{\ominus}$, it is easy to use Equation 11.4.2 to demonstrate that:

$$\lim_{P \to 0} \frac{f}{P} = 1, \tag{11.4.3}$$

in other words, any non-ideal gas will approach the ideal gas behavior as $P \to 0$. This condition, in conjunction with the $T \to \infty$ behavior obtained in the previous section, results in the following statement:

The highest chances for any gas to behave ideally happen at high temperature and low pressure.

We can now return our attention to the definition of fugacity. Remembering that the chemical potential is the molar Gibbs free energy of a substance, we can write:

$$d\mu_{\text{ideal}} = \overline{V}_{\text{ideal}} dP, \tag{11.4.4}$$

and:

$$d\mu_{\text{non-ideal}} = \overline{V}_{\text{non-ideal}} dP, \tag{11.4.5}$$

Subtracting Equation 11.4.4 from Equation 11.4.5, we obtain:

$$d\mu_{\text{non-ideal}} - d\mu_{\text{ideal}} = \left(\overline{V}_{\text{non-ideal}} - \overline{V}_{\text{ideal}}\right) dP, \tag{11.4.6}$$

which we can then integrate between 0 and P:

$$\mu_{\text{non-ideal}} - \mu_{\text{ideal}} = \int_0^P \left(\overline{V}_{\text{non-ideal}} - \overline{V}_{\text{ideal}}\right) dP. \tag{11.4.7}$$

Using eqs. 11.4.1 and 11.4.2 we can then replace the definition of chemical potentials, resulting into:

$$\ln f - \ln P = \frac{1}{RT} \int_0^P \left(\overline{V}_{\text{non-ideal}} - \overline{V}_{\text{ideal}}\right) dP, \tag{11.4.8}$$

which gives us a mathematical definition of the fugacity, as:

$$f = P \cdot \underbrace{\exp\left[\frac{1}{RT}\int_0^P \left(\overline{V}_{\text{non-ideal}} - \overline{V}_{\text{ideal}}\right) dP\right]}_{\text{fugacity coefficient, } \phi(T,P)}. \tag{11.4.9}$$

The exponential term in Equation 11.4.9 is complicated to write, but it can be interpreted as a coefficient—unique to each non-ideal gas—that can be measured experimentally. Such coefficients are dependent on pressure and temperature and are called the *fugacity coefficients*. Using letter ϕ to represent the fugacity coefficient, we can rewrite Equation 11.4.9 as:

$$f = \phi P, \tag{11.4.10}$$

which gives us a straightforward interpretation of the fugacity as an effective pressure. As such, the fugacity will have the same unit as the pressure, while the fugacity coefficients will be adimensional.

As we already saw in chapter 10, the fugacity can be used to replace the pressure in the definition of the equilibrium constant for reactions that involve non-ideal gases. The new constant is usually called K_f, and is obtained from:

$$K_f = \prod_i f_{i,\text{eq}}^{\nu_i} = K_P \prod_i \phi_i^{\nu_i}. \tag{11.4.11}$$

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12: PHASE EQUILIBRIUM

12.1: Phase Stability
12.2: Gibbs Phase Rule
12.3: PT Phase Diagrams
12.4: The Clausius-Clapeyron Equation

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12.1: Phase Stability

We have already encountered the gas, liquid, and solid phases and already discussed some of their properties. These terms are intuitive since these are the three most common states of matter.[1] For this reason, we have previously used the terms without the necessity of formally defining their meaning. However, a formal definition of "phase" is necessary to discuss several concepts in this chapter and the following ones:

Definition: Phase

A region of the system with homogeneous chemical composition and physical state.

Let's now use the total differential of the chemical potential and the definition of molar Gibbs free energy for one component:

$$\begin{aligned} d\mu &= \left(\frac{\partial \mu}{\partial T}\right)_P dT + \left(\frac{\partial \mu}{\partial P}\right)_T dP \\ d\mu &= -SdT + \overline{V}dP, \end{aligned} \tag{12.1.1}$$

to write:

$$\left(\frac{\partial \mu}{\partial T}\right)_P = -S \qquad \left(\frac{\partial \mu}{\partial P}\right)_T = \overline{V}. \tag{12.1.2}$$

We can use these definitions to study the dependence of the chemical potential with respect to changes in pressure and temperature. If we plot μ as a function of T using the first coefficient in Equation 12.1.2, we obtain the diagram in Figure 12.1.1. The diagram presents three curves, each corresponding to one of the three most common states of matter – solid, liquid, and gas. As we saw in several previous chapters, the entropy of a phase is almost constant with respect to temperature,[2] and therefore the three curves are essentially straight, with negative angular coefficients $-S$. This also explains why the solid phase has a basically flat line since, according to the third law, the entropy of a perfect solid is zero and close to zero if the solid is not perfect. The difference between the three lines' angular coefficients is explained by the fact that each of these states has a different value of entropy:

$$\left(\frac{\partial \mu_{\text{solid}}}{\partial T}\right)_P = -S_{\text{s}} \qquad \left(\frac{\partial \mu_{\text{liquid}}}{\partial T}\right)_P = -S_{\text{l}} \qquad \left(\frac{\partial \mu_{\text{gas}}}{\partial T}\right)_P = -S_{\text{g}}, \tag{12.1.3}$$

and since the entropy of a gas is always bigger than the entropy of a liquid, which in turn, is yet bigger than the entropy of a solid ($S_{\text{g}} \gg S_{\text{l}} > S_{\text{s}}$), we obtain three lines with different angular coefficients that intersect each other. At each temperature, the phase with the lowest chemical potential will be the most stable (see red segments in Figure 12.1.1). At each intersection between two lines, the two phases have the same chemical potential, representing the temperature at which they coexist. This temperature is the temperature at which the phase change happens. Recalling from general chemistry, at the junction between the solid and the liquid lines, the fusion (fus) process occurs, and the corresponding temperature is called the melting point T_{m}. At the junction between the liquid and the gas lines, the vaporization (vap) process happens, and the corresponding temperature is called the boiling point T_{b}. Depending on the substance and the pressure at which the process happens, the solid line might intersect the gas line before the liquid line. When that occurs, the liquid phase is never observed, and only the sublimation (subl) process happens at the sublimation point T_{subl}.

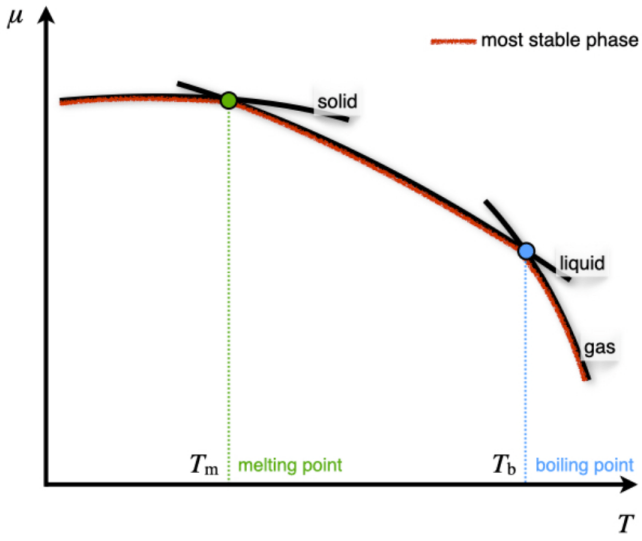


Figure 12.1.1: Dependence of the Chemical Potentials of Solid, Liquid, and Gas Phases on Temperature at Constant Pressure.

The effects of pressure on this diagram can be studied using the second coefficient in Equation 12.1.2. For the majority of substances, $\overline{V}_g \gg \overline{V}_l > \overline{V}_s$, hence the curves will shift to lower values when the pressure is reduced, as in Figure 12.1.2. Notice also that since $\overline{V}_l \cong \overline{V}_s$, the shifts for both the solid and liquid lines is much smaller than the shift for the gas line. These shifts also translate to different values of the junctions, which means the phase changes will occur at different temperatures. Therefore both the melting point and the boiling point in general increase when pressure is increased (and vice versa). Notice how the change for the melting point is always much smaller than the change for the boiling point. Water is a noticeable exception to these trend because $\overline{V}_{H_2O,l} < \overline{V}_{ice}$. This explains the experimental observation that increasing the pressure on ice causes the ice to melt[3]

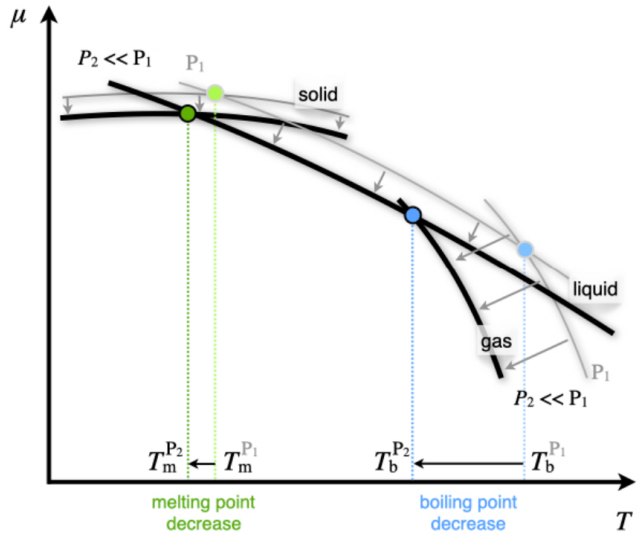


Figure 12.1.2: Effect of Pressure on the Chemical Potential Diagram.

Considering the intersections between two lines, two phases are in equilibrium with each other at each of these points. Therefore their chemical potentials must be equal:

For two or more phases to be in equilibrium, their chemical potential must be equal:

$$\mu_\alpha = \mu_\beta. \tag{12.1.4}$$

If we now change either the temperature or the pressure, the location of the intersection will be shifted (see again Figure 12.1.2 and the discussion above). For infinitesimal changes in variables, the new location will be:

$$\mu_\alpha + d\mu_\alpha = \mu_\beta + d\mu_\beta, \tag{12.1.5}$$

which using Equation 12.1.4, simply becomes:

$$d\mu_\alpha = d\mu_\beta. \tag{12.1.6}$$

Replacing the differential with the definition of chemical potential in Equation ???, we obtain:

$$\begin{aligned} -S_\alpha dT + \overline{V}_\alpha &= -S_\beta dT + \overline{V}_\beta \\ \underbrace{(S_\beta - S_\alpha)}_{\Delta S}\, dT &= \underbrace{\left(\overline{V}_\beta - \overline{V}_\alpha\right)}_{\Delta \overline{V}}, \end{aligned} \tag{12.1.7}$$

which can be rearranged into:

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta \overline{V}}. \tag{12.1.8}$$

This equation is known as the **Clapeyron equation**, and it is the mathematical relation at the basis of the pressure-temperature phase diagrams. Plotting the results of Equation 12.1.8 on a PT phase diagram for common substances results in three lines representing the equilibrium between two different phases. These diagrams are useful to study the relationship between the phases of a substance.

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1. Other states of matter—such as plasma—are possible, but they are not usually observed at the values of temperature and pressure that classical thermodynamics is usually applied to. Discussion of these extreme cases is beyond the scope of this textbook.
2. Think, for example, at the integral $\int S dT$, for which we can assume S independent of temperature to obtain $S\Delta T$. In practice, the entropy increases slightly with the temperature. Therefore the curves in Figure 12.1.1 are slightly concave downwards (remember that they are obtained from values of $-S$, so if S increase with T, the curves bend downwards.)
3. Despite the effect being minimal, it is one of the contributing causes to the fact that we can skate on ice, but we can't on stone. If we increase our pressure on ice by reducing our footprints' surface area using thin skates, ice will slightly melt under our own weight, creating a thin liquid film on which we can skate because of the reduced friction.

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12.2: Gibbs Phase Rule

In chapter 1, we have already seen that the number of independent variables required to describe an ideal gas is two. This number was derived by counting the total number of variables $(3 : P, \overline{V}, T)$, and reduce it by one because the ideal gas law constrains the value of one of them, once the other two are fixed. For a generic system potentially containing more than one chemical substance in several different phases, however, the number of independent variables can be different than two. For a system composed of c components (chemical substances) and p phases, the number of independent variables, f, is given by the Gibbs phase rule:

$$f = c - p + 2. \tag{12.2.1}$$

The Gibbs phase rule derives from the fact that different phases are in equilibrium with each other at some conditions, resulting in the reduction of the number of independent variables at those conditions. More rigorously, when two phases are in thermodynamic equilibrium, their chemical potentials are equal (see Equation 12.1.4). For each equality, the number of independent variables—also called the number of **degrees of freedom**—is reduced by one. For example, the chemical potentials of the liquid and its vapor depend on both T and P. But when these phases are in equilibrium with each other, their chemical potentials must be equal. If either the pressure or the temperature is fixed, the other variable will be uniquely determined by the equality relation. In other terms, when a liquid is in equilibrium with its vapor at a given pressure, the temperature is determined by the fact that the chemical potentials of the two phases is the same, and is denoted as the boiling temperature T_b. Similarly, at a given temperature, the pressure of the vapor is uniquely determined by the same equality relation and is denoted as the vapor pressure, P^*.

The Gibbs phase rule is obtained considering that the number of independent variables is given by the total number of variables minus the constraints. The total number of variables is given by temperature, pressure, plus all the variables required to describe each of the phases. The composition of each phase is determined by $(c-1)$ variables.[1] The number of constraints is determined by the number of possible equilibrium relations, which is $c(p-1)$ since the chemical potential of each component must be equal in all phases. The number of degrees of freedom f is then given by

$$\begin{aligned} f &= (c-1)p + 2 - c(p-1) \\ &= c - p + 2 \end{aligned}$$

which is the Gibbs phase rule, as in Equation 12.2.1.

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1. For a 1-component system $c - 1 = 1 - 1 = 0$, and no additional variable is required to determine the composition of each phase. For a 2-component system, however, each phase will contain both components, hence $c - 1 = 2 - 1 = 1$ additional variable will be required to describe it–the mole fraction.

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12.3: PT Phase Diagrams

Let's now discuss the pressure–temperature diagram of a typical substance, as reported in Figure 12.3.1. Each of the lines reported in the diagram represents an equilibrium between two phases, and therefore it represents a condition that reduces the number of degrees of freedom to one. The lines can be determined using the Clapeyron equation, Equation 12.1.8. The interpretation of each line is as follows:

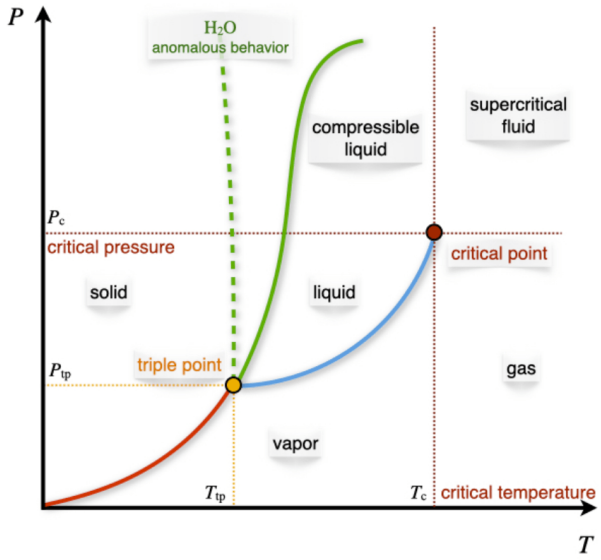


Figure 12.3.1: The Pressure–Temperature Phase Diagram.

Liquid ⇄ Gas equilibrium

For this equilibrium we can use Trouton's rule, Equation 7.1.5, and write:

$$\Delta_{\text{vap}}S = S_{\text{g}} - S_{\text{l}} \cong 88\ \frac{\text{kJ}}{\text{mol}} > 0 \quad \text{always}, \tag{12.3.1}$$

where the entropy of vaporization is always positive, even for cases where the Trouton's rule is violated. The difference in molar volumes is easily obtained, since the volume of the gas is always much greater than the volume of the liquid:

$$\overline{V}_{\text{g}} - \overline{V}_{\text{l}} \cong \overline{V}_{\text{g}} = 22.4\ \frac{\text{L}}{\text{mol}} > 0 \quad \text{always}. \tag{12.3.2}$$

Replacing these values in the Clapeyron equation, we obtain:

$$\frac{dP}{dT} = \frac{88}{22.4}\left(\frac{0.0831}{8.31}\right) = 0.004\ \text{bar} > 0 \quad \text{always}, \tag{12.3.3}$$

which is always positive,regardless of violations to the Trouton's rule. Notice how small this value is, meaning that the liquid–gas equilibrium curve is mostly flat as $T \to 0$.

Solid ⇄ Gas equilibrium

If we look at the signs of each quantity, this case is similar to the previous one:

$$\begin{aligned} \Delta_{\text{subl}} S &> 0 \quad \text{always} \\ \Delta_{\text{subl}} \overline{V} &> 0 \quad \text{always} \\ \\ \frac{dP}{dT} &> 0 \quad \text{always.} \end{aligned} \tag{12.3.4}$$

However, the Trouton's rule is not valid for the solid–gas equilibrium, and $\frac{dP}{dT}$ will be larger than for the previous case.

Solid $\rightleftarrows$ Liquid equilibrium

The final curve is for the solid-liquid equilibrium, for which we have:

$$\Delta_{\text{fus}} S = \frac{\Delta_{\text{fusion}} H}{T_{\text{m}}} > 0 \quad \text{always,} \tag{12.3.5}$$

since fusion is always an exothermic process, $(\Delta_{\text{fus}} H > 0)$. On the other side:

$$\Delta_{\text{fusion}} \overline{V} = \overline{V}_{\text{l}} - \overline{V}_{\text{s}} > 0 \quad \text{generally.}$$

In other words, the difference of the molar volume of the liquid and that of the solid is positive for most substances, but it might be negative (for example for H_2O). As such:

$$\frac{dP}{dT} > 0 \quad \text{generally.} \tag{12.3.6}$$

For H_2O and a few other substances, $\frac{dP}{dT} < 0$, an anomalous behavior that has crucial consequences for the existence of life on earth.[1] For this importance, this behavior is also depicted in Figure $12.3.1$ using a dashed green line.

Since the differences in molar volumes between the solid and the liquid phases are usually small (changes are generally of the order of 10^{-3} L), $\frac{dP}{dT}$ is always much larger than for the previous two cases. The resulting lines for the solid–liquid equilibria are still almost vertical, regardless of the signs of their angular coefficients.

The triple point and the critical point

The only point in the PT diagram where all the three phases coexist is called the triple point. The number of degrees of freedom at the triple point for every 1-component diagram is $f = 1 - 3 + 2 = 0$. The fact that the triple point has zero degrees of freedom means that its coordinates, $T_{\text{tp}}, P_{\text{tp}}, \overline{V}_{\text{tp}}$, are uniquely determined for each chemical substance. For this reason, the value of the triple point of water was fixed by definition—rather than measured—until 2019. This definition was necessary to establish the base unit of the thermodynamic temperature scale in the SI (the Kelvin).[2]

In addition to the triple point where the solid, liquid, and gas phases meet, a triple point may involve more than one condensed phase. Triple points are common for substances with multiple solid phases (polymorphs), involving either two solid phases and a liquid one or three solid phases. Helium is a special case that presents a triple point involving two different fluid phases, called the lambda point. Since the number of degrees of freedom cannot be negative, the Gibbs phase rule for a 1-component diagram sets the limit to how many phases can coexist to just three. Therefore, quadruple points (or higher coexistence points) are not possible for pure substances, even for polymorphs.[3]

Another point with a fixed position in the PT diagram is the critical point, $T_{\text{c}}, P_{\text{c}}, \overline{V}_{\text{c}}$. We have already given the definition of the critical temperature in Definition: Critical Temperature. This point represents the end of the liquid–gas equilibrium curve. This point is also semantically important to define different regions of the phase diagram, as in Figure $12.3.1$. A gas whose pressure and temperature are below the critical point is called a *vapor*. A gas whose temperature is above the critical one and the pressure is below its critical one is called a *supercritical fluid*. Finally, a liquid whose pressure is above the critical point is called a *compressible liquid*.[4]

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1. As is well explained by Wikipedia: "The unusual density curve and lower density of ice than of water is vital to life—if water were most dense at the freezing point, then in winter the very cold water at the surface of lakes and other water bodies would

sink, lakes could freeze from the bottom up, and all life in them would be killed. Furthermore, given that water is a good thermal insulator (due to its heat capacity), some frozen lakes might not completely thaw in summer.[34] The layer of ice that floats on top insulates the water below. Water at about 4 °C (39 °F) also sinks to the bottom, thus keeping the temperature of the water at the bottom constant."

2. For more information on the 2019 redefinition of the SI units, see this Wikipedia page.
3. Notice that quadruple points are possible for 2-component diagrams.
4. Notice that the temperature of a liquid must be below the critical point, otherwise it is no longer a liquid but rather a supercritical fluid.

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12.4: The Clausius-Clapeyron Equation

Let's now take a closer look at the equilibrium between a condensed phase and the gas phase. For both the vaporization and sublimation processes, Clausius showed that the Clapeyron equation can be simplified by using:

$$\Delta_{\text{vap}}S = \frac{\Delta_{\text{vap}}H}{T} \qquad \Delta\overline{V} = \overline{V}_{\text{g}} - \overline{V}_{\text{l}} \cong \overline{V}_{\text{g}}, \tag{12.4.1}$$

resulting in:

$$\frac{dP}{dT} = \frac{\Delta_{\text{vap}}S}{\Delta\overline{V}} \cong \frac{\Delta_{\text{vap}}H}{T\overline{V}_{\text{g}}}. \tag{12.4.2}$$

Using the ideal gas law to replace the molar volume of the gas, we obtain:

$$\frac{dP}{dT} = \frac{P\Delta_{\text{vap}}H}{RT^2}, \tag{12.4.3}$$

which can be rearranged as:

$$\frac{dP}{P} = \frac{\Delta_{\text{vap}}H}{R}\frac{dT}{T^2}. \tag{12.4.4}$$

Equation 12.4.4 is known as the **Clausius–Clapeyron equation**, and it measures the dependence of the vapor pressure of a substance as a function of the temperature. The Clausius–Clapeyron equation can be integrated to obtain:

$$\begin{aligned} \int_{P_i}^{P_f}\frac{dP}{P} &= \frac{\Delta_{\text{vap}}H}{R}\int_{T_i}^{T_f}\frac{dT}{T^2} \\ \ln\frac{P_f}{P_i} &= -\frac{\Delta_{\text{vap}}H}{R}\left(\frac{1}{T_f} - \frac{1}{T_i}\right). \end{aligned} \tag{12.4.5}$$

The integrated Clausius–Clapeyron equation shows that the vapor pressure depends exponentially on the temperature. Thus, even a small change in the temperature will result in a significant change in the vapor pressure. In fact, we daily use the fact that the vapor pressure of water changes drastically when we increase its temperature for cooking most of our food. For example, at an external pressure of 1 bar, it rapidly grows from $P^* = 0.02\ \text{bar}$ to $P^* = 1\ \text{bar}$ when the temperature is increased from $T = 293\ \text{K}$ (around room temperature) to $T = 373\ \text{K}$ (boiling point). The integrated Clausius–Clapeyron equation is also often used to determine the enthalpy of vaporization from measurements of vapor pressure at different temperatures.

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13: MULTI-COMPONENT PHASE DIAGRAMS

We now move from studying 1-component systems to multi-component ones. Systems that include two or more chemical species are usually called *solutions*. Solutions are possible for all three states of matter:

Type:	Solvent	Solute	Examples:
Solid solutions	Solid	Solid	Alloys: brass, bronze
	Solid	Liquid	Dental amalgam
	Solid	Gas	Hydrogen stored in Palladium
Liquid solutions	Liquid	Solid	Saltwater, bleach
	Liquid	Liquid	Alcoholic beverages, vinegar
	Liquid	Gas	Carbonated drinks
Gaseous solutions	Gas	Solid	Smoke, smog
	Gas	Liquid	Aerosols and perfumes
	Gas	Gas	Air

The number of degrees of freedom for binary solutions (solutions containing two components) is calculated from the Gibbs phase rules at $f = 2 - p + 2 = 4 - p$. When one phase is present, binary solutions require $4 - 1 = 3$ variables to be described, usually temperature (T), pressure (P), and mole fraction (y_i in the gas phase and x_i in the liquid phase). Single-phase, 1-component systems require three-dimensional T, P, x_i diagram to be described. When two phases are present (e.g., gas and liquid), only two variables are independent: pressure and concentration. Thus, we can study the behavior of the partial pressure of a gas–liquid solution in a 2-dimensional plot. If the gas phase in a solution exhibits properties similar to those of a mixture of ideal gases, it is called an *ideal solution*. The obvious difference between ideal solutions and ideal gases is that the intermolecular interactions in the liquid phase cannot be neglected as for the gas phase. The main advantage of ideal solutions is that the interactions between particles in the liquid phase have similar mean strength throughout the entire phase. We will consider ideal solutions first, and then we'll discuss deviation from ideal behavior and non-ideal solutions.

13.1: Raoult's Law and Phase Diagrams of Ideal Solutions

13.2: Phase Diagrams of Non-Ideal Solutions

13.3: Phase Diagrams of 2-Components/2-Condensed Phases Systems

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13.1: Raoult's Law and Phase Diagrams of Ideal Solutions

The behavior of the vapor pressure of an ideal solution can be mathematically described by a simple law established by François-Marie Raoult (1830–1901). **Raoult's law** states that the partial pressure of each component, i, of an ideal mixture of liquids, P_i, is equal to the vapor pressure of the pure component P_i^* multiplied by its mole fraction in the mixture x_i:

$$P_i = x_i P_i^*. \tag{13.1.1}$$

One volatile component

Raoult's law applied to a system containing only one volatile component describes a line in the Px_B plot, as in Figure 13.1.1.

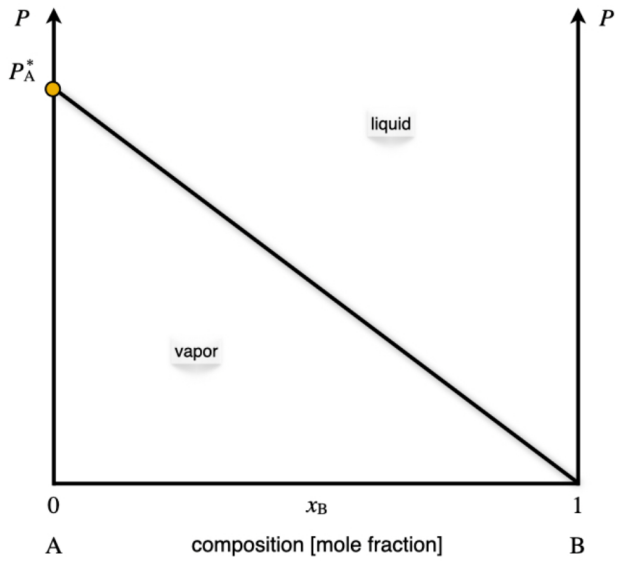


Figure 13.1.1: The Pressure–Composition Phase Diagram of an Ideal Solution Containing a Single Volatile Component at Constant Temperature.

As emerges from Figure 13.1.1, Raoult's law divides the diagram into two distinct areas, each with three degrees of freedom.[1] Each area contains a phase, with the vapor at the bottom (low pressure), and the liquid at the top (high pressure). Raoult's law acts as an additional constraint for the points sitting on the line. Therefore, the number of independent variables along the line is only two. Once the temperature is fixed, and the vapor pressure is measured, the mole fraction of the volatile component in the liquid phase is determined.

Two volatile components

In an ideal solution, every volatile component follows Raoult's law. Since the vapors in the gas phase behave ideally, the total pressure can be simply calculated using Dalton's law as the sum of the partial pressures of the two components $P_\mathrm{TOT} = P_\mathrm{A} + P_\mathrm{B}$. The corresponding diagram is reported in Figure 13.1.2. The total vapor pressure, calculated using Dalton's law, is reported in red. The Raoult's behaviors of each of the two components are also reported using black dashed lines.

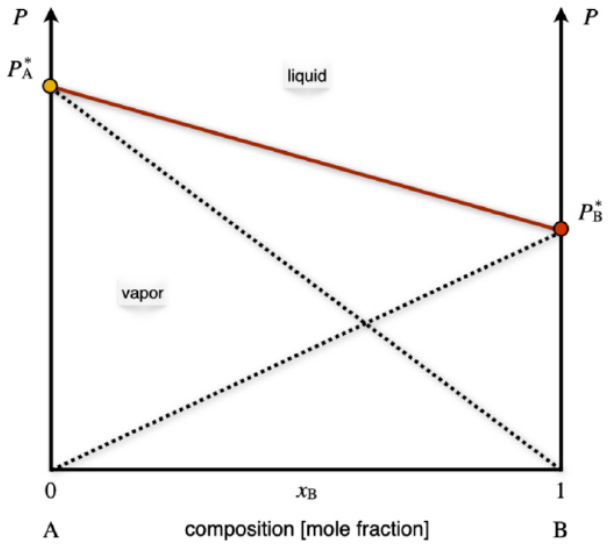


Figure 13.1.2: The Pressure–Composition Phase Diagram of an Ideal Solution Containing Two Volatile Components at Constant Temperature.

Exercise 13.1.1

Calculate the mole fraction in the vapor phase of a liquid solution composed of 67% of toluene (A) and 33% of benzene (B), given the vapor pressures of the pure substances: $P_A^* = 0.03\ \text{bar}$, and $P_B^* = 0.10\ \text{bar}$.

Answer available at the end of this section.

As is clear from the results of Exercise 13.1.1, the concentration of the components in the gas and vapor phases are different. We can also report the mole fraction in the vapor phase as an additional line in the Px_B diagram of Figure 13.1.2. When both concentrations are reported in one diagram—as in Figure 13.1.3—the line where x_B is obtained is called the *liquidus line*, while the line where the y_B is reported is called the *Dew point line*.

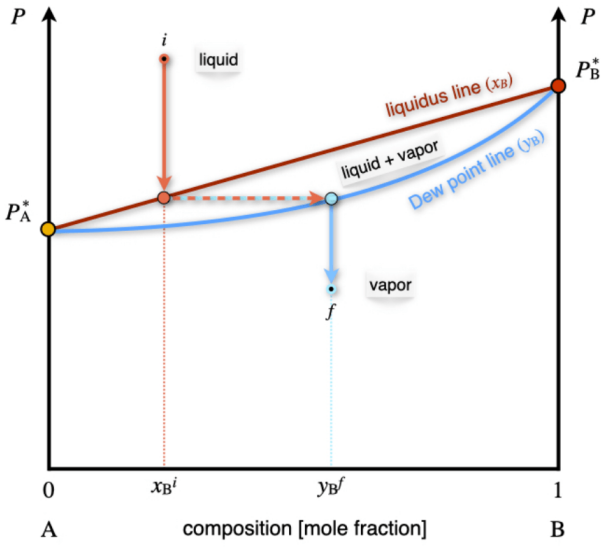


Figure 13.1.3: The Pressure–Composition Phase Diagram of an Ideal Solution Containing Two Volatile Components at Constant Temperature. Both the Liquidus and Dew Point Line are Emphasized in this Plot.

The liquidus and Dew point lines determine a new section in the phase diagram where the liquid and vapor phases coexist. Since the degrees of freedom inside the area are only 2, for a system at constant temperature, a point inside the coexistence area has

fixed mole fractions for both phases. We can reduce the pressure on top of a liquid solution with concentration x_{B}^{i} (see Figure 13.1.3) until the solution hits the liquidus line. At this pressure, the solution forms a vapor phase with mole fraction given by the corresponding point on the Dew point line, y_{B}^{f}.

T_{B} phase diagrams and fractional distillation

We can now consider the phase diagram of a 2-component ideal solution as a function of temperature at constant pressure. The T_{B} diagram for two volatile components is reported in Figure 13.1.4.

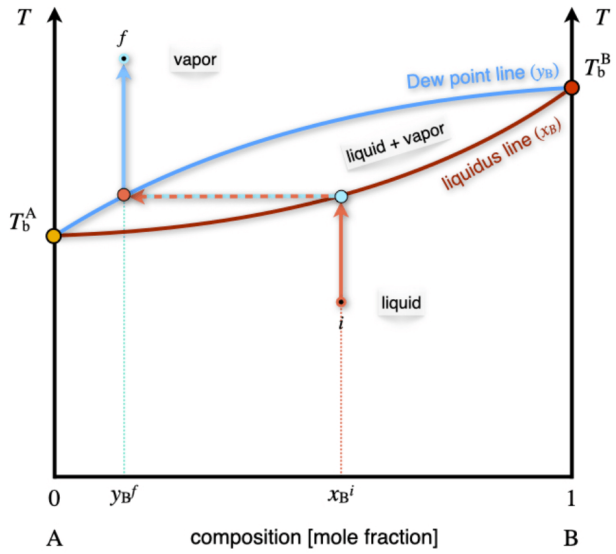


Figure 13.1.4: The Temperature–Composition Phase Diagram of an Ideal Solution Containing Two Volatile Components at Constant Pressure.

Compared to the Px_{B} diagram of Figure 13.1.3, the phases are now in reversed order, with the liquid at the bottom (low temperature), and the vapor on top (high Temperature). The liquidus and Dew point lines are curved and form a lens-shaped region where liquid and vapor coexists. Once again, there is only one degree of freedom inside the lens. As such, a liquid solution of initial composition x_{B}^{i} can be heated until it hits the liquidus line. At this temperature the solution boils, producing a vapor with concentration y_{B}^{f}. As is clear from Figure 13.1.4, the mole fraction of the B component in the gas phase is lower than the mole fraction in the liquid phase. This fact can be exploited to separate the two components of the solution. In particular, if we set up a series of consecutive evaporations and condensations, we can distill fractions of the solution with an increasingly lower concentration of the less volatile component B. This is exemplified in the industrial process of fractional distillation, as schematically depicted in Figure 13.1.5.

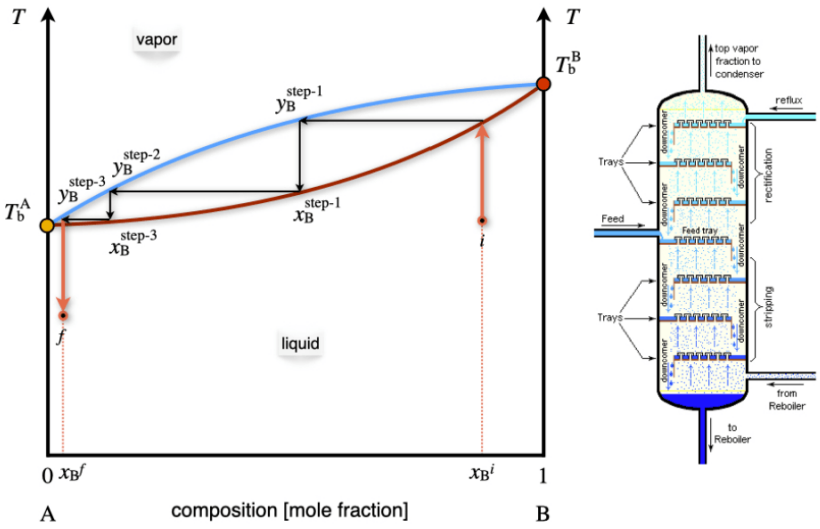


Figure 13.1.5: The Fractional Distillation Process and Theoretical Plates Calculated on a Temperature–Composition Phase Diagram.

Each of the horizontal lines in the lens region of the Tx_{B} diagram of Figure 13.1.5 corresponds to a condensation/evaporation process and is called a *theoretical plate*. These plates are industrially realized on large columns with several floors equipped with condensation trays. The temperature decreases with the height of the column. A condensation/evaporation process will happen on each level, and a solution concentrated in the most volatile component is collected. The theoretical plates and the Tx_{B} are crucial for sizing the industrial fractional distillation columns.

---

1. Only two degrees of freedom are visible in the Px_{B} diagram. Temperature represents the third independent variable.

Answers

Exercise 13.1.1

The data available for the systems are summarized as follows:

$$\begin{array}{cc} x_{\mathrm{A}} = 0.67 & x_{\mathrm{B}} = 0.33 \\ P^*_{\mathrm{A}} = 0.03 \text{ bar} & P^*_{\mathrm{B}} = 0.10 \text{ bar} \\ & P_{\mathrm{TOT}} = ? \\ y_{\mathrm{A}} = ? & y_{\mathrm{B}} = ? \end{array} \tag{13.1.2}$$

The total pressure of the vapors can be calculated combining Dalton's and Roult's laws:

$$\begin{aligned} P_{\mathrm{TOT}} &= P_{\mathrm{A}} + P_{\mathrm{B}} = x_{\mathrm{A}} P^*_{\mathrm{A}} + x_{\mathrm{B}} P^*_{\mathrm{B}} \\ &= 0.67 \cdot 0.03 + 0.33 \cdot 0.10 \\ &= 0.02 + 0.03 = 0.05 \text{ bar} \end{aligned} \tag{13.1.3}$$

We can then calculate the mole fraction of the components in the vapor phase as:

$$\begin{array}{cc} y_{\mathrm{A}} = \dfrac{P_{\mathrm{A}}}{P_{\mathrm{TOT}}} & y_{\mathrm{B}} = \dfrac{P_{\mathrm{B}}}{P_{\mathrm{TOT}}} \\ y_{\mathrm{A}} = \dfrac{0.02}{0.05} = 0.40 & y_{\mathrm{B}} = \dfrac{0.03}{0.05} = 0.60 \end{array} \tag{13.1.4}$$

Notice how the mole fraction of toluene is much higher in the liquid phase, $x_{\mathrm{A}} = 0.67$, than in the vapor phase, $y_{\mathrm{A}} = 0.40$.

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13.2: Phase Diagrams of Non-Ideal Solutions

Non-ideal solutions follow Raoult's law for only a small amount of concentrations. The typical behavior of a non-ideal solution with a single volatile component is reported in the Px_{B} plot in Figure $13.2.1$.

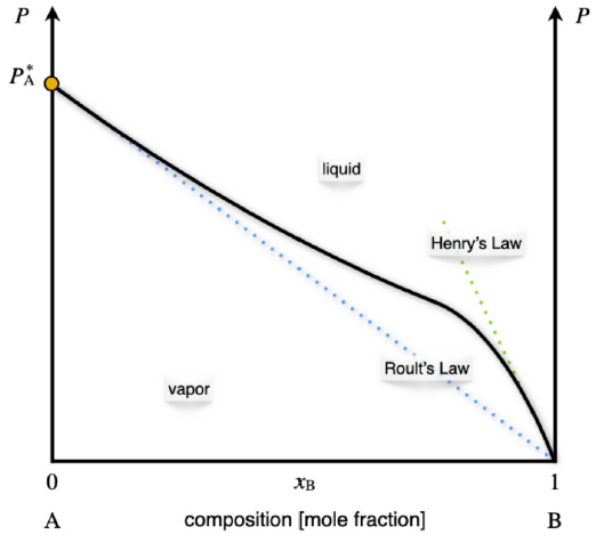


Figure $13.2.1$: The Pressure–Composition Phase Diagram of a Non-Ideal Solution Containing a Single Volatile Component at Constant Temperature.

Raoult's behavior is observed for high concentrations of the volatile component. This behavior is observed at $x_{\mathrm{B}} \to 0$ in Figure $13.2.1$, since the volatile component in this diagram is A. At low concentrations of the volatile component $x_{\mathrm{B}} \to 1$ in Figure $13.2.1$, the solution follows a behavior along a steeper line, which is known as **Henry's law**. William Henry (1774–1836) has extensively studied the behavior of gases dissolved in liquids. His studies resulted in a simple law that relates the vapor pressure of a solution to a constant, called Henry's law solubility constants:

$$P_{\mathrm{B}} = k_{\mathrm{AB}} x_{\mathrm{B}}, \tag{13.2.1}$$

where k_{AB} depends on the chemical nature of A and B. The corresponding diagram for non-ideal solutions with two volatile components is reported on the left panel of Figure $13.2.2$. The total pressure is once again calculated as the sum of the two partial pressures. Positive deviations on Raoult's ideal behavior are not the only possible deviation from ideality, and negative deviation also exits, albeit slightly less common. An example of a negative deviation is reported in the right panel of Figure $13.2.2$.

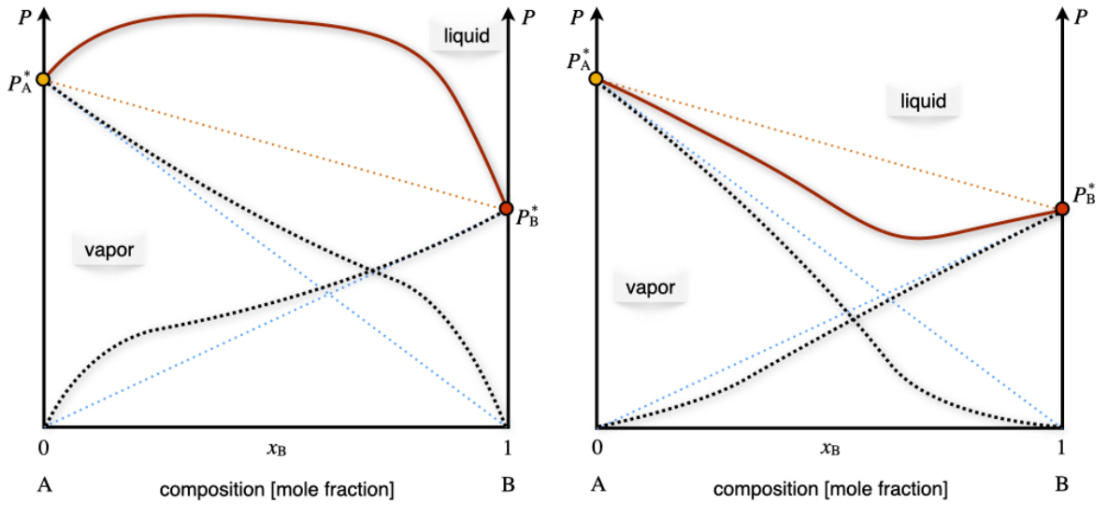


Figure 13.2.2: The Pressure–Composition Phase Diagram of Non-Ideal Solutions Containing Two Volatile Components at Constant Temperature.

If we move from the Px_B diagram to the Tx_B diagram, the behaviors observed in Figure 13.2.2 will correspond to the diagram in Figure 13.2.3.

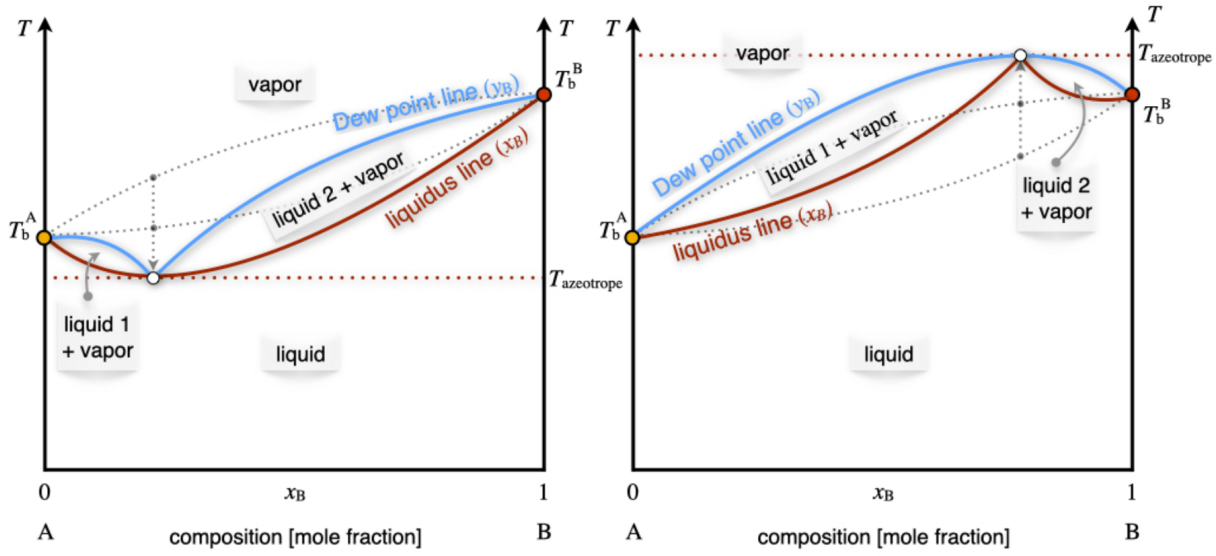


Figure 13.2.3: The Temperature–Composition Phase Diagram of Non-Ideal Solutions Containing Two Volatile Components at Constant Pressure.

The minimum (left plot) and maximum (right plot) points in Figure 13.2.3 represent the so-called **azeotrope**.

An azeotrope is a constant boiling point solution whose composition cannot be altered or changed by simple distillation. This happens because the liquidus and Dew point lines coincide at this point. Therefore, the liquid and the vapor phases have the same composition, and distillation cannot occur. Two types of azeotropes exist, representative of the two types of non-ideal behavior of solutions. The first type is the positive azeotrope (left plot in Figure 13.2.3). A notorious example of this behavior at atmospheric pressure is the ethanol/water mixture, with composition 95.63% ethanol by mass. This positive azeotrope boils at $T = 78.2\ ^\circ\text{C}$, a temperature that is lower than the boiling points of the pure constituents, since ethanol boils at $T = 78.4\ ^\circ\text{C}$ and water at $T = 100\ ^\circ\text{C}$. The second type is the negative azeotrope (right plot in Figure 13.2.3). An example of this behavior at atmospheric pressure is the hydrochloric acid/water mixture with composition 20.2% hydrochloric acid by mass. This negative azeotrope boils at $T = 110\ ^\circ\text{C}$, a temperature that is higher than the boiling points of the pure constituents, since hydrochloric acid boils at $T = -84\ ^\circ\text{C}$ and water at $T = 100\ ^\circ\text{C}$.

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13.3: Phase Diagrams of 2-Components/2-Condensed Phases Systems

We now consider equilibria between two condensed phases: liquid/liquid, liquid/solid, and solid/solid. These equilibria usually occur in the low-temperature region of a phase diagram (or high pressure). Three situations are possible, depending on the constituents and concentration of the mixture.

Totally miscible

We have already encountered the situation where the components of a solution mix entirely in the liquid phase. All the diagrams that we've discussed up to this point belong to this category.

Totally immiscible

A more complicated case is that for components that do not mix in the liquid phase. The liquid region of the temperature–composition phase diagram for a solution with components that do not mix in the liquid phase below a specific temperature is reported in Figure $13.3.1$.

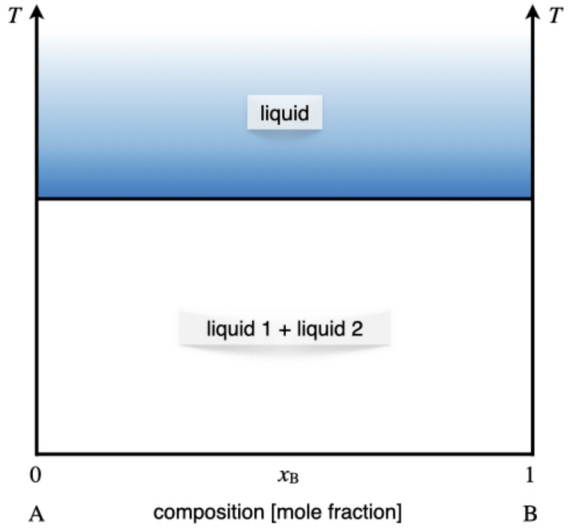


Figure $13.3.1$: The Liquid Region of the Temperature–Composition Phase Diagram of Solutions Containing Two Components that are Completely Immiscible in the Liquid Phase.

While the liquid 1+liquid 2 region (white area in Figure $13.3.1$) might seem similar to the liquid region that sits on top of it (blue area in Figure $13.3.1$), it is substantially different in nature. To prove this, we can calculate the degrees of freedom in each region using the Gibbs phase rule. For the liquid region at the top of the diagram, at constant pressure, we have $f = 2 - 1 + 1 = 2$. In other words, the temperature and the composition are independent, and their values can be changed regardless of each other. In the liquid 1+liquid 2 at the bottom, however, we have $f = 2 - 2 + 1 = 1$, which means that only one variable is independent of the others. The white region in Figure $13.3.1$ is a 2-phase region, and it behaves similarly to the other 2-phases regions that we encountered before, such as the inner portion of the lens in Figure 13.1.4. In other words, since the two components are entirely immiscible, once we set the temperature at a value below the immiscibility line, the concentration of the two liquids will be determined by tracing a horizontal line and by reading the concentrations on the left and right of the diagram (corresponding to 100% A and 100% B, respectively).

Partially miscible

The third and final case is undoubtedly the most interesting since several behaviors are possible. In fact, there might be components that are partially miscible at low temperatures but totally miscible at higher temperatures, for which the diagram will assume the general shape depicted in Figure 13.3.2. A typical example of this behavior is the mixture between water and phenol, whose liquids are completely miscible at $T > 66\ ^{\circ}\mathrm{C}$, and only partially miscible below this temperature. The composition of the 2-phases region (white area in Figure 13.3.2) is determined by tracing a horizontal line and reading the mole fraction on the line that delimits the area, as for the previous case.[1]

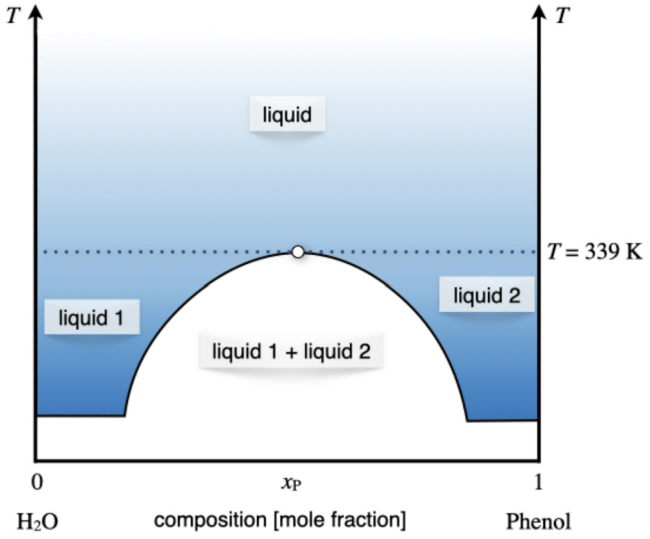


Figure 13.3.2: The Liquid Region of the Temperature–Composition Phase Diagram of Solutions Containing Two Components that are Partially Immiscible at Low Temperature in the Liquid Phase, but Completely Miscible at High Temperatures

On the opposite side of the spectrum, the diagram for a mixture whose components are partially miscible at high temperature, but completely miscible at lower temperatures is depicted in Figure 13.3.3. A typical example of this behavior is the mixture between water and triethylamine, whose liquids are completely miscible at $T < 18.5\ ^{\circ}\mathrm{C}$, and only partially miscible above this temperature.

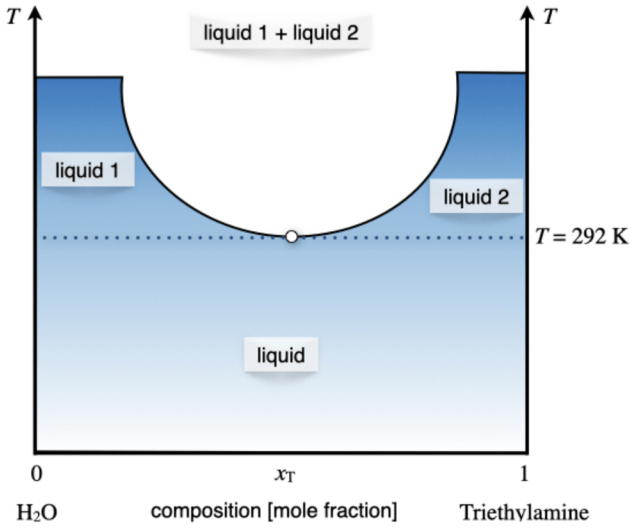


Figure 13.3.3: The Liquid Region of the Temperature–Composition Phase Diagram of Solutions Containing Two Components that are Partially Immiscible at High Temperature in the Liquid Phase, but Completely Miscible at Low Temperatures.

Finally, both situations described above are possible simultaneously. For some particular solutions, there exists a range of

temperature where the two components are only partially miscible. A typical example of this behavior is given by the water/nicotine mixture, whose liquids are completely miscible at $T > 210\ ^{\circ}\mathrm{C}$ and $T < 61\ ^{\circ}\mathrm{C}$, but only partially miscible in between these two temperatures, as in the diagram of Figure 13.3.4.

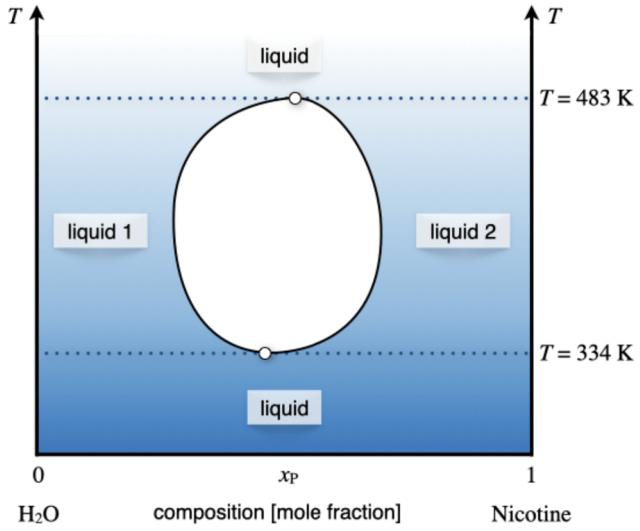


Figure 13.3.4 : The Liquid Region of the Temperature–Composition Phase Diagram of Solutions Containing Two Components that are Partially Immiscible Only Between Two Temperatures.

Eutectic systems

For some particular mixture, the temperature of partial miscibility in the liquid/liquid region might be close to the azeotrope temperature. In some cases, these two regions might even overlap. These characteristic behaviors are reported in Figure 13.3.5.

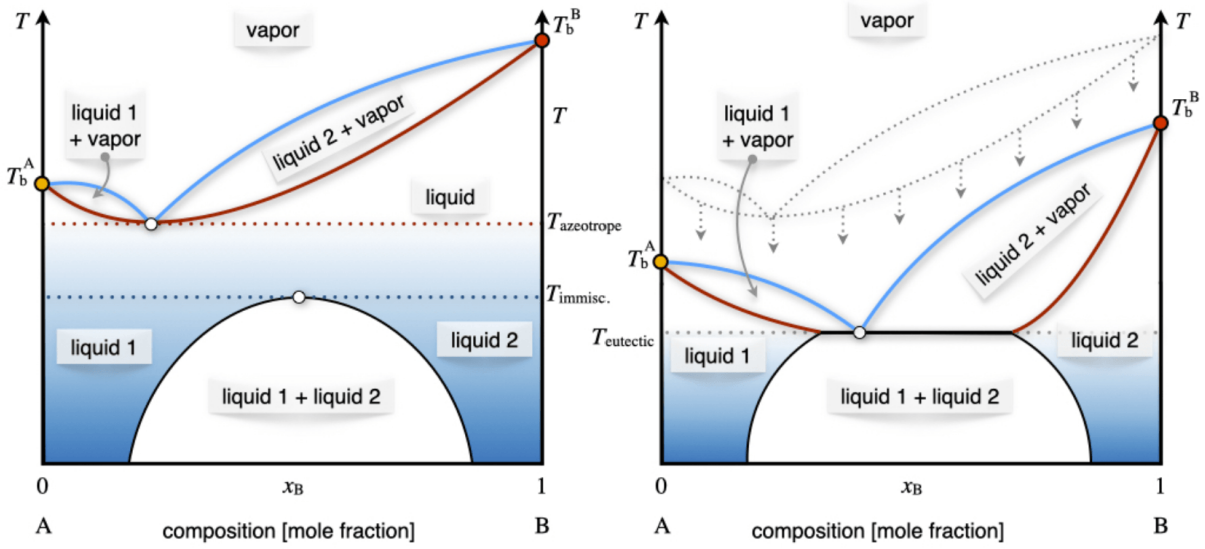


Figure 13.3.5: Interaction Between the Liquid/Gas and Liquid/Liquid Equilibria.

When the azeotrope and partially miscibility temperature overlap, the system forms what is known as an *eutectic*. Eutectic diagrams are possible at the liquid/gas equilibrium. Still, they are widespread at the liquid/solid equilibrium, where two components are completely miscible in the liquid phase, but only partially miscible in the solid phase. Eutectics with completely immiscible components in the solid phase are also very common, as the diagram reported in Figure 13.3.6.

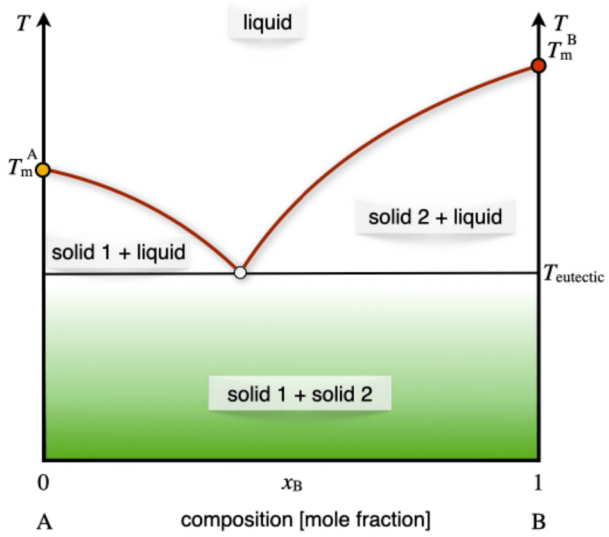


Figure 13.3.6: Typical Eutectic System with Components that are Completely Miscible in the Liquid Phase and Completely Immiscible in the Solid Phase.

1. The only noticeable difference, in this case, is that the two concentrations will be different than 0 and 100% since the component mix partially.

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14: PROPERTIES OF SOLUTIONS

In chapter 13, we have qualitatively described the deviation of real solutions from ideal behavior. In this section, we are discussing it quantitatively. We will be able to do so by using a concept that we have already encountered in chapter 10: Lewis's activity.

14.1: Activity

14.2: Colligative Properties

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14.1: Activity

For non-ideal gases, we introduced in chapter 11 the concept of *fugacity* as an *effective pressure* that accounts for non-ideal behavior. If we extend this concept to non-ideal solution, we can introduce the *activity* of a liquid or a solid, a, as:

$$\mu_{\text{non-ideal}} = \mu^{-\ominus} + RT \ln a, \tag{14.1.1}$$

where μ is the chemical potential of the substance or the mixture, and $\mu^{-\ominus}$ is the chemical potential at standard state. Comparing this definition to Equation 11.4.2, it is clear that the activity is equal to the fugacity for a non-ideal gas (which, in turn, is equal to the pressure for an ideal gas). However, for a liquid and a liquid mixture, it depends on the chemical potential at standard state. This means that the activity is not an absolute quantity, but rather a relative term describing how "active" a compound is compared to standard state conditions. The choice of the standard state is, in principle, arbitrary, but conventions are often chosen out of mathematical or experimental convenience. We already discussed the convention that standard state for a gas is at $P^{-\ominus} = 1 \text{ bar}$, so the activity is equal to the fugacity. The standard state for a component in a solution is the pure component at the temperature and pressure of the solution. This definition is equivalent to setting the activity of a pure component, i, at $a_i = 1$.

For a component in a solution we can use Equation 11.4.2 to write the chemical potential in the gas phase as:

$$\mu_i^{\text{vapor}} = \mu_i^{-\ominus} + RT \ln \frac{P_i}{P^{-\ominus}}. \tag{14.1.2}$$

If the gas phase is in equilibrium with the liquid solution, then:

$$\mu_i^{\text{solution}} = \mu_i^{\text{vapor}} = \mu_i^*, \tag{14.1.3}$$

where μ_i^* is the chemical potential of the pure element. Subtracting Equation 14.1.3 from Equation 14.1.2, we obtain:

$$\mu_i^{\text{solution}} = \mu_i^* + RT \ln \frac{P_i}{P_i^*}. \tag{14.1.4}$$

For an ideal solution, we can use Raoult's law, Equation 13.1.1, to rewrite Equation 14.1.4 as:

$$\mu_i^{\text{solution}} = \mu_i^* + RT \ln x_i, \tag{14.1.5}$$

which relates the chemical potential of a component in an ideal solution to the chemical potential of the pure liquid and its mole fraction in the solution. For a non-ideal solution, the partial pressure in Equation 14.1.4 is either larger (positive deviation) or smaller (negative deviation) than the pressure calculated using Raoult's law. The chemical potential of a component in the mixture is then calculated using:

$$\mu_i^{\text{solution}} = \mu_i^* + RT \ln \left(\gamma_i x_i\right), \tag{14.1.6}$$

where γ_i is a positive coefficient that accounts for deviations from ideality. This coefficient is either larger than one (for positive deviations), or smaller than one (for negative deviations). The activity of component i can be calculated as an *effective mole fraction*, using:

$$a_i = \gamma_i x_i, \tag{14.1.7}$$

where γ_i is defined as the **activity coefficient**. The partial pressure of the component can then be related to its vapor pressure, using:

$$P_i = a_i P_i^*. \tag{14.1.8}$$

Comparing Equation 14.1.8 with Raoult's law, we can calculate the activity coefficient as:

$$\gamma_i = \frac{P_i}{x_i P_i^*} = \frac{P_i}{P_i^{\text{R}}}, \tag{14.1.9}$$

where P_i^{R} is the partial pressure calculated using Raoult's law. This result also proves that for an ideal solution, $\gamma = 1$. Equation 14.1.9 can also be used experimentally to obtain the activity coefficient from the phase diagram of the non-ideal solution. This

is achieved by measuring the value of the partial pressure of the vapor of a non-ideal solution. Examples of this procedure are reported for both positive and negative deviations in Figure 14.1.1.

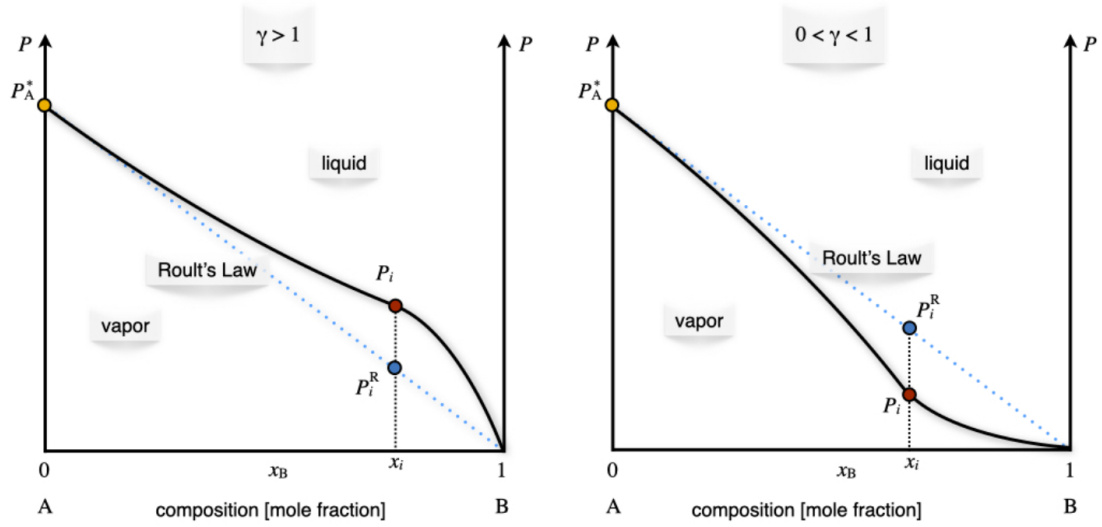


Figure 14.1.1: Positive and Negative Deviation from Raoult's Law in the Pressure–Composition Phase Diagram of Non-Ideal Solutions at Constant Temperature.

- As we already discussed in chapter 10, the activity is the most general quantity that we can use to define the equilibrium constant of a reaction (or the reaction quotient). The advantage of using the activity is that it's defined for ideal and non-ideal gases and mixtures of gases, as well as for ideal and non-ideal solutions in both the liquid and the solid phase.[1]

---

1. Notice that, since the activity is a relative measure, the equilibrium constant expressed in terms of the activities is also a relative concept. In other words, it measures equilibrium relative to a standard state. This fact, however, should not surprise us, since the equilibrium constant is also related to $\Delta_{rxn}G^{-\ominus}$ using Gibbs' relation. This is why the definition of a universally agreed-upon standard state is such an essential concept in chemistry, and why it is defined by the International Union of Pure and Applied Chemistry (IUPAC) and followed systematically by chemists around the globe.

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14.2: Colligative Properties

Colligative properties are properties of solutions that depend on the number of particles in the solution and not on the nature of the chemical species. More specifically, a colligative property depends on the ratio between the number of particles of the solute and the number of particles of the solvent. This ratio can be measured using any unit of concentration, such as mole fraction, molarity, and normality. For diluted solutions, however, the most useful concentration for studying colligative properties is the molality, m, which measures the ratio between the number of particles of the solute (in moles) and the mass of the solvent (in kg):

$$m = \frac{n_{\text{solute}}}{m_{\text{solvent}}}. \tag{14.2.1}$$

Colligative properties usually result from the dissolution of a nonvolatile solute in a volatile liquid solvent, and they are properties of the solvent, modified by the presence of the solute. They are physically explained by the fact that the solute particles displace some solvent molecules in the liquid phase, thereby reducing the concentration of the solvent. This explanation shows how colligative properties are independent of the nature of the chemical species in a solution only if the solution is ideal. For non-ideal solutions, the formulas that we will derive below are valid only in an approximate manner. We will discuss the following four colligative properties: relative lowering of the vapor pressure, elevation of the boiling point, depression of the melting point, and osmotic pressure.

Vapor pressure lowering

As we have already discussed in chapter 13, the vapor pressure of an ideal solution follows Raoult's law. Its difference with respect to the vapor pressure of the pure solvent can be calculated as:

$$\begin{aligned} P^*_{\text{solvent}} - P_{\text{solution}} &= P^*_{\text{solvent}} - x_{\text{solvent}} P^*_{\text{solvent}} \\ &= (1 - x_{\text{solvent}})\, P^*_{\text{solvent}} = x_{\text{solute}} P^*_{\text{solvent}}, \end{aligned} \tag{14.2.2}$$

which shows that the vapor pressure lowering depends only on the concentration of the solute. As such, it is a colligative property.

Boiling point elevation and melting point depression

The following two colligative properties are explained by reporting the changes due to the solute molecules in the plot of the chemical potential as a function of temperature (Figure 14.2.1).

At the boiling point, the chemical potential of the solution is equal to the chemical potential of the vapor, and the following relation can be obtained:

$$\begin{aligned} \mu_{\text{solution}} = \mu_{\text{vap}} &= \mu^{\ominus}_{\text{solvent}} + RT \ln P_{\text{solution}} \\ &= \mu^{\ominus}_{\text{solvent}} + RT \ln \left(x_{\text{solution}} P^*_{\text{solvent}} \right) \\ &= \underbrace{\mu^{\ominus}_{\text{solvent}} + RT \ln P^*_{\text{solvent}}}_{\mu^*_{\text{solvent}}} + RT \ln x_{\text{solution}} \\ &= \mu^*_{\text{solvent}} + RT \ln x_{\text{solution}}, \end{aligned} \tag{14.2.3}$$

and since $x_{\text{solution}} < 1$, the logarithmic term in the last expression is negative, and:

$$\mu_{\text{solution}} < \mu^*_{\text{solvent}}. \tag{14.2.4}$$

Equation ??? proves that the addition of a solute always stabilizes the solvent in the liquid phase, and lowers its chemical potential, as shown in Figure 14.2.1.

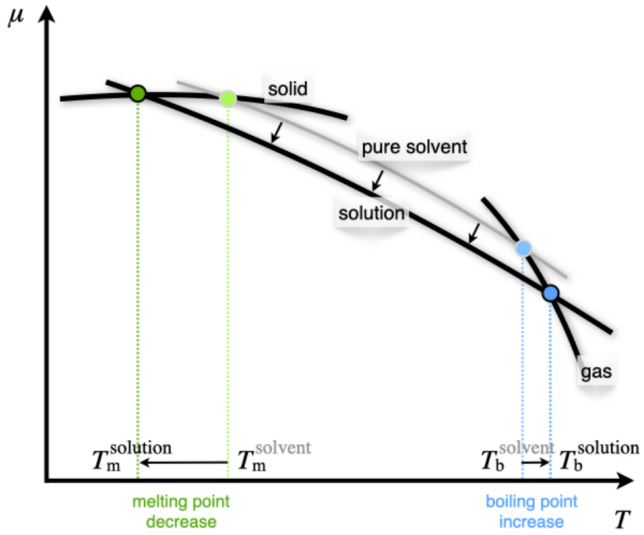


Figure 14.2.1: Reduction of the Chemical Potential of the Liquid Phase Due to the Addition of a Solute.

The elevation of the boiling point can be quantified using:

$$\Delta T_\mathrm{b} = T_\mathrm{b}^\mathrm{solution} - T_\mathrm{b}^\mathrm{solvent} = iK_\mathrm{b}m, \tag{14.2.5}$$

where i is the **van 't Hoff factor**, a coefficient that measures the number of solute particles for each formula unit, K_b is the ebullioscopic constant of the solvent, and m is the molality of the solution, as introduced in Equation 14.2.1 above. For a solute that does not dissociate in solution, $i = 1$. For a solute that dissociates in solution, the number of particles in solutions depends on how many particles it dissociates into, and $i > 1$. For example, the strong electrolyte $\mathrm{CaCl_2}$ completely dissociates into three particles in solution, one $\mathrm{Ca^{2+}}$ and two $\mathrm{Cl^-}$, and $i = 3$. For cases of partial dissociation, such as weak acids, weak bases, and their salts, i can assume non-integer values.

If we assume ideal solution behavior, the ebullioscopic constant can be obtained from the thermodynamic condition for liquid-vapor equilibrium. At the boiling point of the solution, the chemical potential of the solvent in the solution phase equals the chemical potential in the pure vapor phase above the solution:

$$\mu_\mathrm{solution}(T_\mathrm{b}) = \mu^*_\mathrm{solvent}(T_b) + RT\ln x_\mathrm{solvent}, \tag{14.2.6}$$

from which we can derive, using the Gibbs–Helmholtz equation, Equation 9.2.4:

$$K_\mathrm{b} = \frac{RMT_\mathrm{b}^2}{\Delta_\mathrm{vap}H}, \tag{14.2.7}$$

where R is the ideal gas constant, M is the molar mass of the solvent, and $\Delta_\mathrm{vap}H$ is its molar enthalpy of vaporization.

The reduction of the melting point is similarly obtained by:

$$\Delta T_\mathrm{m} = T_\mathrm{m}^\mathrm{solution} - T_\mathrm{m}^\mathrm{solvent} = -iK_\mathrm{m}m, \tag{14.2.8}$$

where i is the van 't Hoff factor introduced above, K_m is the *cryoscopic constant* of the solvent, m is the molality, and the minus sign accounts for the fact that the melting temperature of the solution is lower than the melting temperature of the pure solvent (ΔT_m is defined as a negative quantity, while i, K_m, and m are all positive). Similarly to the previous case, the cryoscopic constant can be related to the molar enthalpy of fusion of the solvent using the equivalence of the chemical potential of the solid and the liquid phases at the melting point, and employing the Gibbs–Helmholtz equation:

$$K_\mathrm{m} = \frac{RMT_\mathrm{m}^2}{\Delta_\mathrm{fus}H}. \tag{14.2.9}$$

Notice from Figure 14.2.1 how the depression of the melting point is always smaller than the elevation of the boiling point. This is because the chemical potential of the solid is essentially flat, while the chemical potential of the gas is steep. Consequently, the

value of the cryoscopic constant is always bigger than the value of the ebullioscopic constant. For example, for water $K_{\mathrm{m}} = 1.86 \ \frac{\mathrm{K\ kg}}{\mathrm{mol}}$, while $K_{\mathrm{b}} = 0.512 \ \frac{\mathrm{K\ kg}}{\mathrm{mol}}$. This is also proven by the fact that the enthalpy of vaporization is larger than the enthalpy of fusion.

Osmotic pressure

The **osmotic pressure** of a solution is defined as the difference in pressure between the solution and the pure liquid solvent when the two are in equilibrium across a semi-permeable (osmotic) membrane. The osmotic membrane is made of a porous material that allows the flow of solvent molecules but blocks the flow of the solute ones. The osmosis process is depicted in Figure 14.2.2.

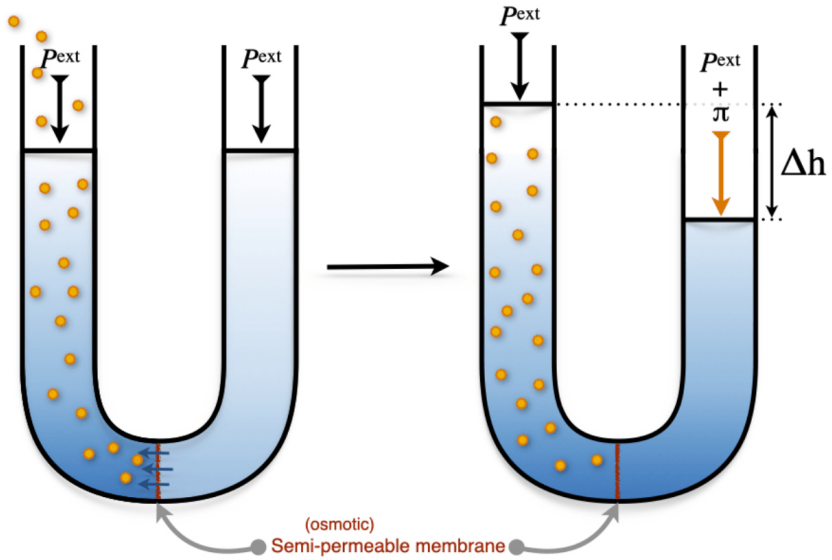


Figure 14.2.2: Osmotic Pressure of a Solution.

Starting from a solvent at atmospheric pressure in the apparatus depicted in Figure 14.2.2, we can add solute particles to the left side of the apparatus. The increase in concentration on the left causes a net transfer of solvent across the membrane. This flow stops when the pressure difference equals the osmotic pressure, π. The formula that governs the osmotic pressure was initially proposed by van 't Hoff and later refined by Harmon Northrop Morse (1848–1920). The **Morse formula** reads:

$$\pi = imRT, \tag{14.2.10}$$

where i is the van 't Hoff factor introduced above, m is the molality of the solution, R is the ideal gas constant, and T the temperature of the solution. As with the other colligative properties, the Morse equation is a consequence of the equality of the chemical potentials of the solvent and the solution at equilibrium.[1]

---

1. For a derivation, see the osmotic pressure Wikipedia page.

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15: CHEMICAL KINETICS

From thermodynamics, we can determine the spontaneity of a reaction and its extent, using ΔG and K_{eq}, respectively. However, thermodynamics does not provide any information on how *fast* the reaction is going to happen. For example, while the reaction that converts solid carbon from its diamond allotropic form into hexagonal graphite is thermodynamically spontaneous, it is so slow as to be virtually non-existent. Diamond is effectively a meta-stable phase. The speed of a chemical reaction is the subject of a branch of physical chemistry called chemical kinetics.

A chemical kinetics study aims to find the *rate* of a reaction and to find the microscopic steps that compose it, determining its *mechanism*.

15.1: Differential and integrated rate laws

15.2: Complex Rate Laws

15.3: Experimental Methods for Determination of Reaction Orders

15.4: Temperature Dependence of the Rate Coefficients

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15.1: Differential and integrated rate laws

The rate law of a chemical reaction is an equation that links the initial rate with the concentrations (or pressures) of the reactants. Rate laws usually include a constant parameter, k, called the *rate coefficient*, and several parameters found at the exponent of the concentrations of the reactants, and are called *reaction orders*. The rate coefficient depends on several conditions, including the reaction type, the temperature, the surface area of an adsorbent, light irradiation, and others. The reaction rate is usually represented with the lowercase letter k, and it should not be confused with the thermodynamic equilibrium constant that is generally designated with the uppercase letter K. Another useful concept in kinetics is the half-life, usually abbreviated with $t_{1/2}$. The half-life is defined as the time required to reach half of the initial reactant concentration.

A reaction that happens in one single microscopic step is called elementary. Elementary reactions have reaction orders equal to the (integer) stoichiometric coefficients for each reactant. As such, only a limited number of elementary reactions are possible (four types are commonly observed), and they are classified according to their overall reaction order. The global reaction order of a reaction is calculated as the sum of each reactant's individual orders and is, at most, equal to three. We examine in detail the four most common reaction orders below.

Zeroth-order reaction

For a zeroth-order reaction, the reaction rate is independent of the concentration of a reactant. In other words, if we have a reaction of the type:

$$\mathrm{A} \longrightarrow \text{products}$$

the differential rate law can be written:

$$-\frac{d[\mathrm{A}]}{dt} = k_0[\mathrm{A}]^0 = k_0, \tag{15.1.1}$$

which shows that any change in the concentration of A will have no effect on the speed of the reaction. The minus sign at the right-hand-side is required because the rate is always defined as a positive quantity, while the derivative is negative because the concentration of the reactant is diminishing with time. Separating the variables $[\mathrm{A}]$ and t of Equation 15.1.1 and integrating both sides, we obtain the integrated rate law for a zeroth-order reaction as:

$$\begin{aligned} \int_{[\mathrm{A}]_0}^{[A]} d[\mathrm{A}] &= -k_0 \int_{t=0}^{t} dt \\ [\mathrm{A}] - [\mathrm{A}]_0 &= -k_0 t \end{aligned} \tag{15.1.2}$$

$$[\mathrm{A}] = [\mathrm{A}]_0 - k_0 t.$$

Using the integrated rate law, we notice that the concentration on the reactant diminishes linearly with respect to time. A plot of $[\mathrm{A}]$ as a function of t, therefore, will result in a straight line with an angular coefficient equal to $-k_0$, as in the plot of Figure 15.1.1.

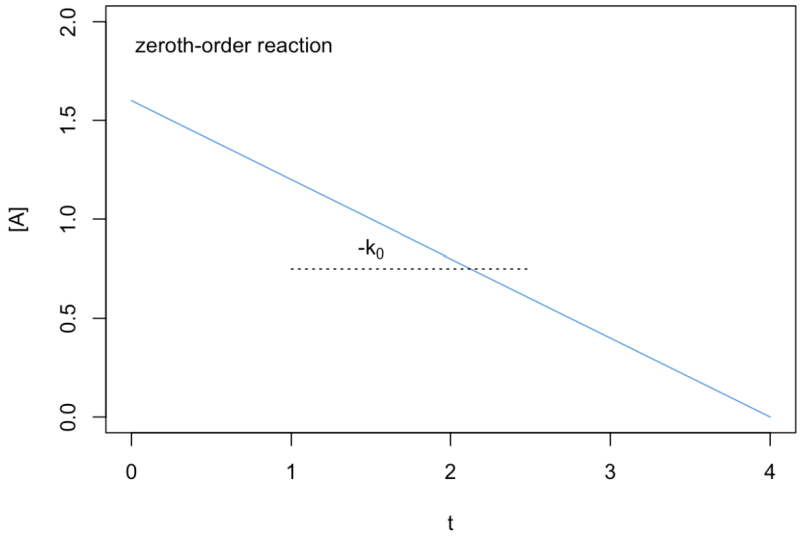


Figure 15.1.1: Reaction Rate Plot for a Zeroth-Order Reaction.

Eq. (15.1.2) also suggests that the units of the rate coefficient for a zeroth-order reaction are of concentration divided by time, typically $\frac{\mathrm{M}}{\mathrm{s}}$, with M being the molar concentration in $\frac{\mathrm{mol}}{\mathrm{L}}$ and s the time in seconds. The half-life of a zero order reaction can be calculated from Equation ???, by replacing $[\mathrm{A}]$ with $\frac{1}{2}[\mathrm{A}]_0$:

$$\begin{aligned} \frac{1}{2}[\mathrm{A}]_0 &= [\mathrm{A}]_0 - k_0 t_{1/2} \\ t_{1/2} &= \frac{[\mathrm{A}]_0}{2k_0}. \end{aligned} \tag{15.1.3}$$

Zeroth-order reactions are common in several biochemical processes catalyzed by enzymes, such as the oxidation of ethanol to acetaldehyde in the liver by the alcohol dehydrogenase enzyme, which is zero-order in ethanol.

First-order reaction

A first-order reaction depends on the concentration of only one reactant, and is therefore also called a *unimolecular reaction*. As for the previous case, if we consider a reaction of the type:

$$\mathrm{A} \rightarrow \text{products}$$

the differential rate law for a first-order reaction is:

$$-\frac{d[\mathrm{A}]}{dt} = k_1[\mathrm{A}]. \tag{15.1.4}$$

Following the usual blueprint of separating the variables, and integrating both sides, we obtain the integrated rate law as:

$$\begin{aligned} \int_{[\mathrm{A}]_0}^{[A]} \frac{d[\mathrm{A}]}{[\mathrm{A}]} &= -k_1 \int_{t=0}^{t} dt \\ \ln \frac{[\mathrm{A}]}{[\mathrm{A}]_0} &= -k_1 t \end{aligned} \tag{15.1.5}$$

$$[\mathrm{A}] = [\mathrm{A}]_0 \exp(-k_1 t).$$

Using the integrated rate law to plot the concentration of the reactant, $[\mathrm{A}]$, as a function of time, t, we obtain an exponential decay, as in Figure 15.1.2.

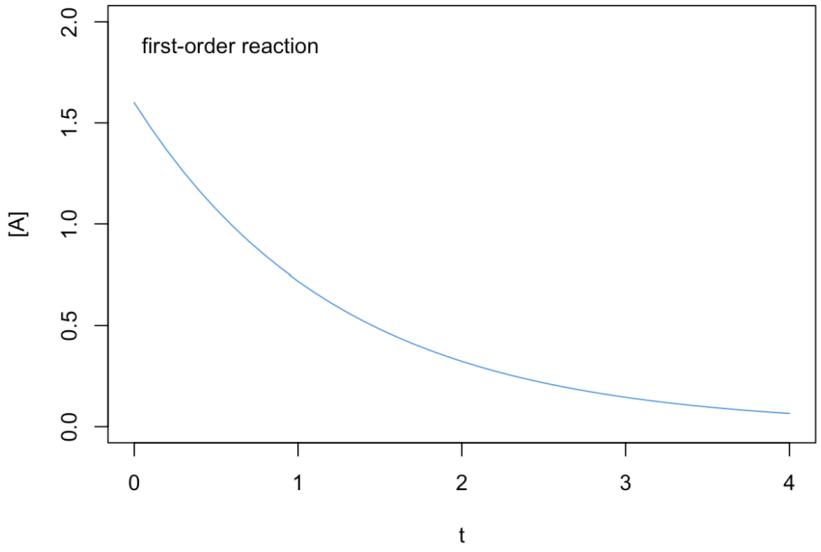


Figure 15.1.2: Reaction Rate Plot for a First-Order Reaction.

However, if we plot the logarithm of the concentration, $\ln[\mathrm{A}]$, as a function of time, we obtain a line with angular coefficient $-k_1$, as in the plot of Figure 15.1.3. From Equation ???, we can also obtain the units for the rate coefficient for a first-order reaction, which typically is $\frac{1}{\mathrm{s}}$, independent of concentration. Since the rate coefficient for first-order reactions has units of inverse time, it is sometimes called the frequency rate.

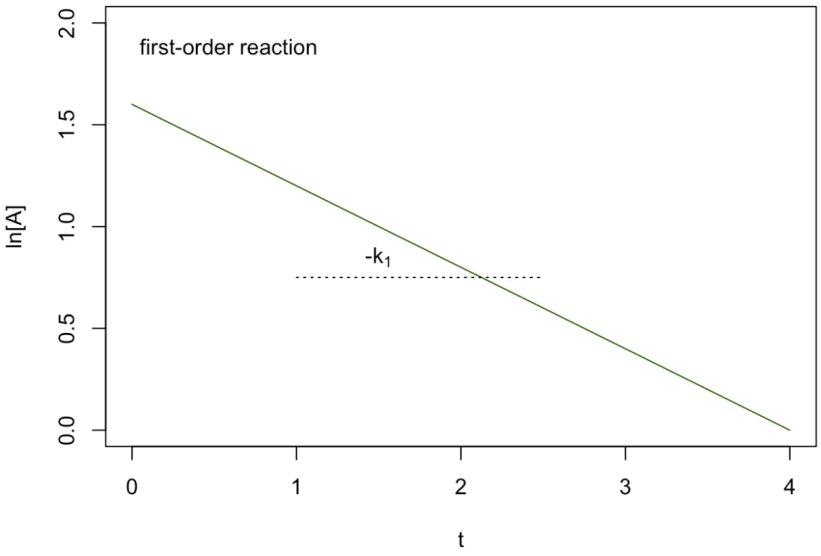


Figure 15.1.3: Linear Plot for a First-Order Reaction. Notice that the Quantity on the y Axes is ln[A].

The half-life of a first-order reaction is:

$$\ln \frac{\frac{1}{2}[\mathrm{A}]_0}{[\mathrm{A}]_0} = -k_1 t_{1/2} \qquad t_{1/2} = \frac{\ln 2}{k_1}. \tag{15.1.6}$$

The half-life of a first-order reaction is independent of the initial concentration of the reactant. Therefore, the half-life can be used in place of the rate coefficient to describe the reaction rate. Typical examples of first-order reactions are radioactive decays. For radioactive isotopes, it is common to report their rate of decay in terms of their half-life. For example, the most stable uranium nucleotide, $^{238}\mathrm{U}$, has a half-life of 4.468×10^9 years, while the most common fissile isotope of uranium, $^{235}\mathrm{U}$, has a half-life of

7.038×10^8 years.[1] Other examples of first-order reactions in chemistry are the class of S_N1 nucleophilic substitution reactions in organic chemistry.

Second-order reaction

A reaction is second-order when the sum of the reaction orders is two. Elementary second-order reactions are also called *bimolecular reactions*. There are two possibilities, a simple one, where the reaction order of one reagent is two, or a more complicated one, with two reagents having each a reaction order of one.

- For the simple case, we can write the reaction as:

$$2\mathrm{A} \rightarrow \text{products}$$

the differential rate law for a first-order reaction is:

$$-\frac{d[\mathrm{A}]}{dt} = k_2[\mathrm{A}]^2. \tag{15.1.7}$$

Following the same procedure used for the two previous cases, we can obtain the integrated rate law as:

$$\begin{aligned} \int_{[\mathrm{A}]_0}^{[A]} \frac{d[\mathrm{A}]}{[\mathrm{A}]^2} &= -k_2 \int_{t=0}^{t} dt \\ \frac{1}{[\mathrm{A}]} - \frac{1}{[\mathrm{A}]_0} &= k_2 t \\ \frac{1}{[\mathrm{A}]} &= \frac{1}{[\mathrm{A}]_0} + k_2 t. \end{aligned} \tag{15.1.8}$$

As for first-order reactions, the plot of the concentration as a function of time shows a non-linear decay. However, if we plot the inverse of the concentration, $\frac{1}{[\mathrm{A}]}$, as a function of time, t, we obtain a line with angular coefficient $+k_2$, as in the plot of Figure 15.1.4.

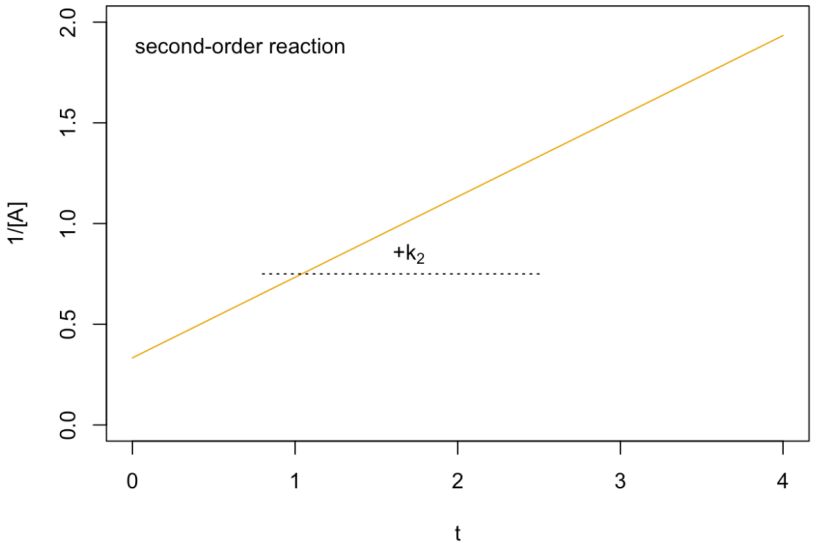


Figure 15.1.4: Linear Plot for a Second-Order Reaction. Notice that the Quantity on the y Axes is 1/[A].

Notice that the line has a *positive* angular coefficient, in contrast with the previous two cases, for which the angular coefficients were negative. The units of k for a simple second order reaction are calculated from Equation ??? and typically are $\frac{1}{\mathrm{M} \cdot \mathrm{s}}$. The half-life of a simple second-order reaction is:

$$\frac{1}{\frac{1}{2}[\mathrm{A}]_0} - \frac{1}{[\mathrm{A}]_0} = k_2 t_{1/2}$$

$$t_{1/2} = \frac{1}{k_2[\mathrm{A}]_0}, \tag{15.1.9}$$

which, perhaps not surprisingly, depends on the initial concentration of the reactant, $[\mathrm{A}]_0$. Therefore, if we start with a higher concentration of the reactant, the half-life will be shorter, and the reaction will be faster. An example of simple second-order behavior is the reaction $\mathrm{NO_2 + CO \rightarrow NO + CO_2}$, which is second-order in $\mathrm{NO_2}$ and zeroth-order in CO.

- For the complex second-order case, the reaction is:

  $$\mathrm{A + B \rightarrow products}$$

  and the differential rate law is:

  $$-\frac{d[\mathrm{A}]}{dt} = k_2'[\mathrm{A}][\mathrm{B}]. \tag{15.1.10}$$

  The differential equation in Equation 15.1.10 has two variables, and cannot be solved exactly unless an additional relationship is specified. If we assume that the initial concentration of the two reactants are equal, then $[\mathrm{A}] = [\mathrm{B}]$ at any time t, and Equation 15.1.10 reduces to Equation 15.1.7. If the concentration of the reactants are different, then the integrated rate law will assume the following shape:

  $$\frac{[\mathrm{A}]}{[\mathrm{B}]} = \frac{[\mathrm{A}]_0}{[\mathrm{B}]_0} \exp\left\{\left([\mathrm{A}]_0 - [\mathrm{B}]_0\right) k_2' t\right\}. \tag{15.1.11}$$

  The units of k for a complex second order reaction can be calculated from Equation 15.1.11, and are the same as those for the simple case, $\frac{1}{\mathrm{M \cdot s}}$. The half-life of a complex second-order reaction cannot be easily written since two different half-lives could, in principle, be defined for each of the corresponding reactants.

Third and higher orders reaction

Although elementary reactions with order higher than two are possible, they are in practice infrequent, and only very few experimental third-order reactions are observed. Fourth-order or higher have never been observed because the probabilities for a simultaneous interaction between four molecules are essentially zero. Third-order elementary reactions are also called *termolelucar reactions*. While termolelucar reactions with three identical reactants are possible in principle, there is no known experimental example. Some complex third-order reactions are known, such as:

$$\mathrm{2NO_{(g)} + O_{2(g)} \longrightarrow 2NO_{2(g)}}$$

for which the differential rate law can be written as:

$$-\frac{dP_{\mathrm{O_2}}}{dt} = k_3 P_{\mathrm{NO}}^2 P_{\mathrm{O_2}}. \tag{15.1.12}$$

---

1. Notice how large these numbers are for uranium. To put these numbers in perspective, we can compare them with the half-life of the most unstable isotope of plutonium, $^{241}\mathrm{Pu}$, which is $t_{1/2} = 14.1$ years.

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15.2: Complex Rate Laws

It is essential to specify that the order of a reaction and its molecularity are equal only for elementary reactions. Reactions that follow complex laws are composed of several elementary steps, and they usually have non-integer reaction orders, for at least one of the reactants.

Consecutive reactions

A reaction that happens following a sequence of two elementary steps can be written as follows:

$$\mathrm{A} \xrightarrow{k_1} \mathrm{B} \xrightarrow{k_2} \mathrm{C}$$

Assuming that each of the steps follows a first order kinetic law, and that only the reagent A is present at the beginning of the reaction, we can write the differential change in concentration of each species with respect to infinitesimal time dt, using the following formulas:

$$\begin{aligned} -\frac{d[\mathrm{A}]}{dt} &= k_1[\mathrm{A}] \Rightarrow [\mathrm{A}] = [\mathrm{A}]_0 \exp(-k_1 t) \\ \frac{d[\mathrm{B}]}{dt} &= k_1[\mathrm{A}] - k_2[\mathrm{B}] \\ \frac{d[\mathrm{C}]}{dt} &= k_2[\mathrm{B}]. \end{aligned} \tag{15.2.1}$$

These three equations represent a system of differential equations with three unknown variables. Unfortunately, these equations are linearly dependent on each other, and they are not sufficient to solve the system for each variable. To do so, we need to include a fourth equation, coming from the conservation of mass:

$$[\mathrm{A}]_0 = [\mathrm{A}] + [\mathrm{B}] + [\mathrm{C}]. \tag{15.2.2}$$

Using the first equation in Equation ???, we can now replace the concentration $[\mathrm{A}]$ in the second equation and solve for $[\mathrm{B}]$:

$$\frac{d[\mathrm{B}]}{dt} + k_2[\mathrm{B}] = k_1[\mathrm{A}]_0 \exp(-k_1 t), \tag{15.2.3}$$

which can be simplified by multiplying both sides by $\exp(k_2 t)$:

$$\begin{aligned} \left(\frac{d[\mathrm{B}]}{dt} + k_2[\mathrm{B}]\right) \exp(k_2 t) &= k_1[\mathrm{A}]_0 \exp[(k_2 - k_1)t] \\ \Rightarrow \frac{d\{[\mathrm{B}]\exp(k_2 t)\}}{dt} &= k_1[\mathrm{A}]_0 \exp[(k_2 - k_1)t], \end{aligned} \tag{15.2.4}$$

which can then be integrated remembering that $[B]_0 = 0$, and $\int \exp(kx) = \frac{1}{k}\exp(kx)$:

$$[\mathrm{B}] = \frac{k_1}{k_2 - k_1}[\mathrm{A}]_0[\exp(-k_1 t) - \exp(-k_2 t)]. \tag{15.2.5}$$

We can then use both $[\mathrm{A}]$, from Equation ???, and $[\mathrm{B}]$, from Equation 15.2.5, in Equation 15.2.2 to solve for $[\mathrm{C}]$:

$$\begin{aligned} [\mathrm{C}] &= [\mathrm{A}]_0 - [\mathrm{A}] - [\mathrm{B}] \\ &= [\mathrm{A}]_0 - [\mathrm{A}]_0 \exp(-k_1 t) - \frac{k_1}{k_2 - k_1}[\mathrm{A}]_0[\exp(-k_1 t) - \exp(-k_2 t)] \\ &= [\mathrm{A}]_0 \left\{1 + \frac{-k_2 \exp(-k_1 t) + k_1 \exp(-k_2 t)}{k_2 - k_1}\right\}. \end{aligned} \tag{15.2.6}$$

From these results, we can distinguish two extreme behaviors. The first one is observed when $k_1 \cong k_2$, and it produces a plot of the concentration of species with respect to time reported in Figure 15.2.1. This behavior is observed when a process undergoing a series of consecutive reactions present a rate-determining step in the middle of the sequence (the second reaction, in the

simple case analyzed above). Once the process is established, its rate will equate the rate of the slowest step.

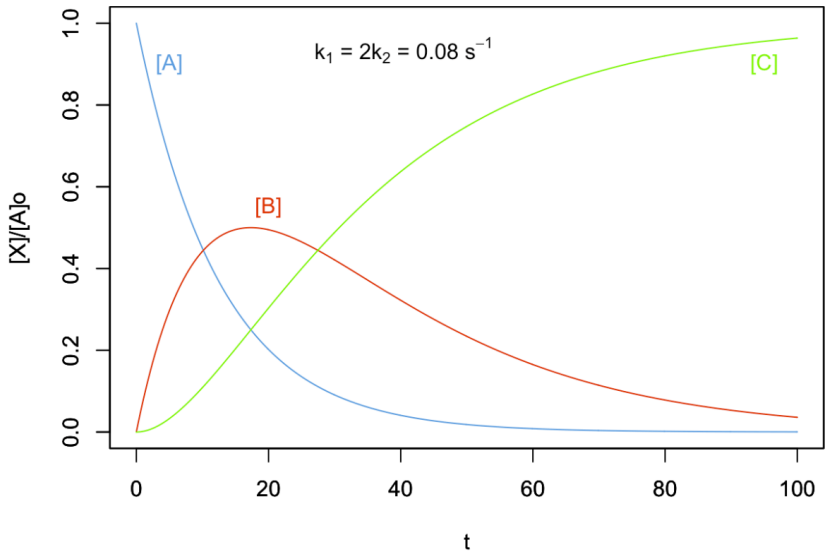


Figure 15.2.1: Concentration Plot for a Process with Two Consecutive Reactions with the Second One Being the Rate-Determining Step.

The second behavior is observed when $k_1 \ll k_2$, and it produces the plot in Figure 15.2.2 In this case, the concentration of the intermediate species B is not relevant throughout the process, and the rate-determining step is the first reaction. As such, the process has the same rate law as an elementary reaction going directly from A to C.

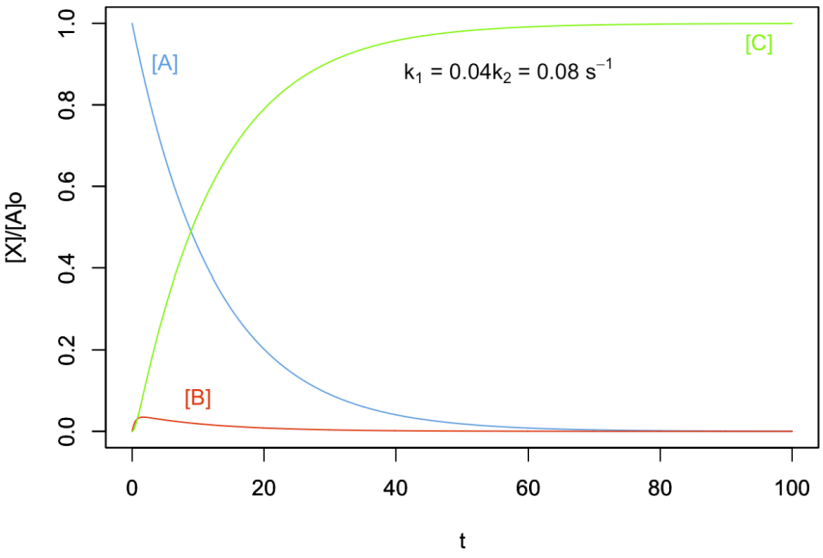


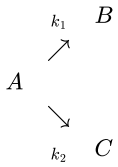
Figure 15.2.2: Concentration Plot for a Process with Two Consecutive Reactions with the First One Being the Rate-Determining Step.

Since the concentration of B is small and relatively constant throughout the process, $\frac{d[\mathrm{B}]}{dT} = 0$. We can then simplify the mathematical treatment of these reactions by eliminating it from the process altogether. This simplification is known as the *steady-state approximation*. It is used in chemical kinetics to study processes that undergo a series of reactions producing intermediate species whose concentrations are constants throughout the entire process.

$$\begin{array}{l} \mathrm{A} \xrightarrow{k_1} \mathrm{I}_1 \xrightarrow{k_2} \mathrm{I}_2 \blacksquare \cdots \xrightarrow{k_n} \text{products} \\ \quad \text{Steady State Approximation:} \\ \mathrm{A} \longrightarrow \text{products} \end{array} \tag{15.2.7}$$

Competitive reactions

A process where two elementary reactions happen in parallel, competing with each can be written as follows:



Assuming that each step follows first order kinetic, we can write:

$$\begin{aligned} -\frac{d[\mathrm{A}]}{dt} &= k_1[\mathrm{A}] + k_2[\mathrm{A}] \Rightarrow [\mathrm{A}] = [\mathrm{A}]_0 \exp\left[-(k_1+k_2)t\right] \\ \frac{d[\mathrm{B}]}{dt} &= k_1[\mathrm{A}] \Rightarrow [\mathrm{B}] = \frac{k_1}{k_1+k_2}[\mathrm{A}]_0 \left\{1 - \exp\left[-(k_1+k_2)t\right]\right\} \\ \frac{d[\mathrm{C}]}{dt} &= k_2[\mathrm{A}] \Rightarrow [\mathrm{C}] = \frac{k_2}{k_1+k_2}[\mathrm{A}]_0 \left\{1 - \exp\left[-(k_1+k_2)t\right]\right\}. \end{aligned} \tag{15.2.8}$$

The concentration of each of the species can then be plotted against time, obtaining the diagram reported in Figure 15.2.3. The final concentrations of the products, $[\mathrm{B}]_f$ and $[\mathrm{C}]_f$, will depend on the values of the two rate coefficients. For example, if $k_1 > k_2$, $[\mathrm{B}]_f > [\mathrm{C}]_f$, as in Figure 15.2.3, but if $k_1 < k_2$, $[\mathrm{B}]_f < [\mathrm{C}]_f$.

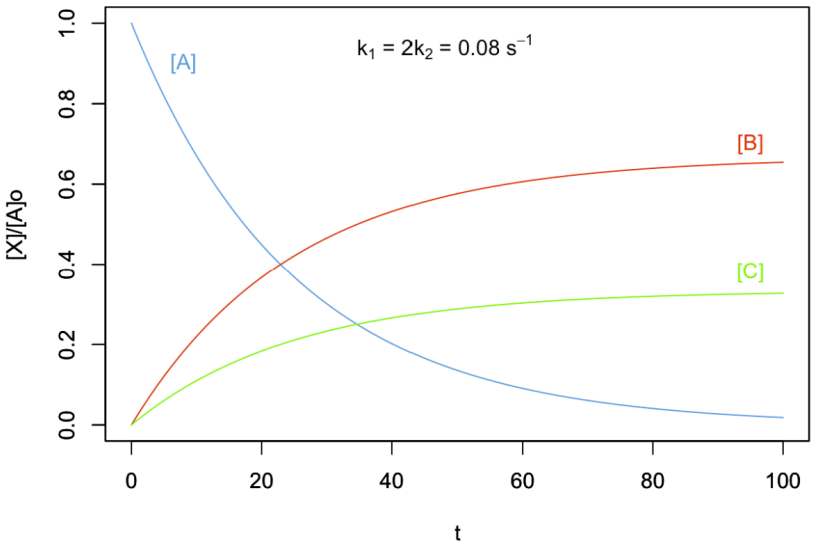


Figure 15.2.3: Concentration Plot for a Process with Two Competitive Reactions.

An important relationship that can be derived from Equation ??? is that:

$$\frac{[\mathrm{B}]}{[\mathrm{C}]} = \frac{k_1}{k_2}.$$

Opposed reactions

Another case of complex kinetic law happens when a pair of forward and reverse reactions occur simultaneously:

$$\mathrm{A} \underset{\blacksquare}{\overset{k_1}{\rightleftharpoons}} \mathrm{B}$$

where the rate coefficients for the forward and backwards reaction, k_1 and k_{-1} respectively, are not necessarily equal to each other, but comparable in magnitude. We can write the rate laws for each of these elementary steps as:

$$
\begin{aligned}
-\frac{d[\mathrm{A}]}{dt} &= k_1[\mathrm{A}] - k_{-1}[\mathrm{B}] = k_1[\mathrm{A}] - k_{-1}\left([\mathrm{A}]_0 - [\mathrm{A}]\right) \\
\frac{d[\mathrm{A}]}{dt} &= -(k_1 + k_{-1})[\mathrm{A}] + k_{-1}[\mathrm{A}]_0,
\end{aligned}
\tag{15.2.9}
$$

which can then be integrated to:

$$
\begin{aligned}
[\mathrm{A}] &= [\mathrm{A}]_0 \frac{k_{-1} + k_1 \exp[-(k_1 + k_{-1})t]}{k_1 + k_{-1}} \\
[\mathrm{B}] &= [\mathrm{A}]_0 \left\{1 - \frac{k_{-1} + k_1 \exp[-(k_1 + k_{-1})t]}{k_1 + k_{-1}}\right\}.
\end{aligned}
\tag{15.2.10}
$$

These formulas can then be used to obtain the plots in Figure 15.2.4.

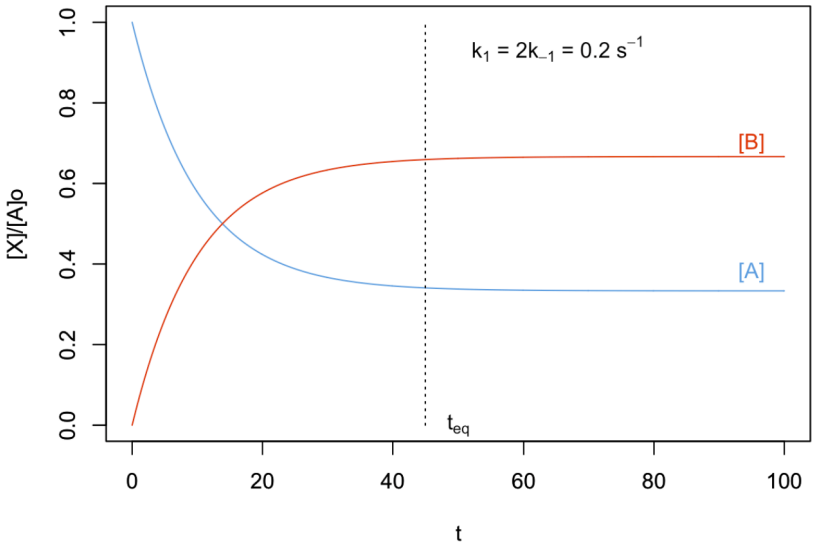


Figure 15.2.4: Concentration Plot for a Process with Two Opposed Reactions.

As can be seen from the plots in Figure 15.2.4, after a sufficiently long time, the systems reach a dynamic equilibrium, where the concentration of A and B don't change. These equilibrium concentrations can be calculated replacing $t = \infty$ in Equation ???:

$$
\begin{aligned}
[\mathrm{A}]_{\mathrm{eq}} &= [\mathrm{A}]_0 \frac{k_{-1}}{k_1 + k_{-1}} \\
[\mathrm{B}]_{\mathrm{eq}} &= [\mathrm{A}]_0 \frac{k_1}{k_1 + k_{-1}}.
\end{aligned}
\tag{15.2.11}
$$

Considering that the concentrations of the species don't change at equilibrium:

$$
\begin{aligned}
-\frac{d[\mathrm{A}]_{\mathrm{eq}}}{dt} = \frac{d[\mathrm{B}]_{\mathrm{eq}}}{dt} &= 0 \\
\Rightarrow\ k_1[\mathrm{A}]_{\mathrm{eq}} &= k_{-1}[\mathrm{B}]_{\mathrm{eq}} \\
\Rightarrow\ \frac{k_1}{k_{-1}} &= \frac{[\mathrm{B}]_{\mathrm{eq}}}{[\mathrm{A}]_{\mathrm{eq}}} = K_C,
\end{aligned}
\tag{15.2.12}
$$

where K_C is the equilibrium constant as defined in chapter 10. This is a rare link between kinetics and thermodynamics and appears only for opposed reactions after sufficient time has passed so that the system can reach the dynamic equilibrium.

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15.3: Experimental Methods for Determination of Reaction Orders

To experimentally measure the reaction rate, we need a method to measure concentration changes with respect to time. The simplest way to determine the reaction rate is to monitor the entire reaction as it proceeds and then plot the resulting data differently until a linear plot is found. A summary of the results obtained in section 15.1 and that is useful for this task is reported in the following table:

	Zeroth-Order	First-Order	Simple Second-Order	Complex Second-Order
Differential Rate Law	$-\frac{d[\mathrm{A}]}{dt} = k_0[\mathrm{A}]^0 = k_0$	$-\frac{d[\mathrm{A}]}{dt} = k_1[\mathrm{A}]$	$-\frac{d[\mathrm{A}]}{dt} = k_2[\mathrm{A}]^2$	$-\frac{d[\mathrm{A}]}{dt} = k_2'[\mathrm{A}][\mathrm{B}]$
Integrated Rate Law	$[\mathrm{A}] = [\mathrm{A}]_0 - k_0 t$	$[\mathrm{A}] = [\mathrm{A}]_0 e^{-k_1 t}$	$\frac{1}{[\mathrm{A}]} = \frac{1}{[\mathrm{A}]_0} + k_2 t$	$\frac{[\mathrm{A}]}{[\mathrm{B}]} = \frac{[\mathrm{A}]_0}{[\mathrm{B}]_0} e^{([\mathrm{A}]_0 - [\mathrm{B}]_0)k_2' t}$
Units of k	$\frac{\mathrm{M}}{\mathrm{s}}$	$\frac{1}{\mathrm{s}}$	$\frac{1}{\mathrm{M}\cdot\mathrm{s}}$	$\frac{1}{\mathrm{M}\cdot\mathrm{s}}$
Linear Plot vs. t	$[\mathrm{A}]$	$\ln[\mathrm{A}]$	$\frac{1}{[\mathrm{A}]}$	$\ln\frac{[\mathrm{A}]_0[\mathrm{B}]}{[\mathrm{B}]_0[\mathrm{A}]}$
Half-life	$t_{1/2} = \frac{[\mathrm{A}]_0}{2k_0}$	$t_{1/2} = \frac{\ln 2}{k_1}$	$t_{1/2} = \frac{1}{k_2[\mathrm{A}]_0}$	not easily defined

However, this method works only if the reaction has few reactants, and it requires several measurements, each of which might be complicated to make. More useful methods to determine the reaction rate are the *initial rate* and the *isolation* methods that we describe below.

Initial rates method

The *initial rates method* involves measuring the rate of a reaction as soon as it starts before any significant change in the concentrations of the reactants occurs. The initial rate method is practical only if the reaction is reasonably slow, but it can measure the rate unambiguously when more than one reactant is involved. For example, if we have a reaction with the following stoichiometry:

$$\alpha\mathrm{A} + \beta\mathrm{B} \xrightarrow{k} \text{products}$$

the initial rate method can be used to determine the coefficients of the rate law:

$$\text{Rate} = k[\mathrm{A}]^{\alpha}[\mathrm{B}]^{\beta} \tag{15.3.1}$$

by designing three experiment, where the initial concentrations of A and B are appropriately changed. For example, let's consider the following experimental data from three different experiments:

	$[\mathrm{A}]_0$ (M)	$[\mathrm{B}]_0$ (M)	initial rate $\left(\frac{M}{s}\right)$
Experiment 1:	0.10	0.10	4.32
Experiment 2:	0.15	0.10	9.70
Experiment 3:	0.10	0.20	4.29

we can calculate α by taking the ratio of the rates measured in experiment 1 and 2:

$$\begin{aligned}\frac{\text{Rate}(1)}{\text{Rate}(2)} &= \frac{k(0.10\ \text{M})^{\alpha}(0.10\ \text{M})^{\beta}}{k(0.15\ \text{M})^{\alpha}(0.10\ \text{M})^{\beta}} \\ \frac{4.32}{9.70} &= \frac{(0.10\ \text{M})^{\alpha}}{(0.15\ \text{M})^{\alpha}} \\ 0.445 &= 0.667^{\alpha} \ \rightarrow\ \ln 0.445 = \alpha \ln 0.667 \\ \alpha &= \frac{-0.81}{-0.405} = 2.\end{aligned} \tag{15.3.2}$$

β can be calculated similarly by taking the ratio between experiments 1 and 3. Alternatively, we can also notice that the reaction rate does not change when the initial concentration $[\text{B}]_0$ is doubled, therefore $\beta = 0$.

Isolation method

Another method that is widely used to determine reaction orders is the *isolation method*. This method is performed by using large excess concentrations of all reactants but one. For example, if we have the following reaction with three reagents and unknown rate law:

$$\alpha\text{A} + \beta\text{B} + \gamma\text{C} \xrightarrow{k} \text{products}$$

we can perform three different experiments, in each of which we use an excessive amount of one of the two reagents, such as:

- Experiment 1: $[\text{A}]_0 = 1\ \text{M}, \quad [\text{B}]_0 = 1000\ \text{M}, \quad [\text{C}]_0 = 1000\ \text{M}$, in which the reaction order with respect to A is measured.
- Experiment 2: $[\text{A}]_0 = 1000\ \text{M}, \quad [\text{B}]_0 = 1\ \text{M}, \quad [\text{C}]_0 = 1000\ \text{M}$, in which the reaction order with respect to B is measured.
- Experiment 3: $[\text{A}]_0 = 1000\ \text{M}, \quad [\text{B}]_0 = 1000\ \text{M}, \quad [\text{C}]_0 = 1\ \text{M}$, in which the reaction order with respect to C is measured.

From each experiment we can determine the *pseudo-order* of the reaction with respect to the reagent that is in minority concentration. For example, for the reaction above, we can write the rate law as:

$$\text{Rate} = k[\text{A}]^{\alpha}[\text{B}]^{\beta}[\text{C}]^{\gamma} \tag{15.3.3}$$

and we can write the initial concentrations, $[X]_0$, and the final concentrations, $[X]_f$, of each of the species in experiment 1, as:

$$\begin{aligned}[\text{A}]_0 = 1\ \text{M} \ &\longrightarrow [\text{A}]_f = 0\ \text{M} && (100\%\ \text{change}) \\ [\text{B}]_0 = 1000\ \text{M} \ &\longrightarrow [\text{B}]_f = 1000 - 1 = 999\ \text{M} \cong [\text{B}]_0 && (0.1\%\ \text{change}) \\ [\text{C}]_0 = 1000\ \text{M} \ &\longrightarrow [\text{C}]_f = 1000 - 1 = 999\ \text{M} \cong [\text{C}]_0\,. && (0.1\%\ \text{change})\end{aligned}$$

The coefficient α can then be determined by incorporating the concentration of the reactants in excess into the rate constant as:

$$\begin{aligned}\text{rate} &= k[\text{A}]^{\alpha}\underbrace{[\text{B}]^{\beta}[\text{C}]^{\gamma}}_{\text{constant}} \\ &= k'[\text{A}]^{\alpha}\end{aligned}$$

and then determine α by verifying which order the data collected for $[\text{A}]$ at various time fit. This can be simply achieved by using the zero-, first-, and second-order kinetic plots, as reported in the table above. We can determine β and γ by repeating the same procedure for the data from the other two experiments. For example, if we find for a specific reaction that $\alpha = 1$, $\beta = 2$, and $\gamma = 0$, we can then say that the reaction is pseudo-order one in A, pseudo-order two in B, and pseudo-order zero in C, with an overall reaction order of three.

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15.4: Temperature Dependence of the Rate Coefficients

The dependence of the rate coefficient, k, on the temperature is given by the **Arrhenius equation**. This formula was derived by Svante August Arrhenius (1859–1927) in 1889 and is based on the simple experimental observation that every chemical process gets faster when the temperature is increased. Working on data from equilibrium reactions previously reported by van 't Hoff, Arrhenius proposed the following simple exponential formula to explain the increase of k when T is increased:

$$k = A \exp\left(\frac{E_a}{RT}\right), \tag{15.4.1}$$

where A is the so-called Arrhenius pre-exponential factor, and E_a is the activation energy. Both of these terms are independent of temperature,[1] and they represent experimental quantities that are unique to each individual reaction. Since there is no known exception to the fact that a temperature increase speeds up chemical reactions, both A and E_a are always positive. The pre-exponential factor units are the same as the rate constant and will vary depending on the order of the reaction. As suggested by its name, the activation energy has units of energy per mole of substance, $\frac{\text{J}}{\text{mol}}$ in SI.

The Arrhenius equation is experimentally useful in its linearized form, which is obtained from two Arrhenius experiments, taken at different temperatures. Applying Equation 15.4.1 to two different experiments, and taking the ratio between the results, we obtain:

$$\ln \frac{k_{T_2}}{k_{T_1}} = -\frac{E_a}{RT}\left(\frac{1}{T_2} - \frac{1}{T_1}\right), \tag{15.4.2}$$

which gives the plot of Figure 15.4.1, from which E_a can be determined.

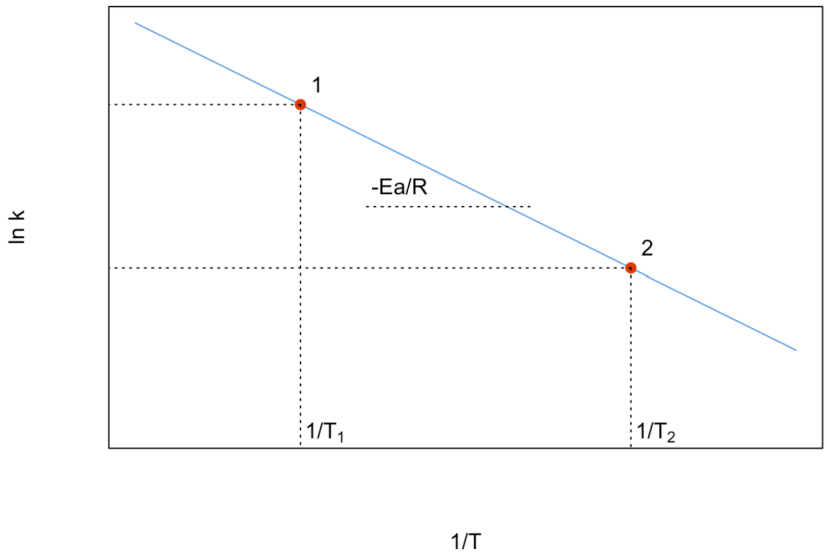


Figure 15.4.1: Arrhenius Plot Obtained Using Experimental Data at Two Different Temperatures.

From empirical arguments, Arrhenius proposed the idea that reactants must acquire a minimum amount of energy before they can form any product. He called this amount of minimum energy the activation energy. We can motivate this assumption by plotting energy of a reaction along the reaction coordinate, as in Figure 15.4.3.[2] The reaction coordinate is defined as the minimum energy path that connects the reactants with the products.

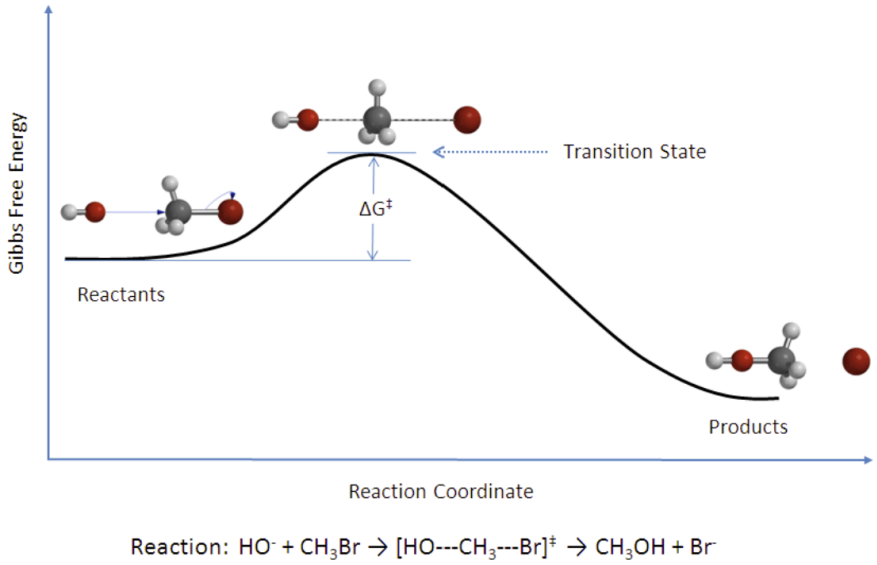


Figure 15.4.3: Reaction Coordinate Diagram for a Typical Reaction.

1. In theory, both A and E_a show a weak temperature dependence. However, they can be considered constants at most experimental conditions, since kinetic studies are usually performed in a small temperature range.
2. This plot is taken from Wikipedia, and have been generated and distributed by Author Grimlock under CC-BY-SA license.

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16: Gas-Phase Reaction Dynamics

- **30.1: The Rate of Bimolecular Gas-Phase Reaction Can Be Estimated Using Hard-Sphere Collision Theory and an Energy-Dependent Reaction Cross Section**
  This page covers collision frequency in bimolecular gas-phase reactions using the Hard Sphere Model, linking collision frequency to reaction rates and introducing a new reaction cross-section that considers energy requirements. It highlights the model's temperature and energy thresholds while noting deviations from the Arrhenius equation.

- **30.2: A Reaction Cross Section Depends Upon the Impact Parameter**
  This page critiques the flawed assumption that all collisions between Q and B particles result in reactions, noting that proper alignment is essential. It discusses the need to modify the reaction cross-section using the line-of-centers model, which takes collision angles into account. Effective collisions depend on the impact parameter, leading to a lower energy available for the reaction than the total kinetic energy.

- **30.3: The Rate Constant for a Gas-Phase Chemical Reaction May Depend on the Orientations of the Colliding Molecules**
  This page discusses a revision of the hard-sphere model for particle collisions, highlighting that not all collisions lead to reactions due to insufficient energy and the importance of proper orientation, particularly for non-spherical particles. The traditional model's assumption of spherical particles overestimates effective collisions, leading to inaccuracies in the reaction rate constant A.

- **30.4: The Internal Energy of the Reactants Can Affect the Cross Section of a Reaction**
  This page discusses modifications to the collision model to account for the internal energy of polyatomic gas particles, including electronic, vibrational, and rotational components. It notes that molecules in high vibrational states could react without additional translational energy, influencing the reaction cross-section σ_r .

- **30.5: A Reactive Collision Can Be Described in a Center-of-Mass Coordinate System**
  This page discusses modeling bimolecular reactions of ideal gases with a center-of-mass coordinate system for enhanced accuracy in reaction kinetics. It explains how reactant molecules' kinetic energy is calculated before collisions, distinguishing between the kinetic energy of the center of mass and the relative motion of reactants. The model emphasizes that only the latter impacts the reaction outcome and addresses the conservation of mass and energy throughout the reaction process.

- **30.6: Reactive Collisions Can be Studied Using Crossed Molecular Beam Machines**
  This page discusses crossed molecular beam experiments, which involve colliding gas-phase atom or molecule beams to study chemical reaction dynamics. Key features include detecting collisions, analyzing product velocities and angles, and using mass spectrometry for energy insights. Originating from Herschbach and Lee, the method has been enhanced with tools like quadrupole filters and supersonic nozzles, broadening its application.

- **30.7: Reactions Can Produce Vibrationally Excited Molecules**
  This page discusses the center of mass reaction model utilized to examine energy distribution in the reaction between fluorine and deuterium. It highlights that for the reaction to be successful, the vibrational energy of $\mathrm{DF(g)}$ must be under 165 kJ/mol. The analysis shows that $\mathrm{DF(g)}$ can occupy vibrational states ranging from $v = 0$ to 4 while adhering to this energy limitation.

- **30.8: The Velocity and Angular Distribution of the Products of a Reactive Collision**
  This page discusses the speed distribution of DF molecules formed from the collision of F and D2, highlighting the connection between products' vibrational energy and their velocity. It notes that vibrational states influence translational energy and speed, analyzing data from crossed molecular beam experiments to explore angular distribution and velocity.

- **30.9: Not All Gas-Phase Chemical Reactions are Rebound Reactions**
  This page describes two gas-phase reaction types: rebound reactions, where products bounce back (e.g., $\mathrm{D_2}$ with F), and stripping reactions, where products like KI move in the same direction as reactants (e.g., K and

I_2). Stripping reactions show larger experimental collision cross-sections than predicted and involve electron transfer prior to collision.

- **30.10: The Potential-Energy Surface Can Be Calculated Using Quantum Mechanics**
  This page covers Potential Energy Surfaces (PES), which illustrate the potential energy of atomic systems based on their configurations, favoring stable structures at energy minima. It discusses PES in the context of exchange reactions involving hydrogen and deuterium, detailing specific reaction pathways and highlighting transition states.
- **30.E: Gas-Phase Reaction Dynamics (Exercises)**

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17: THE MOTIVATION FOR QUANTUM MECHANICS

17.1: Introduction
17.2: Quantum Mechanics is Bizarre
17.3: The Ultraviolet Catastrophe
17.4: The Photoelectric Effect
17.5: Wave-Particle Duality

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17.1: Introduction

Quantum mechanics is an important intellectual achievement of the 20th century. It is one of the more sophisticated field in physics that has affected our understanding of nano-meter length scale systems important for chemistry, materials, optics, and electronics. The existence of orbitals and energy levels in atoms can only be explained by quantum mechanics. Quantum mechanics can explain the behaviors of insulators, conductors, semi-conductors, and giant magneto-resistance. It can explain the quantization of light and its particle nature in addition to its wave nature. Quantum mechanics can also explain the radiation of hot body, and its change of color with respect to temperature. It explains the presence of holes and the transport of holes and electrons in electronic devices. Quantum mechanics has played an important role in photonics, quantum electronics, and micro-electronics. But many more emerging technologies require the understanding of quantum mechanics; and hence, it is important that scientists and engineers understand quantum mechanics better. One area is nano-technologies due to the recent advent of nano-fabrication techniques. Consequently, nano-meter size systems are more common place. In electronics, as transistor devices become smaller, how the electrons move through the device is quite different from when the devices are bigger: nano-electronic transport is quite different from micro-electronic transport. The quantization of electromagnetic field is important in the area of nano-optics and quantum optics. It explains how photons interact with atomic systems or materials. It also allows the use of electromagnetic or optical field to carry quantum information. Moreover, quantum mechanics is also needed to understand the interaction of photons with materials in solar cells, as well as many topics in material science. When two objects are placed close together, they experience a force called the Casimir force that can only be explained by quantum mechanics. This is important for the understanding of micro/nano-electromechanical sensor systems (M/NEMS). Moreover, the understanding of spins is important in spintronics, another emerging technology where giant magneto-resistance, tunneling magneto-resistance, and spin transfer torque are being used. Quantum mechanics is also giving rise to the areas of quantum information, quantum communication, quantum cryptography, and quantum computing. It is seen that the richness of quantum physics will greatly affect the future generation technologies in many aspects.

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17.2: Quantum Mechanics is Bizarre

The development of quantum mechanics is a great intellectual achievement, but at the same time, it is bizarre. The reason is that quantum mechanics is quite different from classical physics. The development of quantum mechanics is likened to watching two players having a game of chess, but the watchers have not a clue as to what the rules of the game are. By observations, and conjectures, finally the rules of the game are outlined. Often, equations are conjectured like conjurors pulling tricks out of a hat to match experimental observations. It is the interpretations of these equations that can be quite bizarre. Quantum mechanics equations were postulated to explain experimental observations, but the deeper meanings of the equations often confused even the most gifted. Even though Einstein received the Nobel prize for his work on the photo-electric effect that confirmed that light energy is quantized, he himself was not totally at ease with the development of quantum mechanics as charted by the younger physicists. He was never comfortable with the probabilistic interpretation of quantum mechanics by Born and the Heisenberg uncertainty principle: “God doesn’t play dice,” was his statement assailing the probabilistic interpretation. He proposed “hidden variables” to explain the random nature of many experimental observations. He was thought of as the “old fool” by the younger physicists during his time. Schrödinger came up with the bizarre “Schrödinger cat paradox” that showed the struggle that physicists had with quantum mechanics’s interpretation. But with today’s understanding of quantum mechanics, the paradox is a thing of yesteryear. The latest twist to the interpretation in quantum mechanics is the parallel universe view that explains the multitude of outcomes of the prediction of quantum mechanics. All outcomes are possible, but with each outcome occurring in different universes that exist in parallel with respect to each other.[1]

The development of quantum mechanics was initially motivated by two observations which demonstrated the inadeqacy of classical physics. These are the “ultraviolet catastrophe” and the photoelectric effect.

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1. This section was adapted in part from Prof. Weng Cho CHEW’s Quantum Mechanics Made Simple Lecture Notes available here.

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17.3: The Ultraviolet Catastrophe

The ultraviolet (UV) catastrophe, also called the Rayleigh–Jeans catastrophe, is the prediction of classical electromagnetism that the intensity of the radiation emitted by an ideal black body at thermal equilibrium goes to infinity as wavelength decreases (see figure 17.3.1)[1].

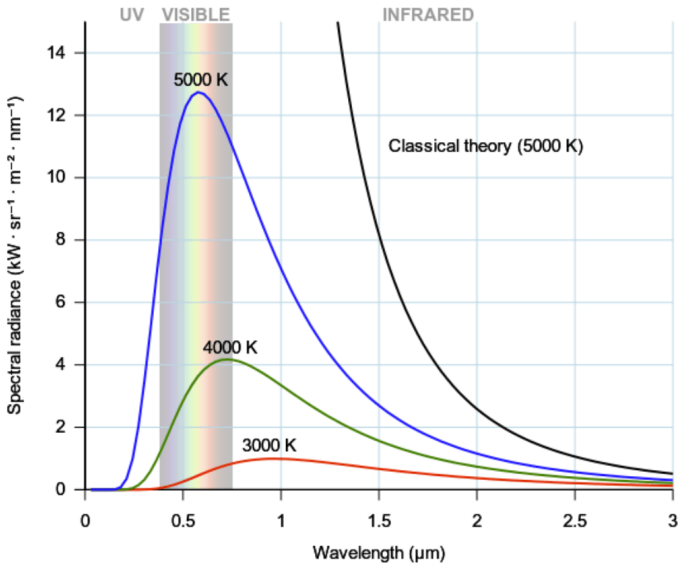


Figure 17.3.1: The ultraviolet catastrophe is the error at short wavelengths in the Rayleigh–Jeans law for the energy emitted by an ideal black body. The error, much more pronounced for short wavelengths, is the difference between the Rayleigh–Jeans law —black—and Planck's law—blue.

A black body is an idealized object that absorbs and emits all frequencies. Classical physics can be used to derive an approximated equation describing the intensity of a black body radiation as a function of frequency for a fixed temperature. The result is known as the Rayleigh-Jeans law, which for wavelength λ, is:

$$B_\lambda(T) = \frac{2ck_\mathrm{B}T}{\lambda^4} \tag{17.3.1}$$

where B_λ is the intensity of the radiation —expressed as the power emitted per unit emitting area, per steradian, per unit wavelength (spectral radiance)— c is the speed of light, k_B is the Boltzmann constant, and T is the temperature in kelvins. The paradox —or rather the breakdown of the Rayleigh–Jeans formula— happens at small wavelength λ. If we take the limit for $\lambda \to 0$ in Equation 17.3.1, we obtain that $B_\lambda \to \infty$. In other words, as the wavelength of the emitted light gets smaller (approaching the UV range), the intensity of the radiation approaches infinity, and the black body emits an infinite amount of energy. This divergence for low wavelength (high frequencies) is called the ultraviolet catastrophe, and it is clearly unphysical.

Max Planck explained the black body radiation in 1900 by assuming that the energies of the oscillations of the electrons responsible for the radiation must be proportional to integral multiples of the frequency, i.e.,

$$E = nh\nu = nh\frac{c}{\lambda} \tag{17.3.2}$$

Planck's assumptions led to the correct form of the spectral function for a black body:

$$B_\lambda(\lambda, T) = \frac{2hc^2}{\lambda^5}\frac{1}{e^{hc/(\lambda k_\mathrm{B}T)} - 1}. \tag{17.3.3}$$

If we now take the limit for $\lambda \to 0$ of Equation 17.3.3, it is easy to prove that B_λ goes to zero, in agreement with the experimental results, and our intuition. Planck also found that for $h = 6.626 \times 10^{-34}$ J s, the experimental data could be reproduced exactly. Nevertheless, Planck could not offer a good justification for his assumption of energy quantization. Physicists did not take this energy quantization idea seriously until Einstein invoked a similar assumption to explain the photoelectric effect.

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17.4: The Photoelectric Effect

In 1886 and 1887, Heinrich Hertz discovered that ultraviolet light can cause electrons to be ejected from a metal surface. According to the classical wave theory of light, the intensity of the light determines the amplitude of the wave, and so a greater light intensity should cause the electrons on the metal to oscillate more violently and to be ejected with a greater kinetic energy. In contrast, the experiment showed that the kinetic energy of the ejected electrons depends on the frequency of the light. The light intensity affects only the number of ejected electrons and not their kinetic energies. Einstein tackled the problem of the photoelectric effect in 1905. Instead of assuming that the electronic oscillators had energies given by Planck's formula, Equation 17.3.2, Einstein assumed that the radiation itself consisted of packets of energy $E = h\nu$, which are now called photons. Einstein successfully explained the photoelectric effect using this assumption, and he calculated a value of h close to that obtained by Planck.

Two years later, Einstein showed that not only is light quantized, but so are atomic vibrations. Classical physics predicts that the molar heat capacity at constant volume (C_V) of a crystal is $3R$, where R is the molar gas constant. This works well for high temperatures, but for low temperatures C_V actually falls to zero. Einstein was able to explain this result by assuming that the oscillations of atoms about their equilibrium positions are quantized according to $E = nh\nu$, Planck's quantization condition for electronic oscillators. This demonstrated that the energy quantization concept was important even for a system of atoms in a crystal, which should be well-modeled by a system of masses and springs (i.e., by classical mechanics).

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17.5: Wave-Particle Duality

Einstein had shown that the momentum of a photon is

$$p = \frac{h}{\lambda}. \tag{17.5.1}$$

This can be easily shown as follows. Assuming $E = h\nu$ for a photon and $\lambda\nu = c$ for an electromagnetic wave, we obtain

$$E = \frac{hc}{\lambda} \tag{17.5.2}$$

Now we use Einstein's relativity result, $E = mc^2$, and the definition of mementum $p = mc$, to find:

$$\lambda = \frac{h}{p}, \tag{17.5.3}$$

which is equivalent to Equation 17.5.1. Note that m refers to the relativistic mass, not the rest mass, since the rest mass of a photon is zero. Since light can behave both as a wave (it can be diffracted, and it has a wavelength), and as a particle (it contains packets of energy $h\nu$), de Broglie reasoned in 1924 that matter also can exhibit this wave-particle duality. He further reasoned that matter would obey the same Equation 17.5.3 as light. In 1927, Davisson and Germer observed diffraction patterns by bombarding metals with electrons, confirming de Broglie's proposition.[1]

Rewriting the previous equations in terms of the wave vector, $k = \frac{2\pi}{\lambda}$, and the angular frequency, $\omega = 2\pi\nu$, we obtain the following two equations

$$\begin{aligned} p &= \hbar k \\ E &= \hbar\omega, \end{aligned} \tag{17.5.4}$$

which are known as **de Broglie's equations**. We will use those equation to develop wave mechanics in the next chapters.

---

1. The previous 3 sections were adapted in part from Prof. C. David Sherrill's A Brief Review of Elementary Quantum Chemistry Notes available here.

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18: CLASSICAL MECHANICS

Quantum mechanics cannot be derived from classical mechanics, but classical mechanics can inspire quantum mechanics. Quantum mechanics is richer and more sophisticated than classical mechanics. Quantum mechanics was developed during the period when physicists had rich knowledge of classical mechanics. In order to better understand how quantum mechanics was developed in this environment, it is better to understand some fundamental concepts in classical mechanics. Classical mechanics can be considered as a special case of quantum mechanics. We will review some classical mechanics concepts here.

18.1: Newtonian Formulation

18.2: Lagrangian Formulation

18.3: Hamiltonian Mechanics

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18.1: Newtonian Formulation

Classical mechanics as formulated by Isaac Newton (1652-1727) is all about forces. Newtonian mechanics works well for problems where we know the forces and have a reasonable coordinate system. In these cases, the net force acting on a system at position q is simply:

$$F_{\text{net}}(q) = m\ddot{q} = m\frac{d^2q}{dt^2}. \tag{18.1.1}$$

Or, in other words, if we know the net force acting on a system of mass m at position q at some time t_0, we can use Equation 18.1.1 to calculate the position of the system at any future (or past) time. We have completely determined the dynamical evolution of the system.[1]

Example 18.1.1

A ball of mass m is at ground level and tossed straight up from an initial position q_0 with an initial velocity $\dot{q}_0$ and subject to gravity alone. Calculate the equation of motion for the ball (i.e. where is the ball going to be after some time t?).[2]

Answer available at the end of this section.

Exercise 18.1.2

How much time will a ball ejected from a height of $1\ \text{m}$ at an initial velocity of $10\ \text{m/s}$ take to hit the floor?

Answer available at the end of this section.

The formula of Newtonian mechanics are not the only one we can use to solve a problem in classical mechanics. We have at least two other equivalent approaches to the same problem that might end up being more useful in certain situations.

---

1. Notice that, in principle, $q \overset{\text{int}}{\in} \mathbb{R}^n$ is the position vector and $\dot{q} \overset{\text{int}}{\in} \mathbb{R}^n$ is the velocity vector. As such, all the equation of classical mechanics are vector equation, and not just simple numerical equation, as we present them here! For our purposes, we can restrict ourselves to a 1-dimensional space, hence forgetting the complications of vector algebra.
2. This example is based on Rhett Allain's blog post that can be found (here)[https://rhettallain.com/2018/10/31/classical-mechanics-newtonian-lagrangian-and-hamiltonian/] ⮈
3. Can you write a python program to do this calculation?

Answers

Example 18.1.1

Since the only force acting on the ball is gravity, we can use the equation for the gravitational force to start our derivation:

$$F_{\text{gravity}} = -mG,$$

with G the usual gravitational constant ($G = 9.8\ \text{m/s}^2$). We can then replace this expression into Equation 18.1.1, to obtain:

$$\begin{aligned} -mG &= m\ddot{q} \\ -G &= \ddot{q} \\ -G &= \frac{d\dot{q}}{dt}, \end{aligned}$$

which can then be integrated with respect to time, to obtain:

$$\begin{aligned} -G\int_{t=0}^{t} dt &= \int_{\dot{q}_0}^{\dot{q}} d\dot{q} \\ \dot{q} &= \dot{q}_0 - Gt \\ \frac{dq}{dt} &= \dot{q}_0 - Gt, \end{aligned}$$

which can be further integrated with respect to time, to give:

$$\int_{q_0}^{q} dq = \int_{t=0}^{t} \dot{q}_0 dt - G \int_{t=0}^{t} t dt$$
$$q = q_0 + \dot{q}_0 t - \frac{1}{2} G t^2.$$

This final equation is the equation of motion for the ball, from which we can calculate the position of the ball at any time t. Notice how the equation of motion does not depend on the mass of the ball!

Exercise 18.1.2

We can use the equation of motion obtained above to solve this problem, and obtain for this specific case $t \simeq 2.12 \text{ s}$.[3]

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18.2: Lagrangian Formulation

Another way to derive the equations of motion for classical mechanics is via the use of the Lagrangian and the principle of least action. The Lagrangian formulation is obtained by starting from the definition of the Lagrangian of the system:

$$L = K - V, \tag{18.2.1}$$

where K is the kinetic energy, and V is the potential energy. Both are expressed in terms of the coordinates $(q, \dot{q})$. Notice that for a fixed time, t, q and $\dot{q}$ are independent variables, since $\dot{q}$ cannot be derived from q alone.

The time integral of the Lagrangian is called the **action**, and is defined as:

$$S = \int_{t_1}^{t_2} L\, dt, \tag{18.2.2}$$

which is a functional: it takes in the Lagrangian function for all times between t_1 and t_2 and returns a scalar value. The equations of motion can be derived from the principle of least action,[1] which states that the true evolution of a system $q(t)$ described by the coordinate q between two specified states $q_1 = q(t_1)$ and $q_2 = q(t_2)$ at two specified times t_1 and t_2 is a minimum of the action functional. For a minimum point:

$$\delta S = \frac{dS}{dq} = 0 \tag{18.2.3}$$

Requiring that the true trajectory $q(t)$ minimizes the action functional S, we obtain the equation of motion (Figure 18.2.1).[2] This can be achieved applying classical variational calculus to the variation of the action integral S under perturbations of the path $q(t)$, Equation 18.2.3. The resulting equation of motion (or set of equations in the case of many dimensions) is sometimes also called the Euler—Lagrange equation:[3]

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}}\right) = \frac{\partial L}{\partial q}. \tag{18.2.4}$$

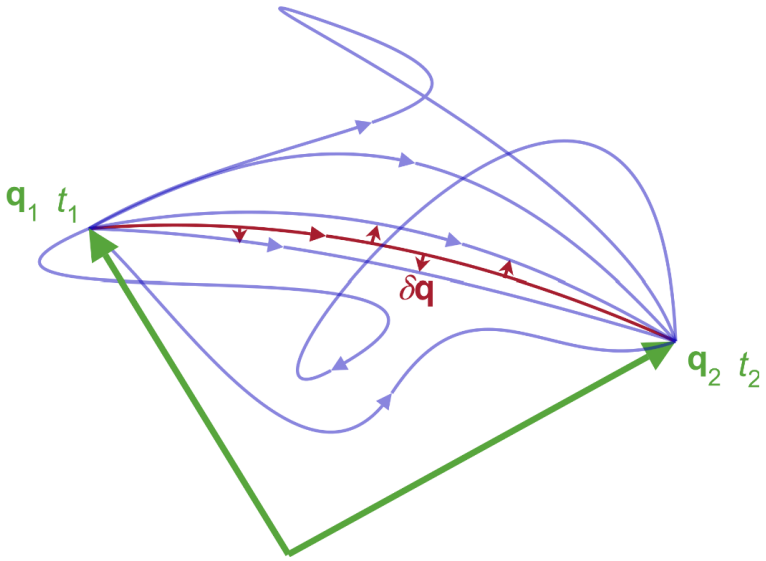


Figure 18.2.1: Principle of least action: As the system evolves, q traces a path through configuration space (only some are shown). The path taken by the system (red) has a stationary action under small changes in the configuration of the system.

Example 18.2.1

Let's apply the Lagrangian mechanics formulas to the same problem as in the previous Example.

Solution

The expression of the kinetic energy, the potential energy, and the Lagrangian for our system are:

$$\begin{aligned} K &= \frac{1}{2}m\dot{q}^2 \\ V &= mGq \\ L &= K - V = \frac{1}{2}m\dot{q}^2 - mGq. \end{aligned}$$

To get the equation of motion using Equation 18.2.4, we need to first take the partial derivative of L with respect to q (right hand side):

$$\frac{\partial L}{\partial q} = -mG,$$

and then we need the derivative with respect to t the derivative of the Lagrangian with respect to $\dot{q}$ at the hand side:

$$\frac{d}{dt}\frac{\partial L}{\partial \dot{q}} = \frac{d\left(\frac{1}{2}m\dot{q}^2 - mGq\right)}{dt} = m\ddot{q}.$$

Putting this together, we get:

$$\begin{aligned} m\ddot{q} &= -mG \\ \ddot{q} &= -G \end{aligned}$$

Which is the same result as obtained from the Newtonian method. Integrating twice, we get the exact same formulas that we can use the same way.

The advantage of Lagrangian mechanics is that it is not constrained to use a coordinate system. For example, if we have a bead moving along a wire, we can define the coordinate system as the distance along the wire, making the formulas much simpler than in Newtonian mechanics. Also, since the Lagrangian depends on kinetic and potential energy it does a much better job with constraint forces.

---

1. Sometimes also called principle of stationary action, or variational principle, or Hamilton's principle.
2. This diagram is taken from Wikipedia by user Maschen, and distributed under CC0 license
3. The mathematical derivation of the Euler—Lagrange equaiton is rather long and unimportant at this stage. For the curious, it can be found here.

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18.3: Hamiltonian Mechanics

A third way of obtaining the equation of motion is Hamiltonian mechanics, which uses the generalized momentum in place of velocity as a coordinate. The generalized momentum is defined in terms of the Lagrangian and the coordinates $(q, \dot{q})$:

$$p = \frac{\partial L}{\partial \dot{q}}. \tag{18.3.1}$$

The Hamiltonian is defined from the Lagrangian by applying a Legendre transformation as:[1]

$$H(p, q) = p\dot{q} - L(q, \dot{q}), \tag{18.3.2}$$

The Lagrangian equation of motion becomes a pair of equations known as the Hamiltonian system of equations:

$$\begin{aligned} \dot{p} &= \frac{dp}{dt} = -\frac{\partial H}{\partial q} \\ \dot{q} &= \frac{dq}{dt} = +\frac{\partial H}{\partial p}, \end{aligned} \tag{18.3.3}$$

where $H = H(q, p, t)$ is the Hamiltonian of the system, which often corresponds to its total energy. For a closed system, it is the sum of the kinetic and potential energy in the system:

$$H = K + V. \tag{18.3.4}$$

Notice the difference between the Hamiltonian, Equation 18.3.4, and the Lagrangian, Equation 18.2.1. In Newtonian mechanics, the time evolution is obtained by computing the total force being exerted on each particle of the system, and from Newton's second law, the time evolutions of both position and velocity are computed. In contrast, in Hamiltonian mechanics, the time evolution is obtained by computing the Hamiltonian of the system in the generalized momenta and inserting it into Hamilton's equations. This approach is equivalent to the one used in Lagrangian mechanics, since the Hamiltonian is the Legendre transform of the Lagrangian. The main motivation to use Hamiltonian mechanics instead of Lagrangian mechanics comes from the more simple description of complex dynamic systems.

Example 18.3.1

Let's apply the Hamiltonian mechanics formulas to the same problem in the previous examples.

Solution

Using Equation 18.3.2, the Hamiltonian can be written as:

$$H = m\dot{q}\dot{q} - \frac{1}{2}m\dot{q}^2 + mGq = \frac{1}{2}m\dot{q}^2 + mGq. \tag{18.3.5}$$

Since the Hamiltonian really depends on position and momentum, we need to get this in terms of q and p, with $p = m\dot{q}$ for the momentum. This is not always the case, since it depends on the choice of coordinate system. For a trivial coordinate system for our simple 1-dimensional problem, we have:

$$H = \frac{p^2}{2m} + mGq,$$

from which we can use eqs. ??? to get:

$$\begin{aligned} \dot{q} &= \frac{\partial H}{\partial p} = \frac{p}{m} \\ \dot{p} &= -\frac{\partial H}{\partial q} = -mG. \end{aligned}$$

These equations represent a major diffference of the Hamiltonian method, since we describe the system using two first-order differential equations, rather than one second-order differential equation. In order to get the equation of motion, we need to take the derivative of $\dot{q}$:

$$\ddot{q} = \frac{d}{dt}\left(\frac{p}{m}\right) = \frac{\dot{p}}{m},$$

and then replacing the definition of $\dot{p}$ obtained above, we get:

$$\ddot{q} = \frac{-mG}{m} = -G$$

which—once again—is the same result obtained for the two previous cases. Integrating this twice, we get the familiar equation of motion for our problem.

---

1. We have already encountered Legendre transform in The Live Textbook of Physical Chemistry 1 when transforming from the thermodynamic energy to any of the other thermodynamic potentials.

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19: THE SCHRÖDINGER EQUATION

In 1925, Erwin Schrödinger and Werner Heisenberg independently developed the new quantum theory. Schrödinger's method involves partial differential equations, whereas Heisenberg's method employs matrices; however, a year later the two methods were shown to be mathematically equivalent. Most textbooks begin with Schrödinger's equation, since it seems to have a better physical interpretation via the classical wave equation. Indeed, the Schrödinger equation can be viewed as a form of the wave equation applied to matter waves.

19.1: The Time-Independent Schrödinger Equation

19.2: The Time-Dependent Schrödinger Equation

19.3: Analytically Soluble Models

19.4: The Hydrogen Atom

19.4.1: Operators and Mathematical Background

19.4.1.1: Operators in Quantum Mechanics

19.4.1.2: Eigenfunctions and Eigenvalues

19.4.1.3: Common Operators in Quantum Mechanics

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19.1: The Time-Independent Schrödinger Equation

We can start the derivation of the single-particle time-independent Schrödinger equation (TISEq) from the equation that describes the motion of a wave in classical mechanics:

$$\psi(x,t) = \exp[i(kx - \omega t)], \tag{19.1.1}$$

where x is the position, t is time, $k = \frac{2\pi}{\lambda}$ is the wave vector, and $\omega = 2\pi\nu$ is the angular frequency of the wave. If we are not concerned with the time evolution, we can consider uniquely the derivatives of Equation 19.1.1 with respect to the location, which are:

$$\begin{aligned} \frac{\partial \psi}{\partial x} &= ik \exp[i(kx - \omega t)] = ik\psi, \\ \frac{\partial^2 \psi}{\partial x^2} &= i^2 k^2 \exp[i(kx - \omega t)] = -k^2 \psi, \end{aligned} \tag{19.1.2}$$

where we have used the fact that $i^2 = -1$.

Assuming that particles behaves as wave—as proven by de Broglie's we can now use the first of de Broglie's equation, Equation 17.5.4, we can replace $k = \frac{p}{\hbar}$ to obtain:

$$\frac{\partial^2 \psi}{\partial x^2} = -\frac{p^2 \psi}{\hbar^2}, \tag{19.1.3}$$

which can be rearranged to:

$$p^2 \psi = -\hbar^2 \frac{\partial^2 \psi}{\partial x^2}. \tag{19.1.4}$$

The total energy associated with a wave moving in space is simply the sum of its kinetic and potential energies:

$$E = \frac{p^2}{2m} + V(x), \tag{19.1.5}$$

from which we can obtain:

$$p^2 = 2m[E - V(x)], \tag{19.1.6}$$

which we can then replace into Equation 19.1.4 to obtain:

$$2m[E - V(x)]\psi = -\hbar^2 \frac{\partial^2 \psi}{\partial x^2}, \tag{19.1.7}$$

which can then be rearranged to the famous **time-independent Schrödinger equation (TISEq)**:

$$-\frac{\hbar^2}{2m}\frac{\partial^2 \psi}{\partial x^2} + V(x)\psi = E\psi, \tag{19.1.8}$$

A two-body problem can also be treated by this equation if the mass m is replaced with a reduced mass $\mu = \frac{m_1 m_2}{m_1 + m_2}$.

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19.2: The Time-Dependent Schrödinger Equation

Unfortunately, the analogy with the classical wave equation that allowed us to obtain the TISEq in the previous section cannot be extended to the time domain by considering the equation that involves the partial first derivative with respect to time. Schrödinger himself presented his time-independent equation first, and then went back and postulated the more general time-dependent equation. We are following here the same strategy and just give the time-independent variable as a postulate. The single-particle time-dependent Schrödinger equation is:

$$i\hbar\frac{\partial\psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\psi(x,t)}{\partial x^2} + V(x)\psi(x,t) \tag{19.2.1}$$

where $V^{\text{int}}\mathbb{R}^n$ represents the potential energy of the system. Obviously, the time-dependent equation can be used to derive the time-independent equation. If we write the wavefunction as a product of spatial and temporal terms, $\psi(x,t) = \psi(x)f(t)$, then Equation 19.2.1 becomes:

$$\psi(x)i\hbar\frac{df(t)}{dt} = f(t)\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right]\psi(x), \tag{19.2.2}$$

which can be rearranged to:

$$\frac{i\hbar}{f(t)}\frac{df(t)}{dt} = \frac{1}{\psi(x)}\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right]\psi(x). \tag{19.2.3}$$

Since the left-hand side of Equation 19.2.3 is a function of t only and the right hand side is a function of x only, the two sides must equal a constant. If we tentatively designate this constant E (since the right-hand side clearly must have the dimensions of energy), then we extract two ordinary differential equations, namely:

$$\frac{1}{f(t)}\frac{df(t)}{dt} = -\frac{iE}{\hbar} \tag{19.2.4}$$

and:

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2} + V(x)\psi(x) = E\psi(x). \tag{19.2.5}$$

The latter equation is the TISEq. The former equation is easily solved to yield

$$f(t) = e^{-iEt/\hbar} \tag{19.2.6}$$

The solutions of Equation 19.2.6, $f(t)$, are purely oscillatory, since $f(t)$ never changes in magnitude. Thus if:

$$\psi(x,t) = \psi(x)\exp\left(\frac{-iEt}{\hbar}\right), \tag{19.2.7}$$

then the total wave function $\psi(x,t)$ differs from $\psi(x)$ only by a phase factor of constant magnitude. There are some interesting consequences of this. First of all, the quantity $|\psi(x,t)|^2$ is time independent, as we can easily show:

$$|\psi(x,t)|^2 = \psi^*(x,t)\psi(x,t) = \psi^*(x)\exp\left(\frac{iEt}{\hbar}\right)\psi(x)\exp\left(\frac{-iEt}{\hbar}\right) = \psi^*(x)\psi(x). \tag{19.2.8}$$

Wave functions of the form of Equation 19.2.7 are called stationary states. The state $\psi(x,t)$ is "stationary," but the particle it describes is not! Of course Equation 19.2.6 represents only a particular solution to the time-dependent Schrödinger equation. The general solution is much more complicated, and the factorization of the temporal part is often not possible:[1]

$$\psi(\mathbf{r},t) = \sum_i c_i e^{-iE_it/\hbar}\psi_i(\mathbf{r})$$

1. This sections was adapted in part from Prof. C. David Sherrill's A Brief Review of Elementary Quantum Chemistry Notes

available here.

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19.3: Analytically Soluble Models

The TISEq can be solved analytically only in a few special cases. In this section, we will analyze the main four. Luckily, we can use these solutions to explain most of the effects in chemistry since we can combine them to describe the hydrogen atom upon which we can build more complex chemical systems, as we will show in the next chapters.

Thumbnail: The quantum wavefunction of a particle in a 2D infinite potential well of dimensions L_x and L_y. The wavenumbers are $n_x = 2$ and $n_y = 2$. (Public Domain; Inductiveload).

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19.4: THE HYDROGEN ATOM

In this chapter we will consider the hydrogen atom as a proton fixed at the origin, orbited by an electron of reduced mass μ. The potential due to electrostatic attraction is:

$$V(r) = -\frac{e^2}{4\pi\varepsilon_0 r}, \tag{19.4.1}$$

where ε_0 is the constant permittivity of vacuum. The kinetic energy term in the Hamiltonian is

$$K = -\frac{\hbar^2}{2\mu}\nabla^2, \tag{19.4.2}$$

where ∇^2 is the Laplace operator (*Laplacian*) representing the divergence of the gradient of a function. Recall that in 1-dimension the kinetic energy is proportional to the second derivative of the wave function with respect to the position. In 3-dimension, the first derivative along all three dimension of space is called gradient, which is written in cartesian coordinates $\nabla = \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right)$. The Laplacian is the divergence $\nabla \cdot$ of the gradient (effectively, it replaces the second derivatives in the 1-D case), and can be written in cartesian coordinates as $\nabla^2 = \nabla \cdot \nabla = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$. The TISEq for the Hydrogen atom is therefore:

$$\left(-\frac{\hbar^2}{2\mu}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r}\right)\psi(r,\theta,\phi) = E\psi(r,\theta,\phi), \tag{19.4.3}$$

which, replacing the Laplacian in spherical coordinates, becomes:

$$-\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}\right] - \frac{e^2}{4\pi\varepsilon_0 r}\psi = E\psi. \tag{19.4.4}$$

This equation seems very complicated, but comparing the term in between square brackets with the TISEq of the rigid rotor, we immediately see some connections. Equation 19.4.4 is a separable, partial differential equation that can be solved by factorizing the wave function $\psi(r,\theta,\phi)$ into $R_{nl}(r)Y_\ell^{m_\ell}(\theta,\phi)$, where $Y_\ell^{m_\ell}(\theta,\phi)$ are again the spherical harmonics that solved the TISEq for the rigid rotor. The radial part $R(r)$ obeys the equation:

$$-\frac{\hbar^2}{2\mu r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)\left[\frac{\hbar^2\ell(\ell+1)}{2\mu r^2} + V(r) - E\right]R(r) = 0, \tag{19.4.5}$$

which is called the radial equation for the hydrogen atom. The solutions of the radial part are:

$$R_{n\ell}(r) = -\left[\frac{(n-\ell-1)!}{2n[(n+\ell)!]^3}\right]^{1/2}\left(\frac{2}{na_0}\right)^{\ell+3/2} r^\ell e^{-r/na_0} L_{n+\ell}^{2\ell+1}\left(\frac{2r}{na_0}\right) \tag{19.4.6}$$

where $0 \le \ell \le n-1$, and $a_0 = \frac{\varepsilon_0 h^2}{\pi\mu e^2}$ is the Bohr radius. The functions $L_{n+\ell}^{2\ell+1}\left(\frac{2r}{na_0}\right)$ are the associated Laguerre functions.

The hydrogen atom eigenfunctions are:

$$\begin{aligned}\psi_{n\ell m_\ell}(r,\theta,\phi) &= R_{n\ell}(r)Y_\ell^{m_\ell}(\theta,\phi) = \\ &= -\left[\frac{(n-\ell-1)!}{2n[(n+\ell)!]^3}\right]^{1/2}\left(\frac{2}{na_0}\right)^{\ell+3/2} r^\ell e^{-r/na_0} L_{n+\ell}^{2\ell+1}\left(\frac{2r}{na_0}\right) Y_\ell^{m_\ell}(\theta,\phi)\end{aligned} \tag{19.4.7}$$

The quantum numbers n, ℓ, m_ℓ can take the following values:

- $n = 1, 2, 3, \ldots, \infty$ (principal quantum number),
- $\ell = 0, 1, 2, \ldots, n-1$ (azimuthal quantum number),
- $m_\ell = -\ell, \ldots, \ell$ (magnetic quantum number).

These functions are called the *hydrogen atom orbitals*, and are usually first encountered in introductory chemistry textbooks.

Notice that—by definition—an orbital is a complex function (i.e., it has both a real and an imaginary component) that describes *exclusively* one electron. Spherical harmonics are orthogonal to each other and they can be linearly combined them to form new solution to the TISEq where the imaginary part is removed. (Because of the orthogonality of spherical harmonics, the energy spectrum will not be affected by this operation.) These corresponding real orbitals are three-dimensional function that are not easily visualized in a three-dimensional space, since they require a four-dimensional one.[1] Since there is no real consensus on what a wave function represent, the interpretation of orbitals is not straightforward.[2] We will return on the interpretation problem in future chapters, but for now it is important to keep in mind these following facts:

- The shape of every hydrogen atom orbital—complex or real—is that of a function on the surface of a sphere (yes, this is true for every single one of them, since they all come from spherical harmonics, which are special functions defined on the surface of a sphere. Hydrogen $2p$ orbitals in real space *do not* have the shape of a dumbbell, as often is said in general chemistry textbooks. Same goes for $d, f, \ldots$ orbitals.)
- Each orbital is the mathematical description of one—and only one—electron (in other words, orbitals do not "contain" electrons, they "are" the functions that describe each electron.)
- Hydrogen orbitals are defined only for stystems that contain one electron. When more than one electron is present in an atom, the TISEq in Equation 19.4.3 does not describe the system anymore. In these more complicated situations the TISEq cannot be solved analytically, and orbitals cannot be easily defined (we will see in chapter 26 how we can circumvent this issue in an approximate manner, and why general chemistry textbook talk of orbitals for every atom and molecule.)

The hydrogen atom eigenvalues are:

$$E_n = -\frac{e^2}{8\pi\varepsilon_0 a_0 n^2} \quad n = 1, 2, \ldots, \infty. \tag{19.4.8}$$

Notice how the eigenvalues (i.e., the energy spectrum) do not depend on the azimuthal and magnetic quantum numbers, ℓ and m. Energy levels with the same n, but different ℓ and/or m are called *degenerate states*, since they all have the same energy. This is, once again, source of misinterpretation in most general chemistry textbook:

- According to the TISEq, the $2s$ and $2p$ orbitals of the hydrogen atom have the same energy.3

---

1. If it is not clear why you need a 4-D space to visualize a 3-D function, think at the fact that we use a 2-D space (the Cartesian plane) to visualize a 1-D function ($f(x)$).
2. At least not as straightforward as it is given in introductory chemistry textbooks.
3. In practice, this is not true, because of a tiny effect called the Lamb shift. The description of this effect requires to go beyond the Schrödinger equation—and essentially beyond quantum mechanics—into the field of quantum electrodynamics. The Lamb shift, however, is not what is usually depicted in general chemistry textbook as the $2s - 2p$ energy difference. The difference that is usually discussed in the context of the aufbau principle is a many-electron effect, as we will discuss in chapter 10, and does not apply to hydrogen.

19.4.1: Operators and Mathematical Background

19.4.1.1: Operators in Quantum Mechanics

19.4.1.2: Eigenfunctions and Eigenvalues

19.4.1.3: Common Operators in Quantum Mechanics

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19.4.1.1: Operators in Quantum Mechanics

The central concept in this new framework of quantum mechanics is that every observable (i.e., any quantity that can be measured in a physical experiment) is associated with an operator. To distinguish between classical mechanics operators and quantum mechanical ones, we use a hat symbol ˆ on top of the latter. Physical pure states in quantum mechanics are represented as unit-norm (probabilities are normalized to one) vectors in a special complex Hilbert space. Following the definition, an operator is a function that projects a vector in the Hilbert space onto the space of physical observables. Since observables are values that come up as the result of the experiment, quantum mechanical operators must yield real eigenvalues.[16] Operators that possess this property are called **Hermitian**. In the wave mechanics formulation of quantum mechanics that we have seen so far, the wave function varies with space and time—or equivalently momentum and time—and observables are differential operators. A completely analogous formulation is possible in terms of matrices. In the matrix formulation of quantum mechanics, the norm of the physical state should stay fixed, so the evolution operator should be unitary, and the operators can be represented as matrices.

The expectation value of an operator $\hat{A}$ for a system with wave function $\psi(\mathbf{r})$ living in a Hilbert space with unit vector $\mathbf{r}$ (i.e., in three-dimensional Cartesian space $\mathbf{r} = \{x, y, z\}$), is given by:

$$\langle A \rangle = \int \psi^*(\mathbf{r}) \hat{A} \psi(\mathbf{r}) d\mathbf{r}, \tag{19.4.1.1.1}$$

and if $\hat{A}$ is a Hermitian operator, all physical observables are represented by such expectation values. It is easy to show that if $\hat{A}$ is a linear operator with an eigenfunction g, then any multiple of g is also an eigenfunction of $\hat{A}$.

Basic Properties of Operators

Most of the properties of operators are obvious, but they are summarized below for completeness. The sum and difference of two operators $\hat{A}$ and $\hat{B}$ are given by:

$$\begin{aligned} (\hat{A} + \hat{B}) f &= \hat{A} f + \hat{B} f \\ (\hat{A} - \hat{B}) f &= \hat{A} f - \hat{B} f. \end{aligned} \tag{19.4.1.1.2}$$

The product of two operators is defined by:

$$\hat{A}\hat{B} f \equiv \hat{A}[\hat{B} f] \tag{19.4.1.1.3}$$

Two operators are equal if

$$\hat{A} f = \hat{B} f \tag{19.4.1.1.4}$$

for all functions f. The identity operator $\hat{1}$ does nothing (or multiplies by 1):

$$\hat{1} f = f \tag{19.4.1.1.5}$$

The associative law holds for operators:

$$\hat{A}(\hat{B}\hat{C}) = (\hat{A}\hat{B})\hat{C} \tag{19.4.1.1.6}$$

The commutative law does not generally hold for operators. In general, $\hat{A}\hat{B} \neq \hat{B}\hat{A}$. It is convenient to define the quantity:

$$[\hat{A}, \hat{B}] \equiv \hat{A}\hat{B} - \hat{B}\hat{A} \tag{19.4.1.1.7}$$

which is called the **commutator** of $\hat{A}$ and $\hat{B}$. Note that the order matters, so that $[\hat{A}, \hat{B}] = -[\hat{B}, \hat{A}]$. If $\hat{A}$ and $\hat{B}$ happen to commute, then $[\hat{A}, \hat{B}] = 0$.

Linear Operators

Almost all operators encountered in quantum mechanics are linear. A linear operator is any operator $\hat{A}$ satisfying the following two conditions:

$$\begin{aligned} \hat{A}(f+g) &= \hat{A}f + \hat{A}g, \\ \hat{A}(cf) &= c\hat{A}f, \end{aligned} \tag{19.4.1.1.8}$$

where c is a constant and f and g are functions. As an example, consider the operators $\frac{d}{dx}$ and $()^2$. We can see that $\frac{d}{dx}$ is a linear operator because:

$$\begin{aligned} \frac{d}{dx}[f(x)+g(x)] &= \frac{d}{dx}f(x) + \frac{d}{dx}g(x), \\ \frac{d}{dx}[cf(x)] &= c(d/dx)f(x). \end{aligned} \tag{19.4.1.1.9}$$

However, $()^2$ is not a linear operator because:

$$(f(x)+g(x))^2 \neq (f(x))^2 + (g(x))^2 \tag{19.4.1.1.10}$$

Hermitian Operators

Hermitian operators are characterized by the self-adjoint property:

$$\int \psi_a^*(\hat{A}\psi_a)d\mathbf{r} = \int \psi_a(\hat{A}\psi_a)^* d\mathbf{r}, \tag{19.4.1.1.11}$$

where the integral is performed over all space. This property guarantees that all the eigenvalues of the operators are real. Defining a as the eigenvalue of operator $\hat{A}$ using:

$$\hat{A}\psi(\mathbf{r}) = a\psi(\mathbf{r}), \tag{19.4.1.1.12}$$

we can prove that a is real by replacing Equation 19.4.1.1.12 into Equation 19.4.1.1.11:

$$\begin{aligned} a\int \psi_a^*\psi_a d\mathbf{r} &= a^* \int \psi_a \psi_a^* d\mathbf{r} \\ (a-a^*)\int |\psi_a|^2 d\mathbf{r} &= 0, \end{aligned} \tag{19.4.1.1.13}$$

and since $|\psi_a|^2$ is never negative, either $a = a^*$ or $\psi_a = 0$. Since $\psi_a = 0$ is not an acceptable wavefunction, $a = a^*$, and a is real.

The following additional properties of Hermitian operators can also be proven with some work:

$$\int \psi^* \hat{A}\psi d\mathbf{r} = \int (\hat{A}\psi)^* \psi d\mathbf{r}, \tag{19.4.1.1.14}$$

and for any two states ψ_1 and ψ_2:

$$\int \psi_1^* \hat{A}\psi_2 d\mathbf{r} = \int (\hat{A}\psi_1)^* \psi_2 d\mathbf{r}. \tag{19.4.1.1.15}$$

Taking ψ_a and ψ_b as eigenfunctions of $\hat{A}$ with eigenvalues a and b with $a \neq b$, and using Equation 19.4.1.1.15, we obtain:

$$\begin{aligned} \int \psi_a^* \hat{A}\psi_b d\mathbf{r} &= \int (\hat{A}\psi_a)^* \psi_b d\mathbf{r} \\ b\int \psi_a^*\psi_b d\mathbf{r} &= a^* \int \psi_a^* \psi_b d\mathbf{r} \\ (b-a)\int \psi_a^*\psi_b d\mathbf{r} &= 0. \end{aligned} \tag{19.4.1.1.16}$$

Thus, since $a = a^*$, and since we assumed $b \neq a$, we must have $\int \psi_a^* \psi_b d\mathbf{r} = 0$, i.e. ψ_a and ψ_b are orthogonal. In other words, eigenfunctions of a Hermitian operator with different eigenvalues are orthogonal (or can be chosen to be so).

---

1. But they might not be strictly real.

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19.4.1.2: Eigenfunctions and Eigenvalues

As we have already seen, an eigenfunction of an operator $\hat{A}$ is a function f such that the application of $\hat{A}$ on f gives f again, times a constant:

$$\hat{A}f = kf, \tag{19.4.1.2.1}$$

where k is a constant called the eigenvalue.

When a system is in an eigenstate of observable A (i.e., when the wave function is an eigenfunction of the operator $\hat{A}$) then the expectation value of A is the eigenvalue of the wave function. Therefore:

$$\hat{A}\psi(\mathbf{r}) = a\psi(\mathbf{r}), \tag{19.4.1.2.2}$$

then:

$$\begin{aligned} \langle A \rangle &= \int \psi^*(\mathbf{r})\hat{A}\psi(\mathbf{r})d\mathbf{r} \\ &= \int \psi^*(\mathbf{r})a\psi(\mathbf{r})d\mathbf{r} \\ &= a\int \psi^*(\mathbf{r})\psi(\mathbf{r})d\mathbf{r} = a, \end{aligned} \tag{19.4.1.2.3}$$

which implies that:

$$\int \psi^*(\mathbf{r})\psi(\mathbf{r})d\mathbf{r} = 1. \tag{19.4.1.2.4}$$

This property of wave functions is called normalization, and in the one-electron TISEq guarantees that the maximum probability of finding an electron over the entire space is one.[1]

A unique property of quantum mechanics is that a wave function can be expressed not just as a simple eigenfunction, but also as a combination of several of them. We have in part already encountered such property in the previous chapter, where complex hydrogen orbitals have been combined to form corresponding linear ones. As a general example, let us consider a wave function written as a linear combination of two eigenstates of $\hat{A}$, with eigenvalues a and b:

$$\psi = c_a\psi_a + c_b\psi_b, \tag{19.4.1.2.5}$$

where $\hat{A}\psi_a = a\psi_a$ and $\hat{A}\psi_b = b\psi_b$. Then, since ψ_a and ψ_b are orthogonal and normalized (usually abbreviated as orthonormal), the expectation value of A is:

$$\begin{aligned} \langle A \rangle &= \int \psi^*\hat{A}\psi d\mathbf{r} \\ &= \int \left[c_a\psi_a + c_b\psi_b\right]^* \hat{A}\left[c_a\psi_a + c_b\psi_b\right] d\mathbf{r} \\ &= \int \left[c_a\psi_a + c_b\psi_b\right]^* \left[ac_a\psi_a + bc_b\psi_b\right] d\mathbf{r} \\ &= a|c_a|^2\int \psi_a^*\psi_a d\mathbf{r} + bc_a^*c_b\int \psi_a^*\psi_b d\mathbf{r} + ac_b^*c_a\int \psi_b^*\psi_a d\mathbf{r} + b|c_b|^2\int \psi_b^*\psi_b d\mathbf{r} \\ &= a|c_a|^2 + b|c_b|^2. \end{aligned} \tag{19.4.1.2.6}$$

This result shows that the average value of A is a weighted average of eigenvalues, with the weights being the squares of the coefficients of the eigenvectors in the overall wavefunction.[2]

---

1. ⚠Imposing the normalization condition is the best way to find the constant A in the solution of the TISEq for the particle in a box, a topic that we delayed in chapter 20.

2. This section was adapted in part from Prof. C. David Sherrill's A Brief Review of Elementary Quantum Chemistry Notes available here.

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19.4.1: OPERATORS AND MATHEMATICAL BACKGROUND

So far, we have seen a few simple examples of how to solve the TISEq. For the general case, the mathematical formulation of quantum mechanics is built upon the concept of an operator. An operator is a function over a space of physical states onto another space of physical states. Operators do not exist exclusively in quantum mechanics, but they can also be used in classical mechanics. In chapter 2, we have seen at least a couple of them, namely the Lagrangian, L, and Hamiltonian, H. In quantum mechanics, however, the concept of an operator is the basis of the complex mathematical treatment that is necessary for more complicated cases. In this chapter, we will discuss the mathematics of quantum mechanical operators, and we will recast the results for the analytical cases in light of the new framework. As we will see, this framework is even simpler than what we have seen in the previous chapter. This simplicity, however, will open the door to the "stranger" side of quantum mechanics.

19.4.1.1: Operators in Quantum Mechanics

19.4.1.2: Eigenfunctions and Eigenvalues

19.4.1.3: Common Operators in Quantum Mechanics

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19.4.1.3: Common Operators in Quantum Mechanics

Some common operators occurring in quantum mechanics are collected in the table below:

Observable Name	Symbol	Operator	Operation
Position	$\mathbf{r}$	$\hat{\mathbf{r}}$	Multiply by $\mathbf{r}$
Momentum	$\mathbf{p}$	$\hat{\mathbf{p}}$	$-i\hbar\left(\hat{\imath}\frac{\partial}{\partial x}+\hat{\jmath}\frac{\partial}{\partial y}+\hat{k}\frac{\partial}{\partial z}\right)$
Kinetic energy	K	$\hat{K}$	$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)$
Potential energy	$V(\mathbf{r})$	$\hat{V}(\mathbf{r})$	Multiply by $V(\mathbf{r})$
Total energy	E	$\hat{H}$	$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)+V(\mathbf{r})$
Angular momentum	L	$\hat{L}^2$	$\hat{L}_x^2+\hat{L}_y^2+\hat{L}_z^2$
	L_x	$\hat{L}_x$	$-i\hbar\left(y\frac{\partial}{\partial z}-z\frac{\partial}{\partial y}\right)$
	L_y	$\hat{L}_y$	$-i\hbar\left(z\frac{\partial}{\partial x}-x\frac{\partial}{\partial z}\right)$
	L_z	$\hat{L}_z$	$-i\hbar\left(x\frac{\partial}{\partial y}-y\frac{\partial}{\partial x}\right)$

In the sections below we analyze in details two main operators for the energy and the angular momentum.

Hamiltonian Operator

The main quantity that quantum mechanics is interested in is the total energy of the system, E. The operator corresponding to this quantity is called *Hamiltonian*:

$$\hat{H}=-\frac{\hbar^2}{2}\sum_i\frac{1}{m_i}\nabla_i^2+V, \tag{19.4.1.3.1}$$

where i is an index over all the particles of the system. Using the formalism of operators in conjunction with Equation 19.4.1.3.1, we can write the TISEq just simply as:

$$\hat{H}\psi=E\psi. \tag{19.4.1.3.2}$$

Comparing Equation 19.4.1.3.1 to the classical analog in Equation 18.3.2, we notice how the first term in the Hamiltonian operator represents the corresponding kinetic energy operator, $\hat{K}$, while the second term represents the potential energy operator, $\hat{V}$. For a one-electron system—such as the ones we studied in chapter 20—we can write:

$$\hat{K}=-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)=\frac{\hbar^2}{2m}\nabla^2, \tag{19.4.1.3.3}$$

which is universal and applies to all systems. The potential energy operator $\hat{V}$ is what differentiate each system. Using Equation 19.4.1.3.2, we can then simply obtain the TISEq for each of the first three models discussed in chapter 20 by simply using:

$$\begin{aligned}\text{Free particle:}&\quad \hat{V}=0,\\ \text{Particle in a box:}&\quad \hat{V}=0 \text{ inside the box, } \hat{V}=\infty \text{ outside the box,}\\ \text{Harmonic oscillator:}&\quad \hat{V}=\frac{1}{2}kx^2.\end{aligned} \tag{19.4.1.3.4}$$

While these three cases are trivial to solve, the case of the rigid rotor is more complicated to solve, since the kinetic energy operator needs to be solved in spherical polar coordinates, as we will show in the next section.

Angular Momentum Operator

To write the kinetic energy operator $\hat{K}$ for the rigid rotor, we need to express the Laplacian, ∇^2, in spherical polar coordinates:

$$\nabla^2 = \nabla_r^2 - \frac{\hat{L}^2}{r^2}, \tag{19.4.1.3.5}$$

where $\nabla_r^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)$ is the radial Laplacian, and $\hat{L}^2$ is the square of the total angular momentum operator, which is:

$$\begin{aligned}\hat{L}^2 = \hat{L}\cdot\hat{L} &= \left(\mathbf{i}\hat{L}_x + \mathbf{j}\hat{L}_y + \mathbf{k}\hat{L}_z\right)\cdot\left(\mathbf{i}\hat{L}_x + \mathbf{j}\hat{L}_y + \mathbf{k}\hat{L}_z\right)\\ &= \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2,\end{aligned} \tag{19.4.1.3.6}$$

with $\{\mathbf{i},\mathbf{j},\mathbf{k}\}$ the unitary vectors in three-dimensional space. The component along each direction, $\left\{\hat{L}_x,\hat{L}_y,\hat{L}_z\right\}$, are then expressed in cartesian coordinates using to the following formulas:

$$\begin{aligned}\hat{L}_x &= -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right),\\ \hat{L}_y &= -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right),\\ \hat{L}_z &= -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right).\end{aligned} \tag{19.4.1.3.7}$$

The eigenvalues equation corresponding to the total angular momentum is:

$$\hat{L}^2 Y(\theta,\varphi) = \hbar^2\ell(\ell+1)Y_\ell^{m_\ell}(\theta,\varphi), \tag{19.4.1.3.8}$$

where ℓ is the azimuthal quantum number and $Y_\ell^m(\theta,\varphi)$ are the spherical harmonics, both of which we already encountered in chapter 20. Recall once again that each energy level E_ℓ is $(2\ell+1)$-fold degenerate in m_ℓ, since m_ℓ can have values $-\ell, -\ell+1, \ldots, \ell-1, \ell$. This means that there are $(2\ell+1)$ states with the same energy E_ℓ, each characterized by the magnetic magnetic quantum number m_ℓ. This quantum number can be determined using the following eigenvalues equation:

$$\hat{L}_z Y(\theta,\varphi) = \hbar m_\ell Y_\ell^{m_\ell}(\theta,\varphi). \tag{19.4.1.3.9}$$

The interpretation of these results is rather complicated, since the angular momenta are quantum operators and they cannot be drawn as vectors like in classical mechanics. Nevertheless, it is common to depict them heuristically as in figure 19.4.1.3.1,[1] where a set of states with quantum numbers $\ell = 2$, and $m_\ell = -2, -1, 0, 1, 2$ are reported. Since $|L| = \sqrt{L^2} = \hbar\sqrt{6}$, the vectors are all shown with length $\hbar\sqrt{6}$. The rings represent the fact that L_z is known with certainty, but L_x and L_y are unknown; therefore every classical vector with the appropriate length and z-component is drawn, forming a cone. The expected value of the angular momentum for a given ensemble of systems in the quantum state characterized by ℓ and m_ℓ, could be somewhere on this cone but it cannot be defined for a single system.

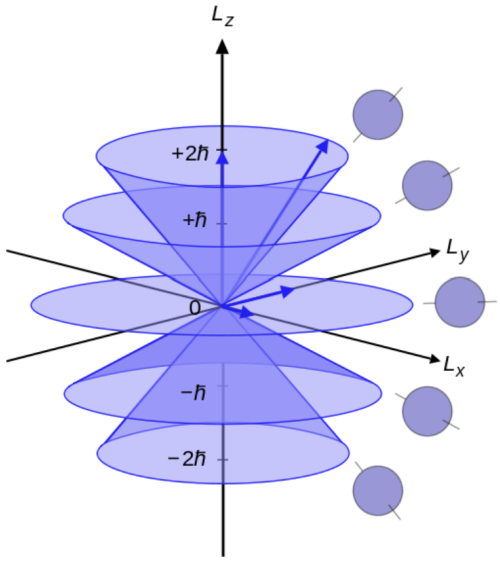


Figure 19.4.1.3.1: Illustration of the vector model of orbital angular momentum.

1. This diagram is taken from Wikipedia by user Maschen, and is of public domain

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20: ANALYTICALLY SOLUBLE MODELS

The TISEq can be solved analytically only in a few special cases. In this section, we will analyze the main four. Luckily, we can use these solutions to explain most of the effects in chemistry since we can combine them to describe the hydrogen atom upon which we can build more complex chemical systems, as we will show in the next chapters.

20.1: The Free Particles

20.2: The Particle in a Box

20.3: The Harmonic Oscillator

20.4: The Rigid Rotor

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20.1: The Free Particles

By definition, the particle does not feel any external force, therefore $V(x) = 0$, and the TISEq is written simply:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi(x). \tag{20.1.1}$$

This equation can be rearranged to:

$$\frac{d^2\psi}{dx^2} = -\frac{2mE}{\hbar^2}\psi(x), \tag{20.1.2}$$

which corresponds to a mathematical problem where the second derivative of a function should be equal to a constant, $-\frac{2mE}{\hbar^2}$ multiplied by the function itself. Such a problem is easily solved by the function:

$$\psi(x) = A\exp(\pm ikx). \tag{20.1.3}$$

The first and second derivatives of this function are:

$$\begin{aligned}\frac{d\psi(x)}{dx} &= \pm ikA\exp(\pm ikx) = \pm ik\psi(x)\\ \frac{d^2\psi(x)}{dx^2} &= \mp k^2 A\exp(\pm ikx) = -(\pm k^2)\psi(x).\end{aligned} \tag{20.1.4}$$

Comparing the second derivative in Equation ??? with Equation 20.1.2, we immediately see that if we set:

$$k^2 = \frac{2mE}{\hbar^2}, \tag{20.1.5}$$

we solve the original differential equation. Considering de Broglie's equation, Equation 17.5.4, we can replace $k = \frac{p}{\hbar}$, to obtain:

$$E = \frac{k^2\hbar^2}{2m} = \frac{p^2}{2m}, \tag{20.1.6}$$

which is exactly the classical value of the kinetic energy of a free particle moving in one direction of space. Since the function in Equation 20.1.3 solves the Schrödinger equation for the free particle, it is called an *eigenfunction* (or *eigenstate*) of the TISEq. The energy result of Equation 20.1.6 is called *eigenvalue* of the TISEq. Notice that, since k is continuous in the eigenfunction, the energy eigenvalue is also continuous (i.e., all values of E are acceptable).

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20.2: The Particle in a Box

Now we can consider a particle constrained to move in a single dimension, under the influence of a potential $V(x)$ which is zero for $0 \leq x \leq a$ and infinite elsewhere. Since the wavefunction is not allowed to become infinite, it must have a value of zero where $V(x)$ is infinite, so $\psi(x)$ is nonzero only within $[0, a]$. The Schrödinger equation is thus:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi(x) \qquad 0 \leq x \leq a. \tag{20.2.1}$$

In other words, inside the box $\psi(x)$ describes a free particle, but outside the box $\psi(x) = 0$. Since the Schrödinger equation involves derivatives, the function that solves it, $\psi(x)$, must be everywhere continuous and everywhere continuously differentiable. This fact means that the value of the wave function at the two extremes must be equal to zero:

$$\psi(0) = \psi(a) = 0. \tag{20.2.2}$$

Inside the box we can use Euler's formula to write the wave function as a linear combination of the positive and negative solutions:

$$\psi(x) = A\exp(\pm ix) = A\sin kx + B\cos kx, \tag{20.2.3}$$

where A and B are constants that we need to determine using the two constraints in Equation 20.2.2. For B it is straightforward to see that:

$$\psi(0) = 0 + B = 0 \implies B = 0. \tag{20.2.4}$$

For A we have:

$$\psi(a) = A\sin ka = 0, \tag{20.2.5}$$

which is trivially solved by $A = 0$, or by the more interesting condition of $ka = n\pi$. The trivial solution corresponds to a wave function uniformly equal to zero everywhere. This wave function is uninteresting, since it describes no particles in no boxes. The second set of solutions, however, is very interesting, since we can write it as:

$$\psi_n(x) = A\sin\left(\frac{n\pi x}{a}\right) \quad n = 1, 2, \ldots, \infty, \tag{20.2.6}$$

which represents an infinite set of functions, $\psi_n(x)$, determined by a positive integer number n, called *quantum number*. Since these functions solve the TISEq, they are also called *eigenfunctions*, but they are not a continuous set, unlike in the previous case. To calculate the energy eigenvalues, we can replace 20.2.6 into Equation 20.2.1, to obtain:

$$E_n = \frac{h^2 n^2}{8ma^2} \quad n = 1, 2, \ldots, \infty. \tag{20.2.7}$$

A few interesting considerations can be made from the results of Equation 20.2.7. First, although there is an infinite number of acceptable values of the energy (eigenvalues), these values are not continuous. Second, the lowest value of the energy is not zero, and it depends on the size of the box, a, since:

$$E_1 = \frac{h^2}{8ma^2} \neq 0. \tag{20.2.8}$$

This value is called *zero-point energy (ZPE)*, and is a purely quantum mechanical effect. Notice that we did not solve for the constant A. This task is not straightforward, and it can be achieved by requiring the wave function to describe one particle exclusively (we will come back to this task after chapter 23). Extending the problem to three dimensions is relatively straightforward, resulting in a set of three separate quantum numbers (one for each of the 3-dimensional coordinate n_x, n_y, n_z).

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20.3: The Harmonic Oscillator

We now consider a particle subject to a restoring force $F = -kx$, as might arise for a mass-spring system obeying Hooke's Law. The potential is then:

$$V(x) = -\int_{-\infty}^{\infty}(-kx)dx = V_0 + \frac{1}{2}kx^2. \tag{20.3.1}$$

If we choose the energy scale such that $V_0 = 0$ then: $V(x) = \frac{1}{2}kx^2$, and the TISEq looks:

$$-\frac{\hbar^2}{2\mu}\frac{d^2\psi}{dx^2} + \frac{1}{2}kx^2\psi(x) = E\psi(x) \tag{20.3.2}$$

After some effort, the eigenfunctions are:

$$\psi_n(x) = N_n H_n(\alpha^{1/2}x)e^{-\alpha x^2/2} \quad n = 0, 1, 2, \ldots, \infty, \tag{20.3.3}$$

where H_n is the Hermite polynomial of degree n, and α and N_n are defined by

$$\alpha = \sqrt{\frac{k\mu}{\hbar^2}} \qquad N_n = \frac{1}{\sqrt{2^n n!}}\left(\frac{\alpha}{\pi}\right)^{1/4}. \tag{20.3.4}$$

The eigenvalues are:

$$E_n = \hbar\omega\left(n + \frac{1}{2}\right), \tag{20.3.5}$$

with $\omega = \sqrt{k/\mu}$. Notice how, once again, the eigenfunctions and eigenvalues are not continuous. In this case, however, the first eigenvalue corresponds to $n = 0$, but because of the $\frac{1}{2}$ factor in Equation 20.3.5, the lowest energy state is, once again, not zero. In other words, the two masses of a quantum harmonic oscillator are always in motion. The frequencies at which they vibrate do not form a continuous spectrum. That is, the vibration frequency cannot take any value that we can think of, but only those given by Equation 20.3.5. The lowest possible energy (the ZPE) will be $E_0 = \frac{1}{2}\hbar\omega$.

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20.4: The Rigid Rotor

The rigid rotor is a simple model of a rotating stick in three dimensions (or, if you prefer, of a molecule). We consider the stick to consist of two point-masses at a fixed distance. We then reduce the model to a one-dimensional system by considering the rigid rotor to have one mass fixed at the origin, which is orbited by the reduced mass μ, at a distance r. The cartesian coordinates, x, y, z, are then replaced by three spherical polar coordinates: the co-latitude (zenith) angle θ, the longitudinal (azimuth) angle ϕ, and the distance r. The TISEq of the system in spherical coordinates is:

$$-\frac{\hbar^2}{2I}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\psi(r)=E_\ell\psi(r), \tag{20.4.1}$$

where $I=\mu r^2$ is the moment of inertia. After a little effort, the eigenfunctions can be shown to be the spherical harmonics $Y_\ell^{m_\ell}(\theta,\phi)$.[1] The eigenvalues are simply:

$$E_\ell=\frac{\hbar^2}{2I}\ell(\ell+1), \tag{20.4.2}$$

where $\ell=0,1,2,...$ is the *azimuthal quantum number*, and $m_\ell=-\ell,-\ell+1,...,\ell-1,\ell$ is the *magnetic quantum number*. Each energy level E_ℓ is $(2\ell+1)$-fold degenerate in m_ℓ. Notice that the energy does not depend on the second index m_ℓ, and the functions with fixed $m_\ell=-\ell,-\ell+1,...,\ell-1,\ell$ have the same energy. Since this problem was, in fact, a one-dimensional problem, it results in just one quantum number ℓ, similarly to the previous two cases. The index m_ℓ that appears in the spherical harmonics will assume some importance in future chapters.

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1. For a description of the spherical harmonics see here

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21: The Hydrogen Atom

In this chapter we will consider the hydrogen atom as a proton fixed at the origin, orbited by an electron of reduced mass μ. The potential due to electrostatic attraction is:

$$V(r) = -\frac{e^2}{4\pi\varepsilon_0 r}, \tag{21.1}$$

where ε_0 is the constant permittivity of vacuum. The kinetic energy term in the Hamiltonian is

$$K = -\frac{\hbar^2}{2\mu}\nabla^2, \tag{21.2}$$

where ∇^2 is the Laplace operator (*Laplacian*) representing the divergence of the gradient of a function. Recall that in 1-dimension the kinetic energy is proportional to the second derivative of the wave function with respect to the position. In 3-dimension, the first derivative along all three dimension of space is called gradient, which is written in cartesian coordinates $\nabla = \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right)$. The Laplacian is the divergence $\nabla \cdot$ of the gradient (effectively, it replaces the second derivatives in the 1-D case), and can be written in cartesian coordinates as $\nabla^2 = \nabla \cdot \nabla = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$. The TISEq for the Hydrogen atom is therefore:

$$\left(-\frac{\hbar^2}{2\mu}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r}\right)\psi(r,\theta,\phi) = E\psi(r,\theta,\phi), \tag{21.3}$$

which, replacing the Laplacian in spherical coordinates, becomes:

$$-\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}\right] - \frac{e^2}{4\pi\varepsilon_0 r}\psi = E\psi. \tag{21.4}$$

This equation seems very complicated, but comparing the term in between square brackets with the TISEq of the rigid rotor, we immediately see some connections. Equation 21.4 is a separable, partial differential equation that can be solved by factorizing the wave function $\psi(r,\theta,\phi)$ into $R_{nl}(r)Y_\ell^{m_\ell}(\theta,\phi)$, where $Y_\ell^{m_\ell}(\theta,\phi)$ are again the spherical harmonics that solved the TISEq for the rigid rotor. The radial part $R(r)$ obeys the equation:

$$-\frac{\hbar^2}{2\mu r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)\left[\frac{\hbar^2\ell(\ell+1)}{2\mu r^2} + V(r) - E\right]R(r) = 0, \tag{21.5}$$

which is called the radial equation for the hydrogen atom. The solutions of the radial part are:

$$R_{n\ell}(r) = -\left[\frac{(n-\ell-1)!}{2n[(n+\ell)!]^3}\right]^{1/2}\left(\frac{2}{na_0}\right)^{\ell+3/2} r^\ell e^{-r/na_0} L_{n+\ell}^{2\ell+1}\left(\frac{2r}{na_0}\right) \tag{21.6}$$

where $0 \le \ell \le n-1$, and $a_0 = \frac{\varepsilon_0 h^2}{\pi\mu e^2}$ is the Bohr radius. The functions $L_{n+\ell}^{2\ell+1}\left(\frac{2r}{na_0}\right)$ are the associated Laguerre functions.

The hydrogen atom eigenfunctions are:

$$\begin{aligned}\psi_{n\ell m_\ell}(r,\theta,\phi) &= R_{n\ell}(r)Y_\ell^{m_\ell}(\theta,\phi) = \\ &= -\left[\frac{(n-\ell-1)!}{2n[(n+\ell)!]^3}\right]^{1/2}\left(\frac{2}{na_0}\right)^{\ell+3/2} r^\ell e^{-r/na_0} L_{n+\ell}^{2\ell+1}\left(\frac{2r}{na_0}\right) Y_\ell^{m_\ell}(\theta,\phi)\end{aligned} \tag{21.7}$$

The quantum numbers n, ℓ, m_ℓ can take the following values:

- $n = 1, 2, 3, \dots, \infty$ (principal quantum number),
- $\ell = 0, 1, 2, \dots, n-1$ (azimuthal quantum number),
- $m_\ell = -\ell, \dots, \ell$ (magnetic quantum number).

These functions are called the *hydrogen atom orbitals*, and are usually first encountered in introductory chemistry textbooks.

Notice that—by definition—an orbital is a complex function (i.e., it has both a real and an imaginary component) that describes *exclusively* one electron. Spherical harmonics are orthogonal to each other and they can be linearly combined them to form new solution to the TISEq where the imaginary part is removed. (Because of the orthogonality of spherical harmonics, the energy spectrum will not be affected by this operation.) These corresponding real orbitals are three-dimensional function that are not easily visualized in a three-dimensional space, since they require a four-dimensional one.[1] Since there is no real consensus on what a wave function represent, the interpretation of orbitals is not straightforward.[2] We will return on the interpretation problem in future chapters, but for now it is important to keep in mind these following facts:

- The shape of every hydrogen atom orbital—complex or real—is that of a function on the surface of a sphere (yes, this is true for every single one of them, since they all come from spherical harmonics, which are special functions defined on the surface of a sphere. Hydrogen $2p$ orbitals in real space *do not* have the shape of a dumbbell, as often is said in general chemistry textbooks. Same goes for $d, f, \ldots$ orbitals.)
- Each orbital is the mathematical description of one—and only one—electron (in other words, orbitals do not "contain" electrons, they "are" the functions that describe each electron.)
- Hydrogen orbitals are defined only for stystems that contain one electron. When more than one electron is present in an atom, the TISEq in Equation 21.3 does not describe the system anymore. In these more complicated situations the TISEq cannot be solved analytically, and orbitals cannot be easily defined (we will see in chapter 26 how we can circumvent this issue in an approximate manner, and why general chemistry textbook talk of orbitals for every atom and molecule.)

The hydrogen atom eigenvalues are:

$$E_n = -\frac{e^2}{8\pi\varepsilon_0 a_0 n^2} \quad n = 1, 2, \ldots, \infty. \tag{21.8}$$

Notice how the eigenvalues (i.e., the energy spectrum) do not depend on the azimuthal and magnetic quantum numbers, ℓ and m. Energy levels with the same n, but different ℓ and/or m are called *degenerate states*, since they all have the same energy. This is, once again, source of misinterpretation in most general chemistry textbook:

- According to the TISEq, the $2s$ and $2p$ orbitals of the hydrogen atom have the same energy.[3]

---

1. If it is not clear why you need a 4-D space to visualize a 3-D function, think at the fact that we use a 2-D space (the Cartesian plane) to visualize a 1-D function ($f(x)$).
2. At least not as straightforward as it is given in introductory chemistry textbooks.
3. In practice, this is not true, because of a tiny effect called the Lamb shift. The description of this effect requires to go beyond the Schrödinger equation—and essentially beyond quantum mechanics—into the field of quantum electrodynamics. The Lamb shift, however, is not what is usually depicted in general chemistry textbook as the $2s - 2p$ energy difference. The difference that is usually discussed in the context of the aufbau principle is a many-electron effect, as we will discuss in chapter 10, and does not apply to hydrogen.

Thumbnail: Hydrogen atom. (Public Domain; Bensaccount via Wikipedia)

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22: OPERATORS AND MATHEMATICAL BACKGROUND

So far, we have seen a few simple examples of how to solve the TISEq. For the general case, the mathematical formulation of quantum mechanics is built upon the concept of an operator. An operator is a function over a space of physical states onto another space of physical states. Operators do not exist exclusively in quantum mechanics, but they can also be used in classical mechanics. In chapter 2, we have seen at least a couple of them, namely the Lagrangian, L, and Hamiltonian, H. In quantum mechanics, however, the concept of an operator is the basis of the complex mathematical treatment that is necessary for more complicated cases. In this chapter, we will discuss the mathematics of quantum mechanical operators, and we will recast the results for the analytical cases in light of the new framework. As we will see, this framework is even simpler than what we have seen in the previous chapter. This simplicity, however, will open the door to the "stranger" side of quantum mechanics.

22.1: Operators in Quantum Mechanics

22.2: Eigenfunctions and Eigenvalues

22.3: Common Operators in Quantum Mechanics

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22.1: Operators in Quantum Mechanics

The central concept in this new framework of quantum mechanics is that every observable (i.e., any quantity that can be measured in a physical experiment) is associated with an operator. To distinguish between classical mechanics operators and quantum mechanical ones, we use a hat symbol ˆ on top of the latter. Physical pure states in quantum mechanics are represented as unit-norm (probabilities are normalized to one) vectors in a special complex Hilbert space. Following the definition, an operator is a function that projects a vector in the Hilbert space onto the space of physical observables. Since observables are values that come up as the result of the experiment, quantum mechanical operators must yield real eigenvalues.[16] Operators that possess this property are called **Hermitian**. In the wave mechanics formulation of quantum mechanics that we have seen so far, the wave function varies with space and time—or equivalently momentum and time—and observables are differential operators. A completely analogous formulation is possible in terms of matrices. In the matrix formulation of quantum mechanics, the norm of the physical state should stay fixed, so the evolution operator should be unitary, and the operators can be represented as matrices.

The expectation value of an operator $\hat{A}$ for a system with wave function $\psi(\mathbf{r})$ living in a Hilbert space with unit vector $\mathbf{r}$ (i.e., in three-dimensional Cartesian space $\mathbf{r} = \{x, y, z\}$), is given by:

$$\langle A \rangle = \int \psi^*(\mathbf{r}) \hat{A} \psi(\mathbf{r}) d\mathbf{r}, \tag{22.1.1}$$

and if $\hat{A}$ is a Hermitian operator, all physical observables are represented by such expectation values. It is easy to show that if $\hat{A}$ is a linear operator with an eigenfunction g, then any multiple of g is also an eigenfunction of $\hat{A}$.

Basic Properties of Operators

Most of the properties of operators are obvious, but they are summarized below for completeness. The sum and difference of two operators $\hat{A}$ and $\hat{B}$ are given by:

$$\begin{aligned} (\hat{A} + \hat{B}) f &= \hat{A} f + \hat{B} f \\ (\hat{A} - \hat{B}) f &= \hat{A} f - \hat{B} f. \end{aligned} \tag{22.1.2}$$

The product of two operators is defined by:

$$\hat{A}\hat{B} f \equiv \hat{A}[\hat{B} f] \tag{22.1.3}$$

Two operators are equal if

$$\hat{A} f = \hat{B} f \tag{22.1.4}$$

for all functions f. The identity operator $\hat{1}$ does nothing (or multiplies by 1):

$$\hat{1} f = f \tag{22.1.5}$$

The associative law holds for operators:

$$\hat{A}(\hat{B}\hat{C}) = (\hat{A}\hat{B})\hat{C} \tag{22.1.6}$$

The commutative law does not generally hold for operators. In general, $\hat{A}\hat{B} \neq \hat{B}\hat{A}$. It is convenient to define the quantity:

$$[\hat{A}, \hat{B}] \equiv \hat{A}\hat{B} - \hat{B}\hat{A} \tag{22.1.7}$$

which is called the **commutator** of $\hat{A}$ and $\hat{B}$. Note that the order matters, so that $[\hat{A}, \hat{B}] = -[\hat{B}, \hat{A}]$. If $\hat{A}$ and $\hat{B}$ happen to commute, then $[\hat{A}, \hat{B}] = 0$.

Linear Operators

Almost all operators encountered in quantum mechanics are linear. A linear operator is any operator $\hat{A}$ satisfying the following two conditions:

$$\begin{aligned} \hat{A}(f+g) &= \hat{A}f + \hat{A}g, \\ \hat{A}(cf) &= c\hat{A}f, \end{aligned} \tag{22.1.8}$$

where c is a constant and f and g are functions. As an example, consider the operators $\frac{d}{dx}$ and $()^2$. We can see that $\frac{d}{dx}$ is a linear operator because:

$$\begin{aligned} \frac{d}{dx}[f(x)+g(x)] &= \frac{d}{dx}f(x) + \frac{d}{dx}g(x), \\ \frac{d}{dx}[cf(x)] &= c(d/dx)f(x). \end{aligned} \tag{22.1.9}$$

However, $()^2$ is not a linear operator because:

$$(f(x)+g(x))^2 \neq (f(x))^2 + (g(x))^2 \tag{22.1.10}$$

Hermitian Operators

Hermitian operators are characterized by the self-adjoint property:

$$\int \psi_a^*(\hat{A}\psi_a)d\mathbf{r} = \int \psi_a(\hat{A}\psi_a)^* d\mathbf{r}, \tag{22.1.11}$$

where the integral is performed over all space. This property guarantees that all the eigenvalues of the operators are real. Defining a as the eigenvalue of operator $\hat{A}$ using:

$$\hat{A}\psi(\mathbf{r}) = a\psi(\mathbf{r}), \tag{22.1.12}$$

we can prove that a is real by replacing Equation 22.1.12 into Equation 22.1.11:

$$\begin{aligned} a\int \psi_a^*\psi_a d\mathbf{r} &= a^* \int \psi_a \psi_a^* d\mathbf{r} \\ (a-a^*)\int |\psi_a|^2 d\mathbf{r} &= 0, \end{aligned} \tag{22.1.13}$$

and since $|\psi_a|^2$ is never negative, either $a = a^*$ or $\psi_a = 0$. Since $\psi_a = 0$ is not an acceptable wavefunction, $a = a^*$, and a is real.

The following additional properties of Hermitian operators can also be proven with some work:

$$\int \psi^* \hat{A}\psi d\mathbf{r} = \int (\hat{A}\psi)^* \psi d\mathbf{r}, \tag{22.1.14}$$

and for any two states ψ_1 and ψ_2:

$$\int \psi_1^* \hat{A}\psi_2 d\mathbf{r} = \int (\hat{A}\psi_1)^* \psi_2 d\mathbf{r}. \tag{22.1.15}$$

Taking ψ_a and ψ_b as eigenfunctions of $\hat{A}$ with eigenvalues a and b with $a \neq b$, and using Equation 22.1.15, we obtain:

$$\begin{aligned} \int \psi_a^* \hat{A}\psi_b d\mathbf{r} &= \int (\hat{A}\psi_a)^* \psi_b d\mathbf{r} \\ b\int \psi_a^*\psi_b d\mathbf{r} &= a^* \int \psi_a^* \psi_b d\mathbf{r} \\ (b-a)\int \psi_a^*\psi_b d\mathbf{r} &= 0. \end{aligned} \tag{22.1.16}$$

Thus, since $a = a^*$, and since we assumed $b \neq a$, we must have $\int \psi_a^* \psi_b d\mathbf{r} = 0$, i.e. ψ_a and ψ_b are orthogonal. In other words, eigenfunctions of a Hermitian operator with different eigenvalues are orthogonal (or can be chosen to be so).

---

1. But they might not be strictly real.

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22.2: Eigenfunctions and Eigenvalues

As we have already seen, an eigenfunction of an operator $\hat{A}$ is a function f such that the application of $\hat{A}$ on f gives f again, times a constant:

$$\hat{A}f = kf, \tag{22.2.1}$$

where k is a constant called the eigenvalue.

When a system is in an eigenstate of observable A (i.e., when the wave function is an eigenfunction of the operator $\hat{A}$) then the expectation value of A is the eigenvalue of the wave function. Therefore:

$$\hat{A}\psi(\mathbf{r}) = a\psi(\mathbf{r}), \tag{22.2.2}$$

then:

$$\begin{aligned} \langle A \rangle &= \int \psi^*(\mathbf{r})\hat{A}\psi(\mathbf{r})d\mathbf{r} \\ &= \int \psi^*(\mathbf{r})a\psi(\mathbf{r})d\mathbf{r} \\ &= a\int \psi^*(\mathbf{r})\psi(\mathbf{r})d\mathbf{r} = a, \end{aligned} \tag{22.2.3}$$

which implies that:

$$\int \psi^*(\mathbf{r})\psi(\mathbf{r})d\mathbf{r} = 1. \tag{22.2.4}$$

This property of wave functions is called normalization, and in the one-electron TISEq guarantees that the maximum probability of finding an electron over the entire space is one.[1]

A unique property of quantum mechanics is that a wave function can be expressed not just as a simple eigenfunction, but also as a combination of several of them. We have in part already encountered such property in the previous chapter, where complex hydrogen orbitals have been combined to form corresponding linear ones. As a general example, let us consider a wave function written as a linear combination of two eigenstates of $\hat{A}$, with eigenvalues a and b:

$$\psi = c_a\psi_a + c_b\psi_b, \tag{22.2.5}$$

where $\hat{A}\psi_a = a\psi_a$ and $\hat{A}\psi_b = b\psi_b$. Then, since ψ_a and ψ_b are orthogonal and normalized (usually abbreviated as orthonormal), the expectation value of A is:

$$\begin{aligned} \langle A \rangle &= \int \psi^*\hat{A}\psi d\mathbf{r} \\ &= \int \left[c_a\psi_a + c_b\psi_b\right]^* \hat{A}\left[c_a\psi_a + c_b\psi_b\right] d\mathbf{r} \\ &= \int \left[c_a\psi_a + c_b\psi_b\right]^* \left[ac_a\psi_a + bc_b\psi_b\right] d\mathbf{r} \\ &= a|c_a|^2 \int \psi_a^*\psi_a d\mathbf{r} + bc_a^*c_b \int \psi_a^*\psi_b d\mathbf{r} + ac_b^*c_a \int \psi_b^*\psi_a d\mathbf{r} + b|c_b|^2 \int \psi_b^*\psi_b d\mathbf{r} \\ &= a|c_a|^2 + b|c_b|^2. \end{aligned} \tag{22.2.6}$$

This result shows that the average value of A is a weighted average of eigenvalues, with the weights being the squares of the coefficients of the eigenvectors in the overall wavefunction.[2]

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1. ⚠Imposing the normalization condition is the best way to find the constant A in the solution of the TISEq for the particle in a box, a topic that we delayed in chapter 20.

2. This section was adapted in part from Prof. C. David Sherrill's A Brief Review of Elementary Quantum Chemistry Notes available here.

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22.3: Common Operators in Quantum Mechanics

Some common operators occurring in quantum mechanics are collected in the table below:

Observable Name	Symbol	Operator	Operation
Position	$\mathbf{r}$	$\hat{\mathbf{r}}$	Multiply by $\mathbf{r}$
Momentum	$\mathbf{p}$	$\hat{\mathbf{p}}$	$-i\hbar\left(\hat{\imath}\frac{\partial}{\partial x}+\hat{\jmath}\frac{\partial}{\partial y}+\hat{k}\frac{\partial}{\partial z}\right)$
Kinetic energy	K	$\hat{K}$	$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)$
Potential energy	$V(\mathbf{r})$	$\hat{V}(\mathbf{r})$	Multiply by $V(\mathbf{r})$
Total energy	E	$\hat{H}$	$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)+V(\mathbf{r})$
Angular momentum	L	$\hat{L}^2$	$\hat{L}_x^2+\hat{L}_y^2+\hat{L}_z^2$
	L_x	$\hat{L}_x$	$-i\hbar\left(y\frac{\partial}{\partial z}-z\frac{\partial}{\partial y}\right)$
	L_y	$\hat{L}_y$	$-i\hbar\left(z\frac{\partial}{\partial x}-x\frac{\partial}{\partial z}\right)$
	L_z	$\hat{L}_z$	$-i\hbar\left(x\frac{\partial}{\partial y}-y\frac{\partial}{\partial x}\right)$

In the sections below we analyze in details two main operators for the energy and the angular momentum.

Hamiltonian Operator

The main quantity that quantum mechanics is interested in is the total energy of the system, E. The operator corresponding to this quantity is called *Hamiltonian*:

$$\hat{H}=-\frac{\hbar^2}{2}\sum_i\frac{1}{m_i}\nabla_i^2+V, \tag{22.3.1}$$

where i is an index over all the particles of the system. Using the formalism of operators in conjunction with Equation 22.3.1, we can write the TISEq just simply as:

$$\hat{H}\psi=E\psi. \tag{22.3.2}$$

Comparing Equation 22.3.1 to the classical analog in Equation 18.3.2, we notice how the first term in the Hamiltonian operator represents the corresponding kinetic energy operator, $\hat{K}$, while the second term represents the potential energy operator, $\hat{V}$. For a one-electron system—such as the ones we studied in chapter 20—we can write:

$$\hat{K}=-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)=\frac{\hbar^2}{2m}\nabla^2, \tag{22.3.3}$$

which is universal and applies to all systems. The potential energy operator $\hat{V}$ is what differentiate each system. Using Equation 22.3.2, we can then simply obtain the TISEq for each of the first three models discussed in chapter 20 by simply using:

$$\begin{aligned}\text{Free particle:}\quad &\hat{V}=0,\\ \text{Particle in a box:}\quad &\hat{V}=0 \text{ inside the box, } \hat{V}=\infty \text{ outside the box,}\\ \text{Harmonic oscillator:}\quad &\hat{V}=\frac{1}{2}kx^2.\end{aligned} \tag{22.3.4}$$

While these three cases are trivial to solve, the case of the rigid rotor is more complicated to solve, since the kinetic energy operator needs to be solved in spherical polar coordinates, as we will show in the next section.

Angular Momentum Operator

To write the kinetic energy operator $\hat{K}$ for the rigid rotor, we need to express the Laplacian, ∇^2, in spherical polar coordinates:

$$\nabla^2 = \nabla_r^2 - \frac{\hat{L}^2}{r^2}, \tag{22.3.5}$$

where $\nabla_r^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)$ is the radial Laplacian, and $\hat{L}^2$ is the square of the total angular momentum operator, which is:

$$\begin{aligned}\hat{L}^2 = \hat{L}\cdot\hat{L} &= \left(\mathbf{i}\hat{L}_x + \mathbf{j}\hat{L}_y + \mathbf{k}\hat{L}_z\right)\cdot\left(\mathbf{i}\hat{L}_x + \mathbf{j}\hat{L}_y + \mathbf{k}\hat{L}_z\right) \\ &= \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2,\end{aligned} \tag{22.3.6}$$

with $\{\mathbf{i},\mathbf{j},\mathbf{k}\}$ the unitary vectors in three-dimensional space. The component along each direction, $\left\{\hat{L}_x,\hat{L}_y,\hat{L}_z\right\}$, are then expressed in cartesian coordinates using to the following formulas:

$$\begin{aligned}\hat{L}_x &= -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right), \\ \hat{L}_y &= -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right), \\ \hat{L}_z &= -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right).\end{aligned} \tag{22.3.7}$$

The eigenvalues equation corresponding to the total angular momentum is:

$$\hat{L}^2 Y(\theta,\varphi) = \hbar^2\ell(\ell+1)Y_\ell^{m_\ell}(\theta,\varphi), \tag{22.3.8}$$

where ℓ is the azimuthal quantum number and $Y_\ell^m(\theta,\varphi)$ are the spherical harmonics, both of which we already encountered in chapter 20. Recall once again that each energy level E_ℓ is $(2\ell+1)$-fold degenerate in m_ℓ, since m_ℓ can have values $-\ell, -\ell+1, \dots, \ell-1, \ell$. This means that there are $(2\ell+1)$ states with the same energy E_ℓ, each characterized by the magnetic magnetic quantum number m_ℓ. This quantum number can be determined using the following eigenvalues equation:

$$\hat{L}_z Y(\theta,\varphi) = \hbar m_\ell Y_\ell^{m_\ell}(\theta,\varphi). \tag{22.3.9}$$

The interpretation of these results is rather complicated, since the angular momenta are quantum operators and they cannot be drawn as vectors like in classical mechanics. Nevertheless, it is common to depict them heuristically as in figure 22.3.1,[1] where a set of states with quantum numbers $\ell = 2$, and $m_\ell = -2, -1, 0, 1, 2$ are reported. Since $|L| = \sqrt{L^2} = \hbar\sqrt{6}$, the vectors are all shown with length $\hbar\sqrt{6}$. The rings represent the fact that L_z is known with certainty, but L_x and L_y are unknown; therefore every classical vector with the appropriate length and z-component is drawn, forming a cone. The expected value of the angular momentum for a given ensemble of systems in the quantum state characterized by ℓ and m_ℓ, could be somewhere on this cone but it cannot be defined for a single system.

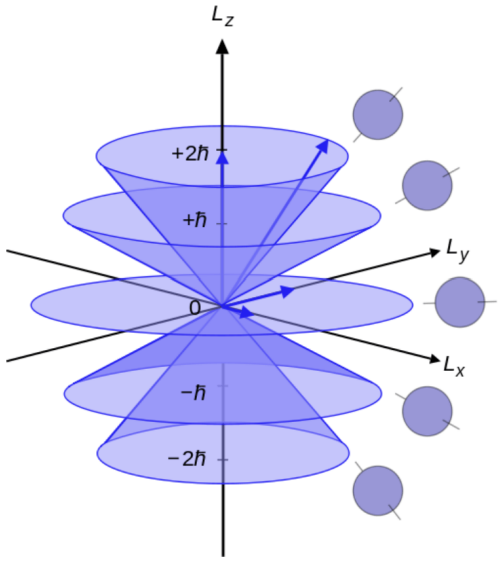


Figure 22.3.1: Illustration of the vector model of orbital angular momentum.

1. This diagram is taken from Wikipedia by user Maschen, and is of public domain

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23: SPIN

Spin is a special property of particles that has no classical analogue. Spin is an intrinsic form of angular momentum carried by elementary particles, such as the electron.

23.1: Stern-Gerlach Experiment

23.2: Sequential Stern-Gerlach Experiments

23.3: Spin Operators

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23.1: Stern-Gerlach Experiment

In 1920, Otto Stern and Walter Gerlach designed an experiment that unintentionally led to the discovery that electrons have their own individual, continuous spin even as they move along their orbital of an atom. The experiment was done by putting a silver foil in an oven to vaporize its atoms. The silver atoms were collected into a beam that passed through an inhomogeneous magnetic field. The result was that the magnetic beam split the beam into two (and only two) separate ones. The Stern–Gerlach experiment demonstrated that the spatial orientation of angular momentum is quantized into two components (up and down). Thus an atomic-scale system was shown to have intrinsically quantum properties. The experiment is normally conducted using electrically neutral particles such as silver atoms. This avoids the large deflection in the path of a charged particle moving through a magnetic field and allows spin-dependent effects to dominate.

If the particle is treated as a classical spinning magnetic dipole, it will precess in a magnetic field because of the torque that the magnetic field exerts on the dipole. If it moves through a homogeneous magnetic field, the forces exerted on opposite ends of the dipole cancel each other out and the trajectory of the particle is unaffected. However, if the magnetic field is inhomogeneous then the force on one end of the dipole will be slightly greater than the opposing force on the other end, so that there is a net force which deflects the particle's trajectory. If the particles were classical spinning objects, one would expect the distribution of their spin angular momentum vectors to be random and continuous. Each particle would be deflected by an amount proportional to its magnetic moment, producing some density distribution on the detector screen. Instead, the particles passing through the Stern–Gerlach apparatus are equally distributed among two possible values, with half of them ending up at an upper spot ("spin up"), and the other half at the lower spot ("spin down"). Since the particles are deflected by a magnetic field, spin is a magnetic property that is associated to some intrinsic form of angular momentum. As we saw in chapter 6, the quantization of the angular momentum gives energy levels that are $(2\ell+1)$-fold degenerate. Since along the direction of the magnet we observe only two possible eigenvalues for the spin, we conclude the following value for s:

$$2s+1=2 \quad \Rightarrow \quad s=\frac{1}{2}. \tag{23.1.1}$$

The Stern-Gerlach experiment proves that electrons are spin-$\frac{1}{2}$ particles. These have only two possible spin angular momentum values measured along any axis, $+\frac{\hbar}{2}$ or $-\frac{\hbar}{2}$, a purely quantum mechanical phenomenon. Because its value is always the same, it is regarded as an intrinsic property of electrons, and is sometimes known as "intrinsic angular momentum" (to distinguish it from orbital angular momentum, which can vary and depends on the presence of other particles).

The act of observing (measuring) the momentum along the z direction corresponds to the operator $\hat{S}_z$, which project the value of the total spin operator $\hat{S}^2$ along the z axis. The eigenvalues of the projector operator are:

$$\hat{S}_z\phi=\hbar m_s\phi, \tag{23.1.2}$$

where $m_s=\{-s,+s\}=\left\{-\frac{1}{2},+\frac{1}{2}\right\}$ is the spin quantum number along the z component. The eigenvalues for the total spin operator $\hat{S}^2$—similarly to the angular momentum operator $\hat{L}^2$ seen in Equation 22.3.6—are:

$$\hat{S}^2\phi=\hbar^2 s(s+1)\phi, \tag{23.1.3}$$

The initial state of the particles in the Stern-Gerlach experiment is given by the following wave function:

$$\phi=c_1\,\phi_\uparrow+c_2\,\phi_\downarrow, \tag{23.1.4}$$

where $\uparrow=+\frac{\hbar}{2}$, $\downarrow=-\frac{\hbar}{2}$, and the coefficients c_1 and c_2 are complex numbers. In this initial state, spin can point in any direction. The expectation value of the operator $\hat{S}_z$ (the quantity that the Stern-Gerlach experiment measures), can be obtained using Equation 22.2.6:

$$\begin{aligned} <S_z> &= \int \phi^*\hat{S}_z\phi\, d\mathbf{s} \\ &= +\frac{\hbar}{2}|c_1|^2-\frac{\hbar}{2}|c_2|^2, \end{aligned} \tag{23.1.5}$$

where the integration is performed along a special coordinate s composed of only two values, and the coefficient c_1 and c_2 are complex numbers. Applying the normalization condition, Equation 6.2.4 we can obtain:

$$|c_1|^2 + |c_2|^2 = 1 \quad \longrightarrow \quad |c_1|^2 = |c_2|^2 = \frac{1}{2}. \tag{23.1.6}$$

This equation is not sufficient to determine the values of the coefficients since they are complex numbers. Equation 23.1.6 , however, tells us that the squared magnitudes of the coefficients can be interpreted as probabilities of outcome from the experiment. This is true because their values are obtained from the normalization condition, and the normalization condition guarantees that the system is observed with probability equal to one. Summarizing, since we started with random initial directions, each of the two states, $\phi_{\uparrow}$ and $\phi_{\downarrow}$, will be observed with equal probability of $\frac{1}{2}$.

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23.2: Sequential Stern-Gerlach Experiments

An interesting result can be obtain if we link multiple Stern–Gerlach apparatuses into one experiment and we perform the measurement along two orthogonal directions in space. As we showed in the previous section, all particles leaving the first Stern-Gerlach apparatus are in an eigenstate of the $\hat{S}_z$ operator (i.e., their spin is either “up or”down” with respect to the z-direction). We can then take either one of the two resulting beams (for simplicity let’s take the “spin up” output), and perform another spin measurement on it. If the second measurement is also aligned along the z-direction then only one outcome will be measured, since all particles are already in the “spin up” eigenstate of $\hat{S}_z$. In other words, the measurement of a particle being in an eigenstate of the corresponding operator leaves the state unchanged.

If, however, we perform the spin measurement along a direction perpendicular to the original z-axis (i.e., the x-axis) then the output will equally distribute among “spin up” or ”spin down” in the x-direction, which in order to avoid confusion, we can call “spin left” and “spin right”. Thus, even though we knew the state of the particles beforehand, in this case the measurement resulted in a random spin flip in either of the measurement directions. Mathematically, this property is expressed by the nonvanishing of the commutator of the spin operators:

$$\left[\hat{S}_z, \hat{S}_x\right] \neq 0. \tag{23.2.1}$$

We can finally repeat the measurement a third time, with the magnet aligned along the original z-direction. According to classical physics, after the second apparatus, we would expect to have one beam with characteristic “spin up” and “spin left”, and another with characteristic “spin up” and “spin right”. The outcome of the third measurement along the original z-axis should be one output with characteristic “spin up”, regardless to which beam the magnet is applied (since the “spin down” component should have been “filtered out” by the first experiment, and the “spin left” and “spin right” component should be filtered out by the third magnet). This is not what is observed. The output of the third measurement is—once again—two beams in the z direction, one with “spin up” characteristric and the other with “spin down”.

This experiment shows that spin is not a classical property. The Stern-Gerlach apparatus does not behave as a simple filter, selecting beams with one specific pre-determined characteristic. The second measurement along the x axis destroys the previous determination of the angular momentum in the z direction. This means that this property cannot be measured on two perpendicular directions at the same time.

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23.3: Spin Operators

The mathematics of quantum mechanics tell us that $\hat{S}_z$ and $\hat{S}_x$ do not commute. When two operators do not commute, the two measurable quantities that are associated with them cannot be known at the same time.

In 3-dimensional space there are three directions that are orthogonal to each other $\{x, y, z\}$. Thus, we can define a third spin projection operator along the y direction, $\hat{S}_y$, corresponding to a new set of Stern-Gerlach experiments where the second magnet is oriented along a direction that is orthogonal to the two that we consider in the previous section. The total spin operator, $\hat{S}^2$, can then be constructed similarly to the total angular momentum operator of Equation 22.3.5, as:

$$\begin{aligned}\hat{S}^2 = \hat{S}\cdot\hat{S} &= \left(\mathbf{i}\hat{S}_x + \mathbf{j}\hat{S}_y + \mathbf{k}\hat{S}_z\right)\cdot\left(\mathbf{i}\hat{S}_x + \mathbf{j}\hat{S}_y + \mathbf{k}\hat{S}_z\right) \\ &= \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2,\end{aligned} \tag{23.3.1}$$

with $\{\mathbf{i}, \mathbf{j}, \mathbf{k}\}$ the unitary vectors in three-dimensional space.

Wolfgang Pauli explicitly derived the relationships between all three spin projection operators. Assuming the magnetic field along the z axis, Pauli's relations can be written using simple equations involving the two possible eigenstates $\phi_\uparrow$ and $\phi_\downarrow$:

$$\begin{aligned}&\hat{S}_x\phi_\uparrow = \frac{\hbar}{2}\phi_\downarrow \qquad \hat{S}_y\phi_\uparrow = \frac{\hbar}{2}i\phi_\downarrow \qquad \hat{S}_z\phi_\uparrow = \frac{\hbar}{2}\phi_\uparrow \\ &\hat{S}_x\phi_\downarrow = \frac{\hbar}{2}\phi_\uparrow \qquad \hat{S}_y\phi_\downarrow = -\frac{\hbar}{2}i\phi_\uparrow \qquad \hat{S}_z\phi_\downarrow = -\frac{\hbar}{2}\phi_\downarrow,\end{aligned} \tag{23.3.2}$$

where i is the imaginary unit ($i^2 = -1$). In other words, for $\hat{S}_z$ we have eigenvalue equations, while the remaining components have the effect of permuting state $\phi_\uparrow$ with state $\phi_\downarrow$ after multiplication by suitable constants. We can use these equations, together with Equation 23.1.7, to calculate the commutator for each couple of spin projector operators:

$$\begin{aligned}\left[\hat{S}_x, \hat{S}_y\right] &= i\hat{S}_z \\ \left[\hat{S}_y, \hat{S}_z\right] &= i\hat{S}_x \\ \left[\hat{S}_z, \hat{S}_x\right] &= i\hat{S}_y,\end{aligned} \tag{23.3.3}$$

which prove that the three projection operators do not commute with each other.

Example 23.3.1

Proof of Commutator Between Spin Projection Operators.

Solution

The equations in ??? can be proved by writing the full eigenvalue equation and solving it using the definition of commutator, Equation 23.1.7, in conjunction with Pauli's relation, Equations ???. For example, for the first couple:

$$\begin{aligned}\left[\hat{S}_x, \hat{S}_y\right]\phi_\uparrow &= \hat{S}_x\hat{S}_y\phi_\uparrow - \hat{S}_y\hat{S}_x\phi_\uparrow \\ &= \hat{S}_x\left(\frac{\hbar}{2}i\phi_\downarrow\right) - \hat{S}_y\left(\frac{\hbar}{2}\phi_\downarrow\right) \\ &= \frac{\hbar}{2}i\left(\frac{\hbar}{2}i\phi_\downarrow\right) - \frac{\hbar}{2}\left(\frac{\hbar}{2}\phi_\downarrow\right) \\ &= \left(\frac{\hbar}{4} + \frac{\hbar}{4}\right)i\phi_\uparrow \\ &= \frac{\hbar}{2}i\phi_\uparrow \\ &= i\hat{S}_z\phi_\uparrow\end{aligned} \tag{23.3.4}$$

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24: POSTULATES OF QUANTUM MECHANICS

In order to understand deeper quantum mechanics, scientists have derived a series of axioms that result in what are called *postulates of quantum mechanics*. These are, in fact, assumptions that we need to make to understand how the measured reality relates with the mathematics of quantum mechanics. It is important to notice that the postulates are necessary for the interpretation of the theory, but not for the mathematics behind it. Regarding of whether we interpret it or not, the mathematics is complete and consistent. In fact, as we will see in the next chapter, several controversies regarding the interpretation of the mathematics are still open, and different philosophies have been developed to rationalize the results. Recall also that there are different ways of writing the equation of quantum mechanics, all equivalent to each other (i.e., Schrödinger's differential formulation and Heisenberg's algebraic formulation that we saw in chapter 3). For these reasons, there is not an agreement on the number of postulates that are necessary to interpret the theory, and some philosophy and/or formulation might require more postulates than others. In this chapter, we will discuss the six postulates, as they are usually presented in chemistry and introductory physics textbooks and as they relate with a basic statistical interpretation of quantum mechanics. Regardless of the philosophical consideration on the meanings and numbers of the postulate, as well as their physical origin, these statements will make the interpretation of the theory a little easier, as we will see in the next chapter.

24.1: Postulate 1- The Wave Function Postulate

24.2: Postulate 2- Experimental Observables

24.3: Postulate 3- Individual Measurements

24.4: Postulate 4- Expectation Values and Collapse of the Wavefunction

24.5: Postulate 5- Time Evolution

24.6: Postulate 6- Pauli Exclusion Principle

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24.1: Postulate 1- The Wave Function Postulate

The state of a quantum mechanical system is completely specified by a function $\Psi(\mathbf{r},t)$ that depends on the coordinates of the particle(s) and on time. This function, called the wave function or state function, has the important property that $\Psi^*(\mathbf{r},t)\Psi(\mathbf{r},t)d\tau$ is the probability that the particle lies in the volume element $d\tau$ located at $\mathbf{r}$ at time t.

The wave function must satisfy certain mathematical conditions because of this probabilistic interpretation. For the case of a single particle, the probability of finding it somewhere is 1, so that we have the normalization condition

$$\int_{-\infty}^{\infty} \Psi^*(\mathbf{r},t)\Psi(\mathbf{r},t)d\tau = 1 \tag{24.1.1}$$

It is customary to also normalize many-particle wave functions to 1. As we already saw for the particle in a box in chapter 20, a consequence of the first postulate is that the wave function must also be single-valued, continuous, and finite, so that derivatives can be defined and calculated at each point in space. This consequence allows for operators (which typically involve derivation) to be applied without mathematical issues.

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24.2: Postulate 2- Experimental Observables

To every observable in classical mechanics there corresponds a linear, Hermitian operator in quantum mechanics. We have in part already discussed this postulate in chapter 22, albeit we didn't call it as such. This postulate is necessary if we require the expectation value of an operator $\hat{A}$ to be real, as it should be.

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24.3: Postulate 3- Individual Measurements

In any measurement of the observable associated with operator $\hat{A}$, the only values that will ever be observed are the eigenvalues a that satisfy the eigenvalue equation:

$$\hat{A}\Psi = a\Psi. \tag{24.3.1}$$

This postulate captures the central point of quantum mechanics: the values of dynamical variables can be quantized (although it is still possible to have a continuum of eigenvalues in the case of unbound states). If the system is in an eigenstate of $\hat{A}$ with eigenvalue a, then any measurement of the quantity A will yield a. Although measurements must always yield an eigenvalue, the state does not have to be an eigenstate of $\hat{A}$ initially.

An arbitrary state can be expanded in the complete set of eigenvectors of $\hat{A}$ $\left(\hat{A}\Psi_i = a_i\Psi_i\right)$ as:

$$\Psi = \sum_i^n c_i\Psi_i, \tag{24.3.2}$$

where n may go to infinity. In this case, we only know that the measurement of A will yield one of the values a_i, but we don't know which one. However, we do know the probability that eigenvalue a_i will occur (it is the absolute value squared of the coefficient, $|c_i|^2$, as we obtained already in chapter 22), leading to the fourth postulate below.

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24.4: Postulate 4- Expectation Values and Collapse of the Wavefunction

If a system is in a state described by a normalized wave function Ψ, then the average value of the observable corresponding to $\hat{A}$ is given by:

$$\langle A \rangle = \int_{-\infty}^{\infty} \Psi^* \hat{A} \Psi d\tau. \tag{24.4.1}$$

An important consequence of the fourth postulate is that, after measurement of Ψ yields some eigenvalue a_i, the wave function immediately "collapses" into the corresponding eigenstate Ψ_i. In other words, measurement affects the state of the system. This fact is used in many experimental tests of quantum mechanics, such as the Stern-Gerlach experiment. Think again at the sequential experiment that we discussed in chapter 23. The act of measuring the spin along one coordinate is not simply a "filtration" of some pre-existing feature of the wave function, but rather an act that changes the nature of the wave function itself, affecting the outcome of future experiments. To this act corresponds the collapse of the wave function, a process that remains unexplained to date. Notice how the controversy is not in the mathematics of the experiment, which we already discussed in the previous chapter without issues. The issues rather arise because we don't know how to define the measurement act in itself (other than the fact that it is some form of quantum mechanical procedure with clear and well-defined macroscopic outcomes). This is the reason why the collapse of the wave function is also sometimes called the *measurement problem* of quantum mechanics, and it is still a source of research and debate among modern scientists.

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24.5: Postulate 5- Time Evolution

The wave function of a system evolves in time according to the time-dependent Schrödinger equation:

$$\hat{H}\Psi(\mathbf{r},t) = i\hbar\frac{\partial\Psi}{\partial t}. \tag{24.5.1}$$

The central equation of quantum mechanics must be accepted as a postulate.

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24.6: Postulate 6- Pauli Exclusion Principle

The total wave function of a system with N spin-$\frac{1}{2}$ particles (also called **fermions**) must be antisymmetric with respect to the interchange of all coordinates of one particle with those of another. For spin-1 particles (also called **bosons**), the wave function is symmetric:

$$\begin{aligned} \Psi\left(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N\right) &= -\Psi\left(\mathbf{r}_2, \mathbf{r}_1, \ldots, \mathbf{r}_N\right) \quad \text{fermions}, \\ \Psi\left(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N\right) &= +\Psi\left(\mathbf{r}_2, \mathbf{r}_1, \ldots, \mathbf{r}_N\right) \quad \text{bosons}. \end{aligned} \tag{24.6.1}$$

Electronic spin must be included in this set of coordinates. As we will see in chapter 26, the mathematical treatment of the antisymmetry postulate gives rise to the Pauli exclusion principle, which states that two or more identical fermions cannot occupy the same quantum state simultaneously (while bosons are perfectly capable of doing so).

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25: QUANTUM WEIRDNESS

In this chapter, we will delve deeper into the strangeness of quantum mechanics. In particular, we will explore quantum phenomena that don't have a classical counterpart, starting from perhaps the most simple but also one of the most revealing: the double-slit experiment.

25.1: The Double-slit Experiment

25.2: Heisenberg's Uncertainty Principle

25.3: Tunneling

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25.1: The Double-slit Experiment

The double-slit experiment is considered by many the seminal experiment in quantum mechanics. The reason why we see it only at this advanced point is that its interpretation is not as straightforward as it might seem from a superficial analysis. The famous physicist Richard Feynman was so fond of this experiment that he used to say that all of quantum mechanics can be understood from carefully thinking through its implications.

The premises of the experiment are very simple: cut two slits in a solid material (such as a sheet of metal), send light or electrons through them, and observe what happens on a screen position at some distance on the other side. The result of this experiment though are far from straightforward.

Let's first consider the single-slit case. If light consisted of classical particles, and these particles were sent in a straight line through a single-slit and allowed to strike a screen on the other side, we would expect to see a pattern corresponding to the size and shape of the slit. However, when this "single-slit experiment" is actually performed, the pattern on the screen is a diffraction pattern in which the light is spread out. The smaller the slit, the greater the angle of spread. This behavior is typical of waves, where diffraction explains the pattern as being the result of the interference of the waves with the slit.

If one illuminates two parallel slits, the light from the two slits again interferes. Here the interference is a more pronounced pattern with a series of alternating light and dark bands. The width of the bands is a property of the frequency of the illuminating light. The pattern observed on the screen is the result of this interference, as shown in figure $25.1.1$.[1]

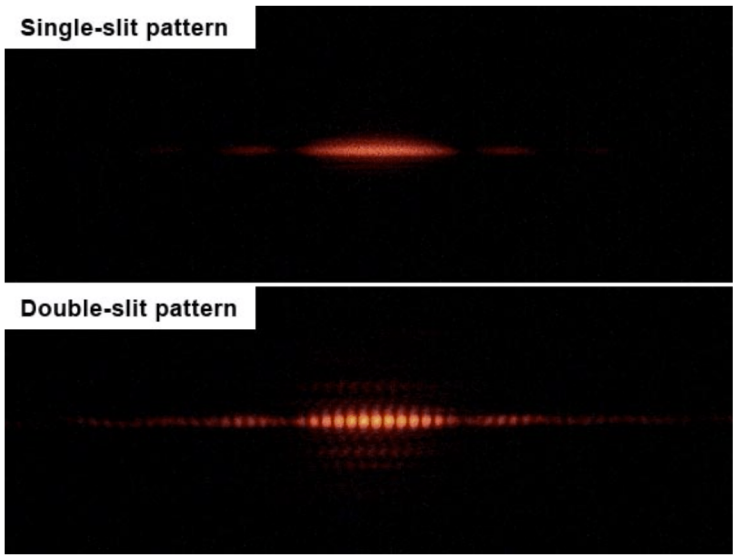


Figure $25.1.1$: Outcomes of single-slit and double-slit experiments.

The interference pattern resulting from the double-slit experiment are observed not only with light, but also with a beam of electrons, and other small particles.

The individual particles experiment

The first twist in the plot is if we perform the experiment by sending individual particles (e.g, either individual photons, or individual electrons). Sending particles through a double-slit apparatus one at a time results in single particles appearing on the screen, as expected. Remarkably, however, an interference pattern emerges when these particles are allowed to build up one by one (figure $25.1.2$)[2]. The resulting pattern on the screen is the same as if each individual particle had passed through both slits.

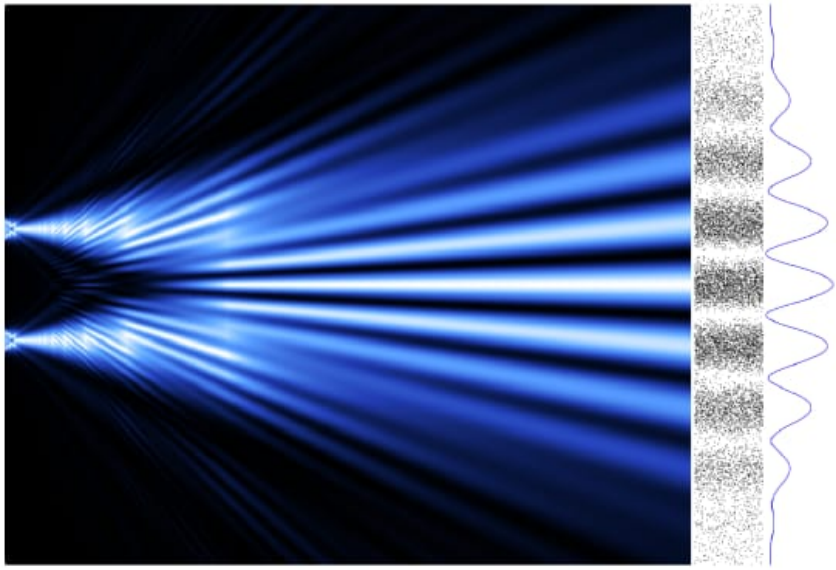


Figure 25.1.2: Numerical simulation of the double-slit experiment with electrons.

This variation of the double-slit experiment demonstrates the wave–particle duality: the particle is measured as a single pulse at a single position, while the wave describes the probability of absorbing the particle at a specific place on the screen.

“Which way” experiment

A second twist happens if we place particle detectors at the slits with the intent of showing through which slit a particle goes. The interference pattern in this case will disappear.

This experiment illustrates that photons (and electrons) can behave as either particles or waves, but cannot be observed as both at the same time. The simplest interpretation of this experiment is that the wave function of the photon collapses into a deterministic position due to the interaction with the detector on the slit, and the interference pattern is therefore lost. This result also proves that in order to measure (detect) a photon, we must interact with it, an act that changes its wave function.

The interpretation of the results of this experiment is not simple. As for other situations in quantum mechanics, the problem arise not because we cannot describe the experiment in mathematical terms, but because the math that we need to describe it cannot be related to the macroscopic classical world we live in. According to the math, in fact, particles in the experiment are described exclusively in probabilistic terms (given by the square of the wave function). The macroscopic world, however, is not probabilistic, and outcomes of experiments can be univocally measured. Several different ways of reediming this controversy have been proposed, including for example the possibility that quantum mechanics is incomplete (the emergence of probability is due to the ignorance of some more fundamental deterministic feature of nature), or assuming that every time a measurement is done on a quantum system, the universe splits, and every possible measurable outcome is observed in different branches of our universe (we only happen to live in one of such branches, so we observe only one non-probabilistic result).[3] The interpretation of quantum mechanics is still an unsolved problem in modern physics (luckily, it does not prevent us from using quantum mechanics in chemistry).

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2. This diagram is taken from Wikipedia by user Alexandre Gondran, and distributed under CC BY-SA 4.0 license
3. The interested student can read more about different interpretations HERE.

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25.2: Heisenberg's Uncertainty Principle

Let's now revisit the simple case of a free particle. As we saw in chapter 20, the wave function that solved the TISEq:

$$\psi(x) = A\exp(\pm ikx), \tag{25.2.1}$$

is the equation of a plane wave along the x direction. This result is in agreement with the de Broglie hypothesis, which says that every object in the universe is a wave. If this wave function describes a particle with mass (such as an electron), freely moving along one spatial direction x, it would be reasonable to ask the question: where is the particle located? Analyzing Equation 25.2.1 , however, it is not possible to answer this question since $\psi(x)$ is delocalized in space from $x = -\infty$ to $x = +\infty$.[1] In other words, the particle position is extremely uncertain because it could be essentially anywhere along the wave.

Thus for a free particle, the particle side of the wave-particle duality seems completely lost. We can, however, bring it back into the picture by writing the wave function as a sum of many plane waves, called a *wave packet*:

$$\psi(x) \propto \sum_n A_n \exp\left(\frac{ip_n x}{\hbar}\right), \tag{25.2.2}$$

where A_n represents the relative contribution of the mode p_n to the overall total. We are allowed to write the wave function this way because each individual plane wave is a solution of the TISEq, and as we already saw in chapter 22 and several other places, the sum of each individual solution is also a solution. An interesting consequence of writing the wave function as a wave packet is that when we sum different waves, they interfere with each other, and they might localize in some region of space. Thus for a wave function written as in Equation 25.2.2, the wave packet can become more localized. We may also make this procedure a step further to the continuum limit, where the wave function goes from a sum to an integral over all possible modes:

$$\psi(x) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \varphi(p) \cdot \exp\left(\frac{ipx}{\hbar}\right) dp, \tag{25.2.3}$$

where $\varphi(p)$ represents the amplitude of these modes and is called the wave function in momentum space. In mathematical terms, we say that $\varphi(p)$ is the Fourier transform of $\psi(x)$ and that x and p are conjugate variables. Adding together all of these plane waves comes at a cost; namely, the momentum has become less precise since it becomes a mixture of waves of many different momenta.

One way to quantify the precision of the position and momentum is the standard deviation, σ. Since $|\psi(x)|^2$ is a probability density function for position, we calculate its standard deviation. The precision of the position is improved—i.e., reduced σ_x—by using many plane waves, thereby weakening the precision of the momentum—i.e., increased σ_p. Another way of stating this is that σ_x and σ_p have an inverse relationship (once we know one with absolute precision, the other becomes completely unknown). This fact was discovered by Werner Heisenberg and is now called the **Heisenberg's uncertainty principle**. The mathematical treatment of this procedure results in the simple formula:

$$\sigma_x \sigma_p \geq \frac{\hbar}{2}. \tag{25.2.4}$$

The uncertainty principle can be extended to any couple of conjugated variables, including, for example, energy and time, angular momentum components along perpendicular directions, spin components along perpendicular directions, etc. It is also easy to show that conjugate variables in quantum mechanics correspond to non-commuting operators.[2]

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1. The time-dependent picture does not help us either, but since it is a little more complicated to work with the TDSEq, we are not showing it here.
2. Therefore, a simpler way of finding if two variables are subject to the uncertainty principle is to check if their corresponding operators commute.

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25.3: Tunneling

Tunneling is a phenomenon where a particle may cross a barrier even if it does not have sufficient kinetic energy to overcome the potential of the barrier itself. In this situation, the particle is said to "tunnel through" the barrier following a purely quantum mechanical phenomenon (figure 25.3.1).[1]

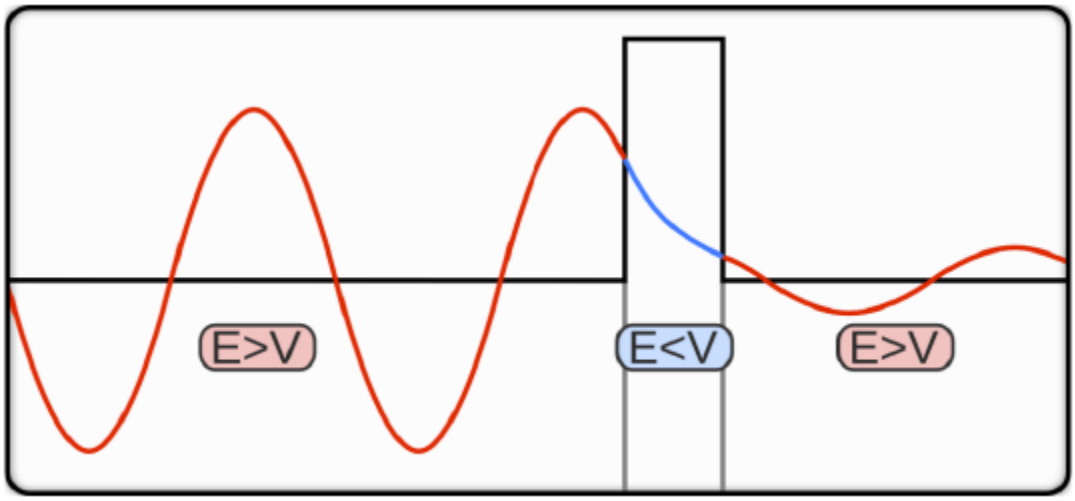


Figure 25.3.1: Quantum tunneling through a barrier. The energy of the tunnelled particle is the same but the probability amplitude is decreased.

To explain tunneling we must resort once again to the TISeq. A traveling or standing wave function incident on a non-infinite potential barrier (V_0) decays in the potential as a function of $A_0 \exp[-\alpha x]$, where A_0 is the amplitude at the boundary, α is proportional to the potential, and x is the distance into the potential. If a second well exists at infinite distance from the first well, the probability goes to zero, so the probability of a particle existing in the second well is zero. If a second well is brought closer to the first well, the amplitude of the wave function at this boundary is not zero, so the particle may tunnel into that well from the first well. It would appear that the particle is "leaking" through the barrier; it can travel through it without having to surmount it. An important point to keep in mind is that tunneling conserves energy. The final sum of the kinetic and potential energy of the system cannot exceed the initial sum. Therefore, the potential on both sides of the barrier does not need to be the same, but the sum of the ground state energy and the potential on the opposite side of the barrier may not be larger than the initial particle energy and potential.

Tunneling can be described using the TISEq, Equation 22.3.1. For the tunneling problem we can take the potential V to be zero for all space, except for the region inside the barrier (between 0 and a):

$$V = \begin{cases} 0 & \text{if } -\infty < x \leq 0 \\ V_0 & \text{if } 0 < x < a \\ 0 & \text{if } a \leq x < \infty \end{cases} . \tag{25.3.1}$$

To solve the TISEq with this potential, we must solve it separately for each region, but we should make sure that the wave function stays single-valued, continuous and everywhere continuously differentiable. The general solution for each region, before applying the boundary conditions, is:

$$\psi = \begin{cases} A\sin(kx) + B\cos(kx) & \text{if } -\infty < x \leq 0 \\ C\exp(-\alpha x) + D\exp(\alpha x) & \text{if } 0 < x < a \\ E\sin(kx) + F\cos(kx) & \text{if } a \leq x < \infty \end{cases} \tag{25.3.2}$$

where $k = \dfrac{\sqrt{2mE}}{\hbar}$, and $\alpha = \dfrac{\sqrt{2m(V_0 - E)}}{\hbar}$. To enforce continuity, we must have at the first boundary:

$$A\sin(0) + B\cos(0) = C\exp(0) + D\exp(0), \tag{25.3.3}$$

which implies that $A = 0$, and $B = C + D$. At the opposite boundary:

$$A\sin(ka) + B\cos(ka) = C\exp(-\alpha a) + D\exp(\alpha a). \tag{25.3.4}$$

We notice that, as a goes to infinity, the right hand side of Equation 25.3.4 goes to infinity, which does not make physical sense. To reconcile this, we must set $D = 0$.

For the final region, E and F, present a potentially intractable problem. However, if one realizes that the value at the boundary a is driving the wave in the region a to infinity, it may also be realized that the wave function could be rewritten as $C\exp[-\alpha a]\cos[k(x - a)]$, phase shifting the wave function by the value of a, and setting the amplitude to the boundary value. Summarizing, the wave function is:

$$\psi = \begin{cases} B\cos(kx) & \text{if } -\infty < x \leq 0 \\ B\exp(-\alpha x) & \text{if } 0 < x < a \\ B\exp(-\alpha a)\cos[k(x-a)] & \text{if } a \leq x < \infty. \end{cases} \tag{25.3.5}$$

Comparing the wave function on the left of the barrier with the one on its right, we notice how the amplitude is attenuated by the barrier as $\exp\left(-a\frac{\sqrt{2m(V_0 - E)}}{\hbar}\right)$, where a is the width of the barrier, and $(V_0 - E)$ is the difference between the potential energy of the barrier and the current energy of the particle. Since the square of the wave function is the probability distribution, the probability of transmission through a barrier is:

$$\exp\left(-2a\frac{\sqrt{2m(V_0 - E)}}{\hbar}\right). \tag{25.3.6}$$

As the barrier width or height approaches zero, the probability of a particle tunneling through the barrier becomes one. We can also note that k is unchanged on the other side of the barrier. This implies that the energy of the particle is exactly the same as it was before it tunneled through the barrier, as stated earlier, the only thing that changes is the quantity of particles going in that direction. The rest is reflected off the barrier, and go back the way it came. On the opposite end, as the barrier width or height approaches infinity, the probability of a particle tunneling through the barrier becomes zero, and the barrier behaves similarly to those that contained the particle in the particle in a box example discussed in chapter 20.

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26: BOLTZMANN FACTOR AND PARTITION FUNCTIONS

UC Davis Chemistry Chemistry 110B

Physical Chemistry II: Properties of Atoms and Molecules

Chem 110A ● Chem 110B ● Chem 110C ● **Agenda** ● **Homework** ● **Worksheet Activities**

Statistical Mechanics provides the connection between microscopic motion of individual atoms of matter and macroscopically observable properties such as temperature, pressure, entropy, free energy, heat capacity, chemical potential, viscosity, spectra, reaction rates, etc. Statistical Mechanics provides the microscopic basis for thermodynamics, which, otherwise, is just a phenomenological theory. Microscopic basis allows calculation of a wide variety of properties not dealt with in thermodynamics, such as structural properties, using distribution functions, and dynamical properties – spectra, rate constants, etc., using time correlation functions. Because a statistical mechanical formulation of a problem begins with a detailed microscopic description, microscopic trajectories can, in principle and in practice, be generated providing a window into the microscopic world. This window often provides a means of connecting certain macroscopic properties with particular modes of motion in the complex dance of the individual atoms that compose a system, and this, in turn, allows for interpretation of experimental data and an elucidation of the mechanisms of energy and mass transfer in a system.

26.1: The Boltzmann Factor Is One of the Most Important Quantities in the Physical Sciences

26.2: The Thermal Boltzman Distribution

26.3: We Postulate That the Average Ensemble Energy Is Equal to the Observed Energy of a System

26.4: The Heat Capacity at Constant Volume

26.5: Express the Pressure in Terms of a Partition Function

26.6: Partition Functions of Systems of Distinguishable Molecules are Products of Molecular Partition Functions

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26.8: A Molecular Partition Function Can Be Decomposed into Partition Functions for Each Degree of Freedom

26.E: Exercises

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26.1: The Boltzmann Factor Is One of the Most Important Quantities in the Physical Sciences

Statistical Mechanics provides the connection between microscopic motion of individual atoms of matter and macroscopically observable properties such as temperature, pressure, entropy, free energy, heat capacity, chemical potential, viscosity, spectra, reaction rates, etc.

The Microscopic Laws of Motion

Consider a system of N classical particles. The particles are confined to a particular region of space by a container of volume V . In classical mechanics, the state of each particle is specified by giving its position and its velocity, i.e., by telling where it is and where it is going. The position of particle i is simply a vector of three coordinates $r_i = (x_i, y_i, z_i)$, and its velocity $\mathbf{v}_i$ is also a vector $(v_{x_i}, v_{y_i}, v_{z_i})$ of the three velocity components. Thus, if we specify, at any instant in time, these six numbers, we know everything there is to know about the state of particle i.

The particles in our system have a finite kinetic energy and are therefore in constant motion, driven by the forces they exert on each other (and any external forces which may be present). At a given instant in time t, the Cartesian positions of the particles are $\mathbf{r}_1(t), \ldots, \mathbf{r}_N(t)$, and the velocities at t are related to the positions by differentiation:

$$\mathbf{v}_i(t) = \frac{d\mathbf{r}_i}{dt} = \dot{\mathbf{r}}_i \tag{26.1.1}$$

In order to determine the positions and velocities as function of time, we need the classical laws of motion, particularly, Newton's second law. Newton's second law states that the particles move under the action of the forces the particles exert on each other and under any forces present due to external fields. Let these forces be denoted $\mathbf{F}_1, \mathbf{F}_2, \ldots, \mathbf{F}_N$. Note that these forces are functions of the particle positions:

$$\mathbf{F}_i = \mathbf{F}_i(\mathbf{r}_1, \ldots, \mathbf{r}_N) \tag{26.1.2}$$

which is known as a force field (because it is a function of positions). Given these forces, the time evolution of the positions of the particles is then given by Newton's second law of motion:

$$m_i \ddot{\mathbf{r}}_i = \mathbf{F}_i(\mathbf{r}_1, \ldots, \mathbf{r}_N)$$

where $\mathbf{F}_1, \ldots, \mathbf{F}_N$ are the forces on each of the N particles due to all the other particles in the system. The notation $\ddot{\mathbf{r}}_i = d^2\mathbf{r}_i/dt^2$.

N Newton's equations of motion constitute a set of $3N$ coupled second order differential equations. In order to solve these, it is necessary to specify a set of appropriate initial conditions on the coordinates and their first time derivatives, $\{\mathbf{r}_1(0), \ldots, \mathbf{r}_N(0), \dot{\mathbf{r}}_1(0), \ldots, \dot{\mathbf{r}}_N(0)\}$. Then, the solution of Newton's equations gives the complete set of coordinates and velocities for all time t.

The Ensemble Concept (Heuristic Definition)

For a typical macroscopic system, the total number of particles is $N \sim 10^{23}$. Since an essentially infinite amount of precision is needed in order to specify the initial conditions (due to exponentially rapid growth of errors in this specification), the amount of information required to specify a trajectory is essentially infinite. Even if we content ourselves with quadrupole precision, however, the amount of memory needed to hold just one phase space point would be about 128 bytes $= 2^7 \sim 10^2$ bytes for each number or $10^2 \times 6 \times 10^{23} \sim 10^{17}$ gigabytes which is also 10^2 yottabytes! The largest computers we have today have perhaps 10^6 gigabytes of memory, so we are off by 11 orders of magnitude just to specify 1 classical state.

Fortunately, we do not need all of this detail. There are enormous numbers of microscopic states that give rise to the same macroscopic observable. Let us again return to the connection between temperature and kinetic energy:

$$\frac{3}{2}NkT = \sum_{i=1}^{N} \frac{1}{2} m_i \mathbf{v}_i^2 \tag{26.1.3}$$

which can be solved to give:

$$T = \frac{2}{3k}\left(\frac{1}{N}\sum_{i=1}^{N}\frac{1}{2}m_i\mathbf{v}_i^2\right) \tag{26.1.4}$$

Here we see that T is related to the average kinetic energy of all of the particles. We can imagine many ways of choosing the particle velocities so that we obtain the same average. One is to take a set of velocities and simply assign them in different ways to the N particles, which can be done in $N!$ ways. Apart from this, there will be many different choices of the velocities, themselves, all of which give the same average.

Since, from the point of view of macroscopic properties, precise microscopic details are largely unimportant, we might imagine employing a construct known as the *ensemble concept* in which a large number of systems with different microscopic characteristics but similar macroscopic characteristics is used to "wash out" the microscopic details via an averaging procedure. This is an idea developed by individuals such as Gibbs, Maxwell, and Boltzmann.

Consider a large number of systems each described by the same set of microscopic forces and sharing a common set of macroscopic thermodynamic variables (e.g. the same total energy, number of moles, and volume). Each system is assumed to evolve under the microscopic laws of motion from a different initial condition so that the time evolution of each system will be different from all the others. Such a collection of systems is called an *ensemble*. The ensemble concept then states that macroscopic observables can be calculated by performing averages over the systems in the ensemble. For many properties, such as temperature and pressure, which are time-independent, the fact that the systems are evolving in time will not affect their values, and we may perform averages at a particular instant in time.

The questions that naturally arise are:

1. How do we construct an ensemble?
2. How do we perform averages over an ensemble?
3. How do we determine which thermodynamic properties characterize an ensemble?
4. How many different types of ensembles can we construct, and what distinguishes them?

These questions will be addresses in the sections ahead.

Thermal energy

A confined monatomic gas can be seen as a box with a whole bunch of atoms in it. Each of these particles can be in one of the states given by the last formula. If all of them have large n values there is obviously a lot of kinetic energy in the system. The lowest energy is when all atoms have 1,1,1 as quantum numbers. Boltzmann realized that this should relate to temperature. When we add energy to the system (by heating it up without changing the volume of the box), the temperature goes up. At higher temperatures we would expect higher quantum numbers, and at lower T, lower ones. But how exactly are the atoms distributed over the various states?

This is a good example of a problem involving a discrete probability distribution. The probability that a certain level (e.g., $n = (n_1, n_2, n_3)$ with energy E_i) is occupied should be a function of temperature: $P_i(T)$. Boltzmann postulated that you could look at temperature as a form of energy. The thermal energy of a system is directly proportional to an absolute temperature.

$$E_{thermal} = kT$$

The proportionality constant k (or k_B) is named after him: the Boltzmann constant. It plays a central role in all statistical thermodynamics. The Boltzmann factor is used to approximate the fraction of particles in a large system. The Boltzmann factor is given by:

$$e^{-\beta E_i} \tag{26.1.5}$$

where:

- E_i is the energy in the state i,
- T is the kelvin temperature, and
- k is Boltzmann constant.

As the following section demonstrates, the term β in Equation 26.1.5 is expressed as:

$$\beta = \frac{1}{kT}$$

The rates of many physical processes are also determined by the Boltzmann factor. For a random particle, its thermal energy of a particle is a small multiple of the energy kT. An increase in temperature results in more particles crossing the energy barrier characteristic of activation processes. If this is to occur, particles need to carry sufficient energy. This energy is needed for the particles to successfully cross the energy barrier and is usually called activation energy. The fraction of molecules that have sufficient energy to escape the original material surface is approximately proportional to the Boltzmann factor.

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Problems

1. How are temperature and the average energy per particle for a system related?
2. What does the Boltzmann factor tell you? Why is it important?
3. When is it possible for particles to get extra energy?
4. Give three examples of activation processes.
5. What do "separate arrangements" mean? What are the differences between these arrangements?

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26.2: The Thermal Boltzman Distribution

Consider a N-particle ensemble. The particles are not necessarily indistinguishable and possibly have mutual potential energy. Since this is a large system, there are many different ways to arrange its particles and yet yield the same thermodynamic state. Only one arrangement can occur at a time. The sum of the probabilities of each separate arrangement equals the total number of separate arrangements. Then the probability of a system is:

$$p_N = W_N p_i$$

where p_N is the probability of the system, W_N is the total number of different possible arrangements of the N particles in the system, and p_i is the probability of each separate arrangement. Heisenberg's uncertainty principle states that it is impossible to simultaneously know the momentum and the position of an object with complete precision. In agreement with the uncertainty principle, the total possible number of combinations can be defined as the total number of distinguishable rearrangements of the N particles.

The most practical ensemble is the canonical ensemble with N, V, and T fixed. We can imagine a collection of boxes with equal volumes and number of particles with the entire collection kept in thermal equilibrium. Based on the Boltzmann factor, we know that for a system that has states with energies e_1, e_2, e_3..., the probability p_j that the system will be in the state j with energy E_j is exponentially proportional to the energy of state j. The partition functions of the state places a very important role in calculating the properties of a system, for example, it can be used to calculate the probability, as well as the energy, heat capacity, and pressure.

The Boltzmann Distribution

We are ultimately interested in the probability that a given distribution will occur. The reason for this is that we must have this information in order to obtain useful thermodynamic averages. Let's consider an ensemble of A systems. We will define a_j as the number of systems in the ensemble that are in the quantum state j. For example, a_1 represents the number of systems in the quantum state 1. The total number of possible microstates is:

$$W(a_1, a_2, ...) = \frac{A!}{a_1! a_2! ...}$$

The overall probability that P_j that a system is in the jth quantum state is obtained by averaging a_j/A over all the allowed distributions. Thus, P_j is given by:

$$\begin{aligned} P_j &= \frac{\langle a_j \rangle}{A} \\ &= \frac{1}{A} \frac{\sum_a W(a) a_j(a)}{\sum_a W(a)} \end{aligned}$$

where the angle brackets indicate an ensemble average. Using this definition we can calculate any average property (i.e. any thermodynamic property):

$$\langle M \rangle = \sum_j M_j P_j \tag{26.2.1}$$

The method of the most probable distribution is based on the idea that the average over P_j is **identical** to the most probable distribution. Physically, this results from the fact that we have so many particles in a typical system that the fluctuations from the mean are extremely (immeasurably) small. The equivalence of the average probability of an occupation number and the most probable distribution is expressed as follows:

$$P_j = \frac{\langle a_j \rangle}{A} = \frac{a_j}{A}$$

The probability function is subject to the following constraints:

- Constraint 1: Conservation of energy requires:

$$E_{total} = \sum_j a_j e_j \tag{26.2.2}$$

  where e_j is the energy of the jth quantum state.
- Constraint 2: Conservation of mass requires:

$$A = \sum_j a_j \tag{26.2.3}$$

  which says only that the total number of all of the systems in the ensemble is A.

As we will learn in later chapters, the system will tend towards the distribution of a_j that maximizes the total number of microstates. This can be expressed as:

$$\sum_j \left(\frac{\partial \ln W}{\partial a_j} \right) = 0$$

Our constraints becomes:

$$\sum_j e_j da_j = 0$$

$$\sum_j da_j = 0$$

The method of Lagrange multipliers (named after Joseph Louis Lagrange is a strategy for finding the local maxima and minima of a function subject to equality constraints. Using the method of LaGrange undetermined multipliers we have:

$$\sum_j \left[\left(\frac{\partial \ln W}{\partial a_j} \right) da_j + \alpha da_j - \beta e_j da_j \right] = 0$$

We can use Stirling's approximation:

$$\ln x! \approx x \ln x – x$$

to evaluate:

$$\left(\frac{\partial \ln W}{\partial a_j} \right)$$

to get:

$$\left(\frac{\partial A!}{\partial a_j} \right) - \sum_i \left(\frac{\partial \ln a_i}{\partial a_j} \right) = 0$$

as outlined below.

Application of Stirling's Approximation

First step is to note that:

$$\ln W = \ln A! - \sum_j \ln a_j ! a \approx A \ln A – A - \sum_j a_j \ln a_j - \sum_j a_j$$

Since (from Equation 26.2.3):

$$A = \sum_j a_j$$

these two cancel to give:

$$\ln W = A \ln A - \sum_j a_j \ln a_j$$

The derivative is:

$$\left(\frac{\partial \ln W}{\partial a_j} \right) = \frac{\partial A \ln A}{\partial a_j} - \sum_i \frac{\partial a_i \ln a_i}{\partial a_j}$$

Therefore we have:

$$\left(\frac{\partial A \ln A}{\partial a_j} \right) = \frac{\partial A}{\partial a_j} \ln A - \frac{\partial A}{\partial a_j} = \ln A - 1$$

$$\left(\frac{\partial a_i \ln a_i}{\partial a_j} \right) = \frac{\partial a_i}{\partial a_j} \ln a_i - \frac{\partial a_i}{\partial a_j} = \ln a_j + 1$$

These latter derivatives result from the fact that:

$$\left(\frac{\partial a_i}{\partial a_i} \right) = 1$$

$$\left(\frac{\partial a_j}{\partial a_i} \right) = 0$$

The simple expression that results from these manipulations is:

$$- \ln \left(\frac{a_j}{A} \right) + \alpha - \beta e_j = 0$$

The most probable distribution is:

$$\frac{a_j}{A} = e^a \sum_j e^{-\beta e_j} \tag{26.2.4}$$

Now we need to find the undetermined multipliers α and β.

The left hand side of Equation 26.2.4 is 1. Thus, we have:

$$P_j = \frac{a_j}{A} = \frac{e^{-\beta e_j}}{\sum_j e^{-\beta e_j}}$$

This determines a and defines the Boltzmann distribution. We will show that β from the optimization procedure of method of Lagrange multipliers is:

$$\beta = \frac{1}{kT}$$

This identification will show the importance of temperature in the Boltzmann distribution. The distribution represents a thermally equilibrated most probable distribution over all energy levels (Figure 17.2.1).

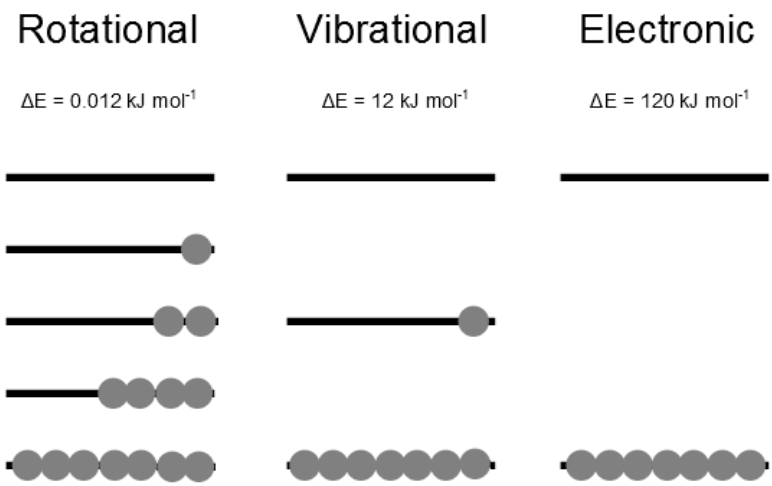


Figure 17.2.1 : At lower temperatures, the lower energy states are more greatly populated. At higher temperatures, there are more higher energy states populated, but each is populated less. $k_BT\ 2.5\ \ kJ\ \ mol^{-1}$ at 300 K. (CC SA-BY 3.0; Mysterioso via Wikiversity).

Boltzmann Distribution

The Boltzmann distribution represents a thermally equilibrated **most probable** distribution over all energy levels. There is always a **higher** population in a state of lower energy than in one of higher energy.

Once we know the probability distribution for energy, we can calculate thermodynamic properties like the energy, entropy, free energies and heat capacities, which are all average quantities (Equation 26.2.1). To calculate P_j, we need the energy levels of a system (i.e., $\{e_i\}$). The energy ("levels") of a system can be built up from the quantum energy levels

> It must always be remembered that no matter how large the energy spacing is, there is always a non-zero probability of the upper level being populated. The only exception is a system that is at absolute zero. This situation is however hypothetical as absolute zero can be approached but not reached.

Partition Function

The sum over all factors $e^{-\beta e_j}$ is given a name. It is called the molecular partition function, q:

$$q = \sum_j e^{-\beta e_j}$$

The molecular partition function q gives an indication of the average number of states that are thermally accessible to a molecule at the temperature of the system. The partition function is a sum over states (of course with the Boltzmann factor β multiplying the energy in the exponent) and is a number. Larger the value of q, larger the number of states which are available for the molecular system to occupy (Figure 17.2.2).

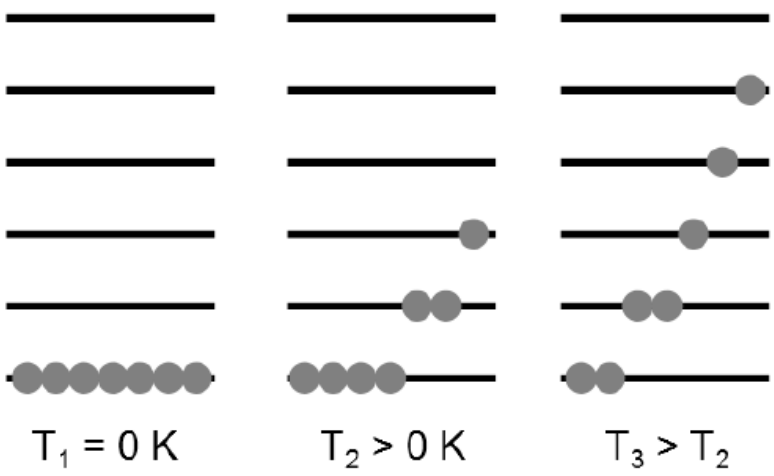


Figure 17.2.2 : At lower temperatures, the lower energy states are more greatly populated. At higher temperatures, there are more higher energy states populated, but each is populated less. (CC SA-BY 3.0; Mysterioso via Wikiversity).

We distinguish here between the partition function of the ensemble, Q and that of an individual molecule, q. Since Q represents a sum over all states accessible to the system it can written as:

$$Q(N,V,T) = \sum_{i,j,k...} e^{-\beta(e_i+e_j+e_k...)}$$

where the indices $i,\ j,\ k$ represent energy levels of **different** particles.

Regardless of the type of particle the molecular partition function, q represents the energy levels of one individual molecule. We can rewrite the above sum as:

$$Q = q_i q_j q_k \ldots$$

or:

$$Q = q^N$$

for N particles. Note that q_i means a sum over states or energy levels accessible to molecule i and q_j means the same for molecule j. The molecular partition function, q counts the energy levels accessible to molecule i only. Q counts not only the states of all of the molecules, but all of the possible combinations of occupations of those states. However, if the particles are not distinguishable then we will have counted $N!$ states too many. The factor of $N!$ is exactly how many times we can swap the indices in $Q(N,V,T)$ and get the same value (again provided that the particles are not distinguishable). See this video for more information.

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Problems

1. Complete the justification of Boltzmann's distribution law by computing the proportionality constant a.
2. A system contains two energy levels E_1, E_2. Using Boltzmann statistics, express the average energy of the system in terms of

E_1, E_2.

3. Consider a system contains N energy levels. Redo problem #2.
4. Use the property of exponential function, derive equation (17.9).
5. What are the uses of partition functions?

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26.3: We Postulate That the Average Ensemble Energy Is Equal to the Observed Energy of a System

We will be restricting ourselves to the canonical ensemble (constant temperature and constant pressure). Consider a collection of N molecules. The probability of finding a molecule with energy E_i is equal to the fraction of the molecules with energy E_i. That is, in a collection of N molecules, the probability of the molecules having energy E_i:

$$P_i = \frac{n_i}{N}$$

This is the directly obtained from the Boltzmann distribution, where the fraction of molecules n_i/N having energy E_i is:

$$P_i = \frac{n_i}{N} = \frac{e^{-E_i/kT}}{Q} \tag{26.3.1}$$

The average energy is obtained by multiplying E_i with its probability and summing over all i:

$$\langle E \rangle = \sum_i E_i P_i \tag{26.3.2}$$

> Equation 26.3.2 is the standard average over a distribution commonly found in quantum mechanics as expectation values. The quantum mechanical version of this Equation is
>
> $$\langle \psi | \hat{H} | \psi \rangle$$
>
> where Ψ^2 is the distribution function that the Hamiltonian operator (e.g., energy) is averaged over; this equation is also the starting point in the Variational method approximation.

Equation 26.3.2 can be solved by plugging in the Boltzmann distribution (Equation 26.3.1):

$$\langle E \rangle = \sum_i \frac{E_i e^{-E_i/kT}}{Q} \tag{26.3.3}$$

Where Q is the partition function:

$$Q = \sum_i e^{-\frac{E_i}{kT}}$$

We can take the derivative of $\ln Q$ with respect to temperature, T:

$$\left(\frac{\partial \ln Q}{\partial T}\right) = \frac{1}{kT^2} \sum_i \frac{E_i e^{-E_i/kT}}{Q} \tag{26.3.4}$$

Comparing Equation 26.3.3 with 26.3.4, we obtain:

$$\langle E \rangle = kT^2 \left(\frac{\partial \ln Q}{\partial T}\right)$$

It is common to write these equations in terms of β, where:

$$\beta = \frac{1}{kT}$$

The partition function becomes:

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

We can take the derivative of $\ln Q$ with respect to β:

$$\left(\frac{\partial \ln Q}{\partial \beta}\right) = -\sum_i \frac{E_i e^{-\beta E_i}}{Q}$$

And obtain:

$$\langle E \rangle = -\left(\frac{\partial \ln Q}{\partial \beta}\right)$$

Replacing $1/kT$ with β often simplifies the math and is easier to use.

> It is not uncommon to find the notation changes: Z instead of Q and $\bar{E}$ instead of $\langle E \rangle$.

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26.4: The Heat Capacity at Constant Volume

The heat capacity at constant volume (C_V) is defined to be the change in internal energy with respect to temperature:

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{N,V} \tag{26.4.1}$$

Since:

$$E = -\frac{\partial \ln Q(N,V,\beta)}{\partial \beta} \tag{26.4.2}$$

We see that:

$$\begin{aligned} C_V &= \frac{\partial U}{\partial T} \\ &= \frac{\partial U}{\partial \beta}\frac{\partial \beta}{\partial T} \\ &= \frac{1}{kT^2}\frac{\partial^2}{\partial \beta^2}\ln Q(N,V,\beta) \\ &= k\beta^2\frac{\partial^2}{\partial \beta^2}\ln Q(N,V,\beta) \end{aligned} \tag{26.4.3}$$

where k is the Boltzmann constant. Energy can be stored in materials/gases via populating the specific degrees of freedom that exist in the sample. Understanding how this occurs requires the usage of Quantum Mechanics.

Dulong-Petit Law on the Heat Capacities of Solids

Pierre Louis Dulong and Alexis Thèrèse Petit conducted experiments in 1819 on three dimensional solid crystals to determine the heat capacities of a variety of these solids (Heat capacity is the solids ability to absorb and retain heat). Dulong and Petit discovered that all investigated solids had a heat capacity of approximately 2.49 x 10^4 J kilomole^{-1} K^{-1} at around 298 K or room temperature. The result from their experiment was explained by considering every atom inside the solid as an oscillator with six degrees of freedom (an oscillator can be thought of as a spring connecting all the atoms in the solid lattice). These springs extend into three dimensional space. The more energy that is added to the solid the more these springs vibrate. Each atom has an energy of $\frac{1}{2}kT$, where k is the Boltzmann constant and T is the absolute temperature. Thus,

$$C_V = \frac{6R}{2} = 3R \qquad \text{(Dulong-Petit Law)}$$

The number 6 in this equation is the number of degrees of freedom for the molecule. Petit and Dulong suggested that these results supported their foundation for the heat capacity of solids. The explanation for Petit and Dulong's experiment was not sufficient when it was discovered that heat capacity decreased as temperature approached absolute zero. The degrees of freedom do not slow down or cease to move when the solid reaches a sufficiently cold temperature. An additional model was proposed to explain this deviance. Two main theories were developed to explain this puzzling deviance in the heat capacity experiments. The first was constructed by Einstein and the second was authored by Debye.

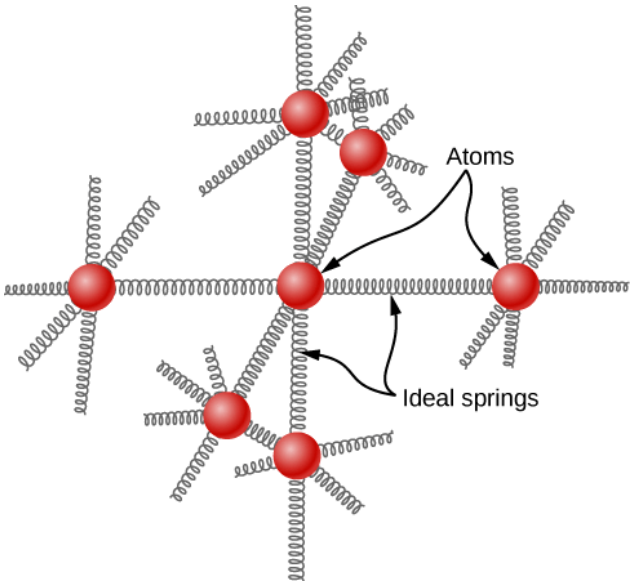


Figure 17.4.1 : In a simple model of a solid element, each atom is attached to others by six springs, two for each possible motion: x, y, and z. Each of the three motions corresponds to two degrees of freedom, one for kinetic energy and one for potential energy. (CC BY-SA 4.0; OpenStax).

Einstein's Theory on the Heat Capacities of Solids

Einstein assumed three things when he investigated the heat capacity of solids. First, he assumed that each solid was composed of a lattice structure consisting of N atoms. Each atom was treated as moving independently in three dimensions within the lattice (3 degrees of freedom). This meant that the entire lattice's vibrational motion could be described by a total of $3N$ motions, or degrees of freedom. Secondly, he assumed that the atoms inside the solid lattice did not interact with each other and thirdly, all of the atoms inside the solid vibrated at the same frequency. The third point highlights the main difference in Einstein's and Debye's two models.

Einstein's first point is accurate because the experimental data supported his hypothesis, however his second point is not because if atoms inside a solid could not interact, sound could not propagate through it. For example, a tuning fork's atoms, when struck, interact with one another to create sound which travels through air to the listener's ear. Atoms also interact in a solid when they are heated. Take for example a frying pan. If the pan is heated on one side, the heat transfers throughout the metal effectively warming the entire pan. Molecules that make up the frying pan interact to transfer heat. Much in the same way the oscillators in a solid interact when energy is added to the system. The extent of these interactions lead to the physically observed heat capacity.

The heat capacity of a solid at a constant volume is

$$\begin{aligned} C_V &= \left(\frac{\partial U}{\partial T}\right)_V \\ &= 3Nk\left(\frac{\theta_E}{T}\right)^2 \\ &= \frac{\exp\left(\frac{\theta_E}{T}\right)}{\left(\exp\frac{\theta_E}{T}-1\right)^2} \end{aligned}$$

where

- $\theta_E = \frac{h\nu}{k}$ is the **Einstein temperature**,
- h is Planck's constant,
- k is Boltzmann's constant, and
- ν is the oscillator frequency of the atoms inside the solid.

The Einstein temperature's accessibility of the vibrational energy inside of a solid molecule determines the heat capacity of that solid. The greater the accessibility the greater the heat capacity. If the vibrational energy is easily accessible the collisions in the molecule have a greater probability of exciting the atom into an upper vibrational level. This is displayed below.

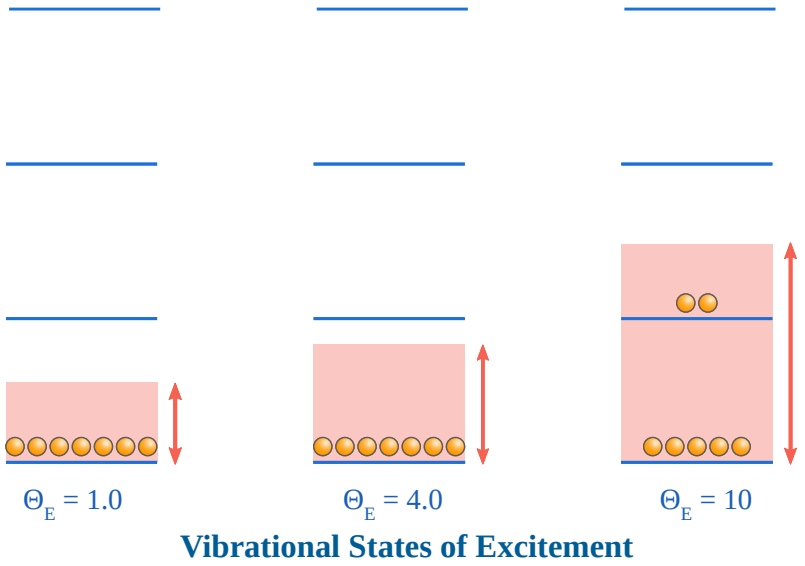


Figure 17.4.2 : This Figure illustrates the effect of the Einstein temperature on the likelihood of an oscillator absorbing energy from a collision and transferring that energy into stored heat or heat capacity. As the Einstein temperature increases, the greater the probability of an oscillator being excited to the next vibrational state. (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

So the Einstein temperature specifically indicates the probability that a molecule has in its degrees of freedom to store energy in its atomic oscillators (or bonds). Comparing the Einstein temperature to the traditional classical values of Heat capacity will illustrate the differences the specific strengths (high temperature) and weaknesses (low temperature) of the Einstein model.

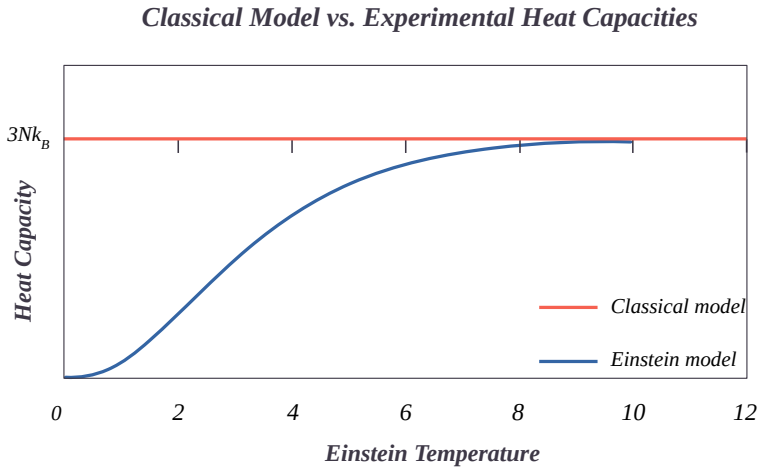


Figure 17.4.3 :This graph shows the accuracy of the of the Einstein temperature at low temperatures. The classical model is effective at temperatures above 10 Einstein Temperatures. (Cc BY-NC; Ümit Kaya via LibreTexts)

Thus, in the high temperature limit ($\frac{\theta_E}{T} \ll 1$) (i.e., the temperature is very large compared to the Einstein temperature) then

$$C_V \approx 3Nk = 3nR. \tag{26.4.4}$$

Einstein's model reveals the accuracy of the Petit and Dulong model and models high temperatures accurately. However, just as Petit and Dulong's model decreased in accuracy as the temperature decreased, so followed Einstein's.

When examining the extremely low temperature limit: $\frac{\theta_E}{T} \gg 1$, it can be seen:

$$C_V = 3Nk\left(\frac{\theta_E}{T}\right)^2 e^{\frac{-\theta_E}{T}} \tag{26.4.5}$$

As temperature (T) goes to zero, the exponential portion of the above equation goes to zero and therefore C_V also approaches zero. This supports the experimental values as temperature approaches zero the heat capacity of the solid likewise decreases to zero.

Einstein's theory also explains solids that exhibit a low heat capacity even at relatively high temperatures. An example of such a solid is diamond. The heat capacity of diamond approaches $3Nk$ as temperature greatly increases. Einstein's model supports this through the definition of an Einstein temperature. As the Einstein temperature increases, ν must increase likewise. This is the equivalent of each atom possessing more energy and therefore vibrating more rapidly within the solid itself. The oscillator frequency, ν, can be written as:

$$\nu = \frac{1}{2\pi}\sqrt{\frac{\kappa}{\mu}} \tag{26.4.6}$$

where κ is the force constant and μ is the reduced mass. This formula better predicts solids with high force constants or low reduced masses. This corrects deviations from the Petit and Dulong model.

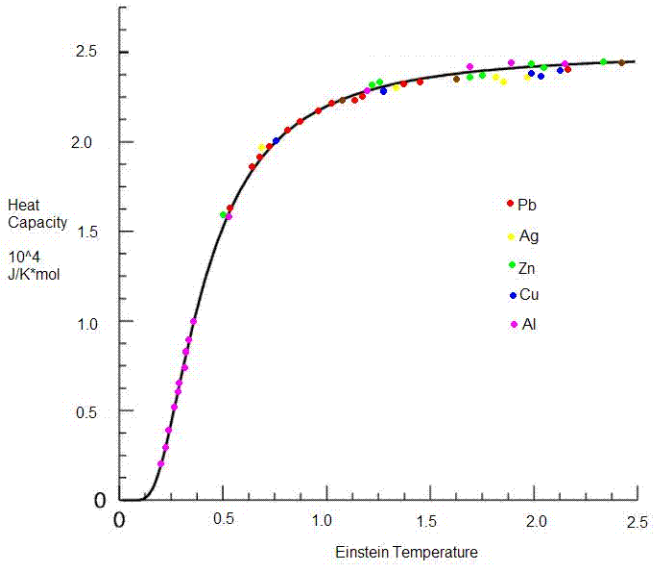


Figure 17.4.4 . This graph indicates the heat capacity of several solid metals as a function of the Einstein temperature: $\theta_E = \frac{hv}{k_B}$.

Essentially the Einstein temperature allows for the heat capacity equation and the vibrational frequencies in the solid to change as the temperature changes. This effectively adjusts for the deviations seen in the Petit/Dulong model. As the temperature increases or decreases, the Einstein temperature increases or decreases likewise to mirror the actual physical activity within the solid.

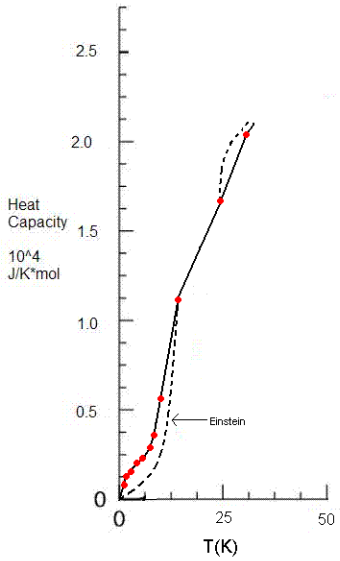


Figure 17.4.5 . This plot shows the heat capacity of lead compared to the expected values calculated from Einstein's model.

Einstein's model predicts relatively low temperatures well. However, when decreasing from approximately 15 K, Einstein's model deviates from experimental values. Also, this can be observed, although not as dramatically, for temperatures from 25 K to 30 K. Clearly a term or correction is still missing from Einstein's model to increase its accuracy.

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26.5: Express the Pressure in Terms of a Partition Function

Pressure can also be derived from the canonical partition function. The average pressure is the sum of the probability times the pressure:

$$\langle P \rangle = \sum_i P_i(N,V,T) P_i(N,V)$$

The pressure of a macroscopic system is:

$$P(N,V) = -\left(\frac{\partial E_i}{\partial V}\right)_N$$

So we can write the average pressure as:

$$\begin{aligned}\langle P \rangle &= \sum_i P_i(N,V,\beta)\left(-\frac{\partial E_i}{\partial V}\right)_N \\ &= \sum_i \left(-\frac{\partial E_i}{\partial V}\right)_N \frac{e^{-E_i(N,V)/kT}}{Q(N,V,T)}\end{aligned}$$

In a few steps we can show that the temperature can be expressed in terms of the partition function:

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

Writing in terms of β instead of temperature:

$$Q(N,V,\beta) = \sum_i e^{-\beta E_i(N,V)}$$

The derivative of the partition function with respect to volume is:

$$\left(\frac{\partial Q}{\partial V}\right)_{N,\beta} = -\beta \sum_i \left(\frac{\partial E_i}{\partial V}\right)_N e^{-\beta E_i(N,V)}$$

The average pressure can then be written as:

$$\langle P \rangle = \frac{kT}{Q(N,V,\beta)}\left(\frac{\partial Q}{\partial V}\right)_{N,\beta}$$

Which shows that the pressure can be expressed solely terms of the partition function:

$$\langle P \rangle = kT\left(\frac{\partial \ln Q}{\partial V}\right)_{N,\beta}$$

We can use this result to derive the ideal gas law. For N particles of an ideal gas:

$$Q(N,V,\beta) = \frac{[q(V,\beta)]^N}{N!}$$

where:

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

is the translational partition function. The utility of expressing the pressure as a logarithm is clear from the fact that we can write:

$$\begin{aligned}\ln Q &= N\ln q - \ln N! \\ &= -\frac{3N}{2}\ln\left(\frac{2\pi m}{h^2\beta}\right) + N\ln V - \ln N!\end{aligned}$$

We have used the property of logarithms that $\ln(AB) = \ln(A) + \ln(B)$ and $\ln(X^Y) = Y\ln(X)$. Only one term in the ln Q depends on V. Taking the derivative of $N\ln V$ with respect to V gives:

$$\left(\frac{\partial \ln Q}{\partial V}\right)_{N,\beta} = \frac{N}{V}$$

Substituting this into the above equation for the pressure gives:

$$P = \frac{NkT}{V}$$

which is the ideal gas law. Recall that $Nk = nR$ where N is the number of molecules and n is the number of moles. R is the universal gas constant (8.314 J/mol-K) which is nothing more than k multiplied by Avagadro's number. $N_A k = R$ converts the constant from a "per molecule" to a "per mole" basis.

Gas Compressed by a Piston

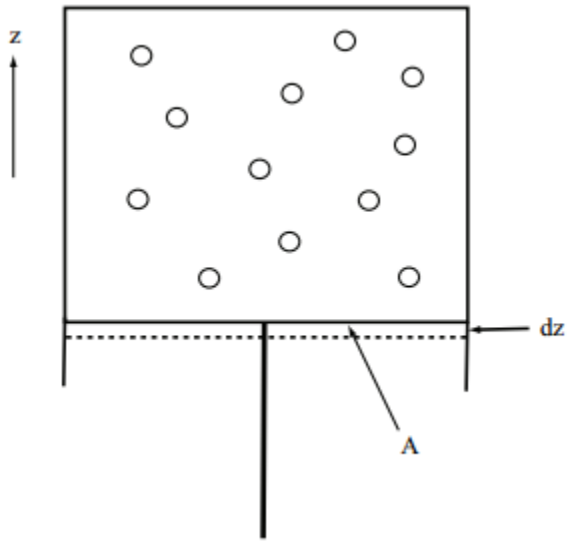


Figure 17.5.1 : Illustration of a thought experiment in which a system is compressed via a piston pushed into the system along the positive z axis.

Let us consider a simple thought experiment, which is illustrated in the figure above: A system of N particles is compressed by a piston pushing in the positive z direction. Since this is a classical thought experiment, we think in terms of forces. The piston exerts a constant force of magnitude F on the system. The direction of the force is purely in the positive z direction, so that we can write the force vector $\mathbf{F}$ as $\mathbf{F} = (0, 0, F)$. At equilibrium (the piston is not moving), the system exerts an equal and opposite force on the piston of the form $(0, 0, -F)$. If the energy of the system is E, then the force exerted by the system on the piston will be given by the negative change in E with respect to z:

$$-F = -\frac{dE}{dz} \tag{26.5.1}$$

or:

$$F = \frac{dE}{dz} \tag{26.5.2}$$

The force exerted by the system on the piston is manifest as an observable pressure P equal to the force F divided by the area A of the piston, $P = F/A$. Given this, the observed pressure is just:

$$P = \frac{dE}{Adz} \tag{26.5.3}$$

Since the volume decreases when the system is compressed, we see that $Adz = -dV$. Hence, we can write the pressure as $P = -dE/dV$.

Of course, the relation $P = -dE/dV$ is a thermodynamic one, but we need a function of x that we can average over the ensemble. The most natural choice is:

$$p(x) = -\frac{d\mathcal{E}(x)}{dV} \tag{26.5.4}$$

so that $P = \langle p(x) \rangle$. Setting up the average, we obtain:

$$P = -\frac{C_N}{Q(N,V,T)} \int \frac{\partial \mathcal{E}}{\partial V} e^{-\beta \mathcal{E}(x)} \tag{26.5.5}$$

$$= \frac{C_N}{Q(N,V,T)} \frac{1}{\beta} \int \frac{\partial}{\partial V} e^{-\beta \mathcal{E}(x)} \tag{26.5.6}$$

$$= \frac{kT}{Q(N,V,T} \frac{\partial}{\partial V} C_N \int e^{-\beta \mathcal{E}(x)} \tag{26.5.7}$$

$$= kT \left(\frac{\partial \ln Q(N,V,T)}{\partial V} \right) \tag{26.5.8}$$

Ideal Gas in the Canonical Ensemble

Recall that the mechanical energy for an ideal gas is:

$$\mathcal{E}(x) = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m} \tag{26.5.9}$$

where all particles are identical and have mass m. Thus, the expression for the canonical partition function $Q(N,V,T)$ is:

$$Q(N,V,T) = \frac{1}{N! h^{3N}} \int dx \, e^{-\beta \sum_{i=1}^{N} \mathbf{p}_i^2 / 2m}$$

Note that this can be expressed as:

$$Q(N,V,T) = \frac{1}{N! h^{3N}} V^N \left[\int dp \, e^{-\beta p^2 / 2m} \right]^{3N}$$

Evaluating the Gaussian integral gives us the final result immediately:

$$Q(N,V,T) = \frac{1}{N!} \left[\frac{V}{h^3} \left(\frac{2\pi m}{\beta} \right)^{3/2} \right]^N$$

The expressions for the energy:

$$E = -\frac{\partial}{\partial \beta} \ln Q(N,V,T)$$

which gives:

$$E = \frac{3}{2} NkT = \frac{3}{2} nRT \tag{26.5.10}$$

and pressure:

$$P = kT \left(\frac{\partial \ln Q(N,V,T)}{\partial V} \right)$$

giving:

$$P = \frac{NkT}{V} = \frac{nRT}{V} \tag{26.5.11}$$

which is the ideal gas law.

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26.6: Partition Functions of Systems of Distinguishable Molecules are Products of Molecular Partition Functions

A system, such as a container of gas, can consist of a large number of subsystems. How is the partition function of the system built up from those of the subsystems? This depends on whether the subsystems are distinguishable or indistinguishable. Let's start with energy. Energy is additive so that:

$$E_{\text{tot}}(N,V) = \epsilon_1(V) + \epsilon_2(V) + \epsilon_3(V) + \cdots$$

Each of the molecules can have their energy distributed over their respective energy states (e.g., vibrations, rotations, etc.). This means that each ϵ_i is already a summation over the states of the molecule. Let us assume that we can somehow distinguish all the molecules as: a, b, c, d... and denote the energy state they are in by i, j, k:

$$E_l(N,V) = \epsilon_i^a(V) + \epsilon_j^b(V) + \epsilon_k^c(V) + \cdots$$

A good example would be the molecules in a molecular crystal. They only move around a fixed site and so we can distinguish by how far molecule 'a' is from a given corner of the crystal. The systems partition function becomes:

$$Q(N,V,\beta) = \sum_i e^{-\beta E_l} = \sum_{i,j,k,\ldots} e^{-\beta(\epsilon_i^a + \epsilon_j^b + \epsilon_k^c)}$$

So far, we have done little effort to distinguish between the partition function of a molecular system q and the whole ensemble Q (e.g. the gas). If the entities that we called systems are **distinguishable** and independent, the whole ensemble partition function is the product of the molecular system partition functions. We get:

$$Q(N,V,\beta) = \prod_i q_i$$

for N distinguishable systems. We can split up the summation into a product of molecular partition functions:

$$Q(N,V,\beta) = \prod_i^N q_i(V,\beta) = q_a(V,\beta)q_b(V,\beta)q_c(V,\beta)\cdots$$

This results in each molecular system partition function being summed over independently:

$$Q(N,V,\beta) = \sum_i e^{-\beta\epsilon_i^a} \sum_j e^{-\beta\epsilon_i^b} \sum_k e^{-\beta\epsilon_i^c} \ldots$$

If the energy states of all the particles are the same, then the equation simplifies to:

$$Q(N,V,\beta) = [q(V,\beta)]^N$$

We can do this if, for example, the particles are embedded in a crystal where we can distinguish them by their location. We will see in the next chapter that for indistinguishable particles, such as those in a gas, we get a different result.

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26.7: Partition Function of Indistinguishable Components

In the previous section, the definition of the the partition function involves a sum of state formulism:

$$Q = \sum_i e^{-\beta E_i}. \tag{26.7.1}$$

However, under most conditions, full knowledge of each member of an ensemble is missing and hence we have to operate with a more reduced knowledge. This is demonstrated via a simple model of two particles in a two-energy level system in Figure 26.7.1 . Each particle (red or blue) can occupy either the $E_1 = 0$ energy level or the $E_2 = \epsilon$ energy level resulting in four possible states that describe the system. The corresponding partition function for this system is then (via Equation 26.7.1):

$$Q_{\text{distinguishable}} = e^0 + e^{-\beta\epsilon} + e^{-\beta\epsilon} + e^{-2\beta\epsilon} = q^2 \tag{26.7.2}$$

and is just the molecular partition function (q) squared.

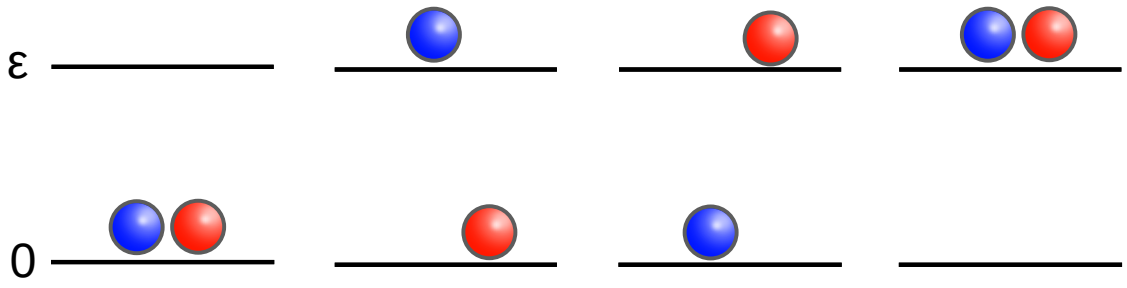


Figure 26.7.1: Four different states can exist for a two-level system with two distinguishable particles (red and blue balls). (CC BY 4.0; Delmar Larsen via LibreTexts)

However, if the two particles are indistinguishable (e.g., both the same color as in Figure 26.7.2) then while four different combinations can be generated like in Figure 26.7.1, there is no discernible way to separate the two middle states. Hence, there are effectively only three states observable for this system.

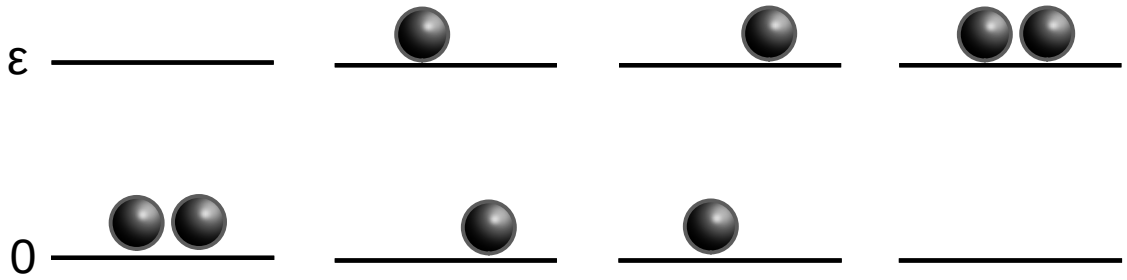


Figure 26.7.2: Three different states can exist for a two-level system with two indistinguishable particles (black balls). The two middle states are indescernable and represent a single state with one particle exited and the other in the ground state. (CC BY 4.0; Delmar Larsen via LibreTexts)

The corresponding partition function for this system (again using Equation 26.7.1) can be constructed:

$$Q(N, V, \beta) = e^0 + e^{-\beta\epsilon} + e^{-2\beta\epsilon} \neq q^2 \tag{26.7.3}$$

and this is not equal to the square of the molecular partition function. If Equation 26.7.2 were used to describe the indistinguishable particle case, then it would overestimate the number of observable states. From combinatorics, using q^N for a large N-particle system of indistinguishable particles will overestimate the number of states by a factor of $N!$. Therefore Equation 26.7.1 requires a slight modification to account for this over counting.

$$Q(N,V,\beta)=\frac{\sum_i e^{-\beta E_i}}{N!} \tag{26.7.4}$$

If we have N molecules, we can perform $N!$ permutations that should not affect the outcome. To avoid over counting (making sure we do not count each state more than once), the partition function becomes:

$$Q(N,V,\beta)=\frac{q(V,\beta)^N}{N!}$$

Note

As you may have noticed, using Equation 26.7.4 to estimate of Q for the two-indistinguishable particle discussed case above with $N=2$ is incorrect (i.e., Equation 26.7.4 is not equal to Equation 26.7.3). That is because the $N!$ factor is only applicable for large N.

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26.8: A Molecular Partition Function Can Be Decomposed into Partition Functions for Each Degree of Freedom

From the previous sections, the partition function for a system of N indistinguishable and independent molecules is:

$$Q(N,V,\beta) = \frac{\sum_i e^{-\beta E_i}}{N!} \tag{26.8.1}$$

And the average energy of the system is:

$$\langle E \rangle = kT^2 \left(\frac{\partial \ln Q}{\partial T} \right) \tag{26.8.2}$$

We can combine these two equations to obtain:

$$\begin{aligned} \langle E \rangle &= kT^2 \left(\frac{\partial \ln Q}{\partial T} \right)_{N,V} \\ &= NkT^2 \left(\frac{\partial \ln q}{\partial T} \right)_V \\ &= N \sum_i \epsilon_i \frac{e^{-\epsilon_i/kT}}{q(V,T)} \end{aligned} \tag{26.8.3}$$

The average energy is equal to:

$$\langle E \rangle = N \langle \epsilon \rangle \tag{26.8.4}$$

where $\langle \epsilon \rangle$ is the average energy of a single particle. If we compare Equation 26.8.2 with Equation 26.8.2, we can see:

$$\langle \epsilon \rangle = \sum_i \epsilon_i \frac{e^{-\epsilon_i/kT}}{q(V,T)}$$

The probability that a particle is in state i, π_i, is given by:

$$\langle \epsilon \rangle = \frac{e^{-\epsilon_i/kT}}{q(V,T)} = \frac{e^{-\epsilon_i/kT}}{\sum_i e^{-\epsilon_i/kT}}$$

The energy of a particle is a sum of the energy of each degree of freedom for that particle. In the case of a molecule, the energy is:

$$\epsilon = \epsilon_{\text{trans}} + \epsilon_{\text{rot}} + \epsilon_{\text{vib}} + \epsilon_{\text{elec}}$$

The molecular partition function is the product of the degree of freedom partition functions:

$$q(V,T) = q_{\text{trans}} q_{\text{rot}} q_{\text{vib}} q_{\text{elec}}$$

The partition function for each degree of freedom follows the same is related to the Boltzmann distribution. For example, the vibrational partition function is:

$$q_{\text{vib}} = \sum_i e^{-\epsilon_i/kT}$$

The average energy of each degree of freedom follows the same pattern as before. For example, the average vibrational energy is:

$$\langle \epsilon_{\text{vib}} \rangle = kT^2 \frac{\partial \ln q_{\text{vib}}}{\partial t} = -\frac{\partial \ln q_{\text{vib}}}{\partial \beta}$$

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26.E: Exercises

In the mid 1920's the German physicist Werner Heisenberg showed that if we try to locate an electron within a region Δx; e.g. by scattering light from it, some momentum is transferred to the electron, and it is not possible to determine exactly how much momentum is transferred, even in principle. Heisenberg showed that consequently there is a relationship between the uncertainty in position Δx and the uncertainty in momentum Δp.

$$\Delta p \Delta x \geq \frac{\hbar}{2} \tag{26.E.1}$$

You can see from Equation 26.E.1 that as Δp approaches 0, Δx must approach ∞, which is the case of the free particle discussed previously.

This uncertainty principle, which also is discussed in Chapter 4, is a consequence of the wave property of matter. A wave has some finite extent in space and generally is not localized at a point. Consequently there usually is significant uncertainty in the position of a quantum particle in space. Activity 1 at the end of this chapter illustrates that a reduction in the spatial extent of a wavefunction to reduce the uncertainty in the position of a particle increases the uncertainty in the momentum of the particle. This illustration is based on the ideas described in the next section.

Exercise $26.E.1$

Compare the minimum uncertainty in the positions of a baseball (mass = 140 gm) and an electron, each with a speed of 91.3 miles per hour, which is characteristic of a reasonable fastball, if the standard deviation in the measurement of the speed is 0.1 mile per hour. Also compare the wavelengths associated with these two particles. Identify the insights that you gain from these comparisons.

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27: PARTITION FUNCTIONS AND IDEAL GASES

UC Davis Chemistry Chemistry 110B

Physical Chemistry II: Properties of Atoms and Molecules

Chem 110A ● Chem 110B ● Chem 110C ● **Agenda** ● **Homework** ● **Worksheet Activities**

In chemistry, we are typically concerned with a collection of molecules. However, if the molecules are reasonably far apart as in the case of a dilute gas, we can approximately treat the system as an ideal gas system and ignore the intermolecular forces. The present chapter deals with systems in which intermolecular interactions are ignored. In ensemble theory, we are concerned with the ensemble probability density, i.e., the fraction of members of the ensemble possessing certain characteristics such as a total energy E, volume V, number of particles N or a given chemical potential μ and so on. The molecular partition function enables us to calculate the probability of finding a collection of molecules with a given energy in a system. The equivalence of the ensemble approach and a molecular approach may be easily realized if we treat part of the molecular system to be in equilibrium with the rest of it and consider the probability distribution of molecules in this subsystem (which is actually quite large compared to systems containing a small number of molecules of the order of tens or hundreds).

27.1: The Translational Partition Function of a Monatomic Ideal Gas

27.2: Most Atoms Are in the Ground Electronic State at Room Temperature

27.3: The Energy of a Diatomic Molecule Can Be Approximated as a Sum of Separate Terms

27.4: Most Molecules Are in the Ground Vibrational State at Room Temperature

27.5: Most Molecules Are in Excited Rotational States at Ordinary Temperatures

27.6: Rotational Partition Functions Contain a Symmetry Number

27.7: The Vibrational Partition Function

27.8: The Rotational Partition Function Depends on the Shape of the Molecule

27.9: Molar Heat Capacities

27.E: Partition Functions and Ideal Gases (Exercises)

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27.1: The Translational Partition Function of a Monatomic Ideal Gas

Let us consider the translational partition function of a monatomic gas particle confined to a cubic box of length L. The particle inside the box has translational energy levels given by:

$$E_{\text{trans}} = \frac{h^2\left(n_x^2 + n_y^2 + n_z^2\right)}{8mL^2}$$

where n_x, n_y and n_z are the quantum numbers in the three directions. The translational partition function is given by:

$$q_{\text{trans}} = \sum_i e^{-\epsilon_i/kT}$$

which is the product of translational partition functions in the three dimensions. We can write the translation partition function as the product of the translation partition function for each direction:

$$q_{\text{trans}} = q_x q_y q_z \tag{27.1.1}$$

$$= \sum_{n_x=1}^{\infty} e^{-\epsilon_x/kT} \sum_{n_y=1}^{\infty} e^{-\epsilon_y/kT} \sum_{n_z=1}^{\infty} e^{-\epsilon_z/kT} \tag{27.1.2}$$

Since the levels are very closely spaced (continuous), we can replace each sum in Equation 27.1.2 with an integral. For example:

$$q_x = \sum_{n_x=1}^{\infty} e^{-\epsilon_x/kT} \tag{27.1.3}$$

$$\approx \int_{n_x=1}^{\infty} e^{-\epsilon_x/kT} \tag{27.1.4}$$

and after substituting the energy for the relevant dimension:

$$\epsilon_x = \frac{h^2 n_x^2}{8mL^2}$$

we can extend the lower limit of integration in the approximation of Equation 27.1.4:

$$q_x = \int_1^{\infty} e^{-\frac{h^2 n_x^2}{8mL^2 kT}} \approx \int_0^{\infty} e^{-\frac{h^2 n_x^2}{8mL^2 kT}}$$

We then use the following solved Gaussian integral:

$$\int_o^{\infty} e^{-an^2} dn = \sqrt{\frac{\pi}{4a}}$$

with the following substitution:

$$a = \frac{h^2}{8mL^2 kT}$$

we get:

$$q_x = \frac{1}{2}\sqrt{\frac{\pi}{a}} = \frac{1}{2}\sqrt{\frac{\pi 8mkT}{h^2}}L$$

or more commonly presented as:

$$q_x = \frac{L}{\Lambda}$$

where Λ is the **de Broglie wavelength** and is given by

$$\Lambda = \frac{h}{\sqrt{2\pi 8mkT}}$$

Multiplying the expressions for q_x, q_y and q_z (Equation 27.1.1) and using V as the volume of the box L^3, we arrive at:

$$q_{\text{trans}} = \left(\frac{\sqrt{2\pi 8mkT}}{h}\right)^{3/2} V = \frac{V}{\Lambda^3} \tag{27.1.5}$$

This is usually a very large number (10^{20}) for volumes of 1 cm^3 for small molecular masses. This means that such a large number of translational states are accessible and available for occupation by the molecules of a gas. This result is very similar to the result of the classical kinetic gas theory that said that the observed energy of an ideal gas is:

$$U = \frac{3}{2}nRT$$

We postulate therefore that the observed energy of a macroscopic system should equal the statistical average over the partition function as shown above. In other words: if you know the particles your system is composed of and their energy states you can use statistics to calculate what you should observe on the whole ensemble.

Example

Calculate the translational partition function of an I_2 molecule at 300K. Assume V to be 1 liter.

Solution

Mass of I_2 is $2 \times 127 \times 1.6606 \times 10^{-27} kg$

$$\begin{aligned} 2\pi mkT &= 2 \times 3.1415 \times (2 \times 127 \times 1.6606 \times 10^{-27}\, kg) \times 1.3807 \times 10^{-23}\, J/K \times 300K \\ &= 1.0969 \times 10^{-44}\, J\, kg \end{aligned}$$

$$\begin{aligned} \Lambda &= \frac{h}{\sqrt{2\pi mkT}} \\ &= \frac{6.6262 \times 10^{-34}\, J\, s}{\sqrt{1.0969 \times 10^{-44}\, J\, kg}} = 6.326 \times 10^{-12}\, m \end{aligned}$$

The via Equation 27.1.5

$$q_{\text{trans}} = \frac{V}{\Lambda^3} = \frac{1000 \times 10^{-6} m^3}{(6.326 \times 10^{-12}\, m)^3} = 3.95 \times 10^{30}$$

This means that 3.95×10^{30} quantum states are thermally accessible to the molecular system

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27.2: Most Atoms Are in the Ground Electronic State at Room Temperature

Writing the electronic energies as $E_1, E_2, E_3, ...$ with corresponding degeneracies $g_1, g_2, g_3, ...$ The electronic partition function is then given by the following summation:

$$q_{el}(T) = g_1 e^{-E_1/kT} + g_2 e^{-E_2/kT} + g_3 e^{-E_3/kT} + ... \tag{27.2.1}$$

Usually, the differences in electronic energies are significantly greater than thermal energy kT:

$$kT \ll E_1 < E_2 < E_3$$

If we treat the lowest energy electronic state E_1 as the reference value of zero of energy, the electronic partition function (Equation 27.2.1) can be approximated as:

$$q_{elec}(T) = g_1 + g_2 e^{-E_2/kT} + g_3 e^{-E_3/kT} + ... \tag{27.2.2}$$

Typically electronic states are tens of thousands of wave numbers above the ground state. For example, the first excited electronic state of nitric oxide (NO) is ~40,000 cm^{-1}. Using this value:

$$\frac{E_2}{kT} = \frac{40000 \text{ cm}^{-1}}{kT} = \frac{10^4 \text{ K}}{T}$$

That means, that even at 1,000 K, the value of the second term in {\reference{3.24}} is:

$$g_2 e^{-10} = g_2 4.5 \times 10^{-5}$$

The result is that the higher electronic states are not accessible under ordinary temperatures. There are some cases, however, where the first excited state lies much closer to the ground state, but these are the exception rather than the rule.

Example 18.2.1

Find the electronic partition of H_2 at 300 K.

Solution

The lowest electronic energy level of H_2 is near $-32\ eV$ and the next level is about $5\ eV$ higher. Taking -32 eV as the zero (or reference value of energy), then

$$q_{el} = e_0 + e^{-5eV/kT} + ...$$

At 300 K, T = 0.02\; eV and

$$q_{el} = 1 + e^{-200} + ...$$
$$\approx 1.0$$

Where all terms other than the first are essentially 0. This implies that $q_{el} = 1$.

The physical meaning of the result from Example 18.2.1 is that only the ground electronic state is generally thermally accessible at room temperature.

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27.3: The Energy of a Diatomic Molecule Can Be Approximated as a Sum of Separate Terms

A monatomic gas has three degrees of freedom per molecule, all of them translational:

1. movement in x-direction
2. movement in y-direction
3. movement in z-direction

A polyatomic gas, including diatomic molecules, has other levels that you can 'stuff' energy into. Polyatomic molecules can rotate and vibrate, and if enough energy is available you could also excite the electrons involved in the σ and π bonds. A reasonable approximation of the partition function of the molecule would become:

$$q_{\text{tot}}(V,T) = q_{\text{trans}} q_{\text{vib}} q_{\text{rot}} q_{\text{elec}}$$

The partition function of a molecular idea gas is then:

$$Q(N,V,T) = \frac{(q_{\text{trans}} q_{\text{vib}} q_{\text{rot}} q_{\text{elec}})^N}{N!}$$

The total energy of the molecule is then the sum of the translation, vibrational, rotational, and electronic energies:

$$E_{tot} = E_{\text{trans}} E_{\text{vib}} E_{\text{rot}} E_{\text{elec}}$$

We will only scratch the surface of the additional degrees of freedom and their partition functions.

Electronic

At room temperature the system is usually in its ground electronic state. This means that the **electronic partition function** $q_{\text{elec}} = 1$. Usually we do not have to worry about these degrees of freedom. If we do, there are usually just a few levels to worry about. This includes their **degeneracy g**. If there is a single state at a certain energy ($g = 1$), two states ($g = 2$), or more states, we must multiply the Boltzmann factor by this degeneracy number.

If there are more than one state to worry about, we could follow the same procedure as we did for the translational states:

1. Define the energy states and their degeneracies
2. Compose the partition function q for the molecule and Q for the gas
3. Use the (β or T) derivative of $\ln Q$ to determine $\langle E \rangle$
4. Use the T derivative of $U \approx \langle E \rangle$ to find the contribution to the heat capacity

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27.4: Most Molecules Are in the Ground Vibrational State at Room Temperature

The vibrational energy levels of a diatomic are given by:

$$E_v = (v + 1/2)h\nu$$

where is ν the vibrational frequency and v is the vibrational quantum number. In this case, it is easy to sum the geometric series shown below:

$$\begin{aligned} q_{\text{vib}} &= \sum_{v=0}^{\infty} e^{-(v+1/2)h\nu/kT} \\ &= e^{-h\nu/2kT}\left(1 + e^{-h\nu/kT} + e^{-2h\nu/kT} + ...\right) \end{aligned}$$

or rewritten as:

$$q_{\text{vib}} = e^{-h\nu/2kT}\left(1 + x + x^2 + x^3 + ...\right) \tag{27.4.1}$$

where $x = e^{-h\nu/kT}$. Given the following power series expansion:

$$\frac{1}{1-x} = 1 + x + x^2 + x^3 + x^4 + ...$$

Equation 27.4.1 can be rewritten as:

$$q_{\text{vib}} = e^{-h\nu/2kT}\left(\frac{1}{1-x}\right)$$

or:

$$q_{\text{vib}} = \frac{e^{-h\nu/2kT}}{1 - e^{-h\nu/kT}} \tag{27.4.2}$$

If the zero of energy scale is at $h\nu/2kT$, then Equation 27.4.2 can be rewritten as:

$$q_{\text{vib}} \approx \frac{1}{1 - e^{-h\nu/kT}} \tag{27.4.3}$$

A vibrational temperature Θ_{vib} may be defined as:

$$\Theta_{\text{vib}} = \frac{hc\tilde{\nu}}{k}$$

where $\tilde{\nu}$ is the vibrational frequency in cm^{-1}. Θ_{vib} is a good way to express the *stiffness* of the vibrating bond in units of the Boltzmann constant. Because the stiffness obviously depends on what bond your are talking about, this is a good way to do the same thing we did for the critical temperature of the non-ideal gases.

Table 27.4.1 : Representative molecular data for a few diatomics

Molecule	g	Bond Length (pm)	ω (cm^{-1})	Θ_{vib} (K)	$\tilde{B}$ (cm^{-1})	Θ_{rot} (K)	Force constant k (dynes/cm)	D_0 (kcal/ mol)
H_2	1	0.7474	4400	6332	60.9	87.6	5.749	103.2
D_2	1	0.7415	3118	4487	30.45	43.8	5.77	104.6
N_2	1	1.097	2358	3393	2.001	2.99	22.94	225.1
O_2	3	1.207	1580	2274	1.446	2.08	11.76	118.0

Molecule	g	Bond Length (pm)	ω (cm^{-1})	Θ_{vib} (K)	$\tilde{B}$ (cm^{-1})	Θ_{rot} (K)	Force constant k (dynes/cm)	D_0 (kcal/ mol)
Cl_2	1	1.987	560	805	0.244	0.351	3.2	57.0
CO	1	1.128	2170	3122	1.931	2.78	19.03	255.8
NO	2	1.15	190	2719	1.695	2.45	15.7	150.0
HCl	1	1.275	2938	4227	10.44	15.02	4.9	102.2
HI	1	1.609	2270	3266	6.46	9.06	3.0	70.5
Na_2	1	3.096	159	229	0.154	0.221	0.17	17.3
K_2	1	3.979	92.3	133	0.0561	0.081	0.10	11.8

Example 18.4.1

The vibrational frequency of of I_2 is $214.57\ \ cm^{-1}$. Calculate the vibrational partition function of I_2 at 300 K.

Solution:

$$\frac{h\nu}{kT} = \frac{214.57}{209.7} = 1.0232$$

so

$$e^{-h\nu/kT} = 0.3595$$

and

$$q_{vib} = \frac{1}{1-0.3595} = 1.561$$

This implies, as before, that very few vibrational states are accessible and much less than rotation states and many orders less than translation states.

Vibrational Heat Capacity

The vibrational energy is given by the above expression and the molar heat capacity at constant volume, $\bar{C}_V$ is given by:

$$\bar{C}_V = \left(\frac{\partial E}{\partial T}\right)_V$$

We have:

$$\frac{\partial}{\partial T} = \frac{\partial \beta}{\partial T}\frac{\partial}{\partial \beta} \tag{27.4.4}$$

$$= \frac{-1}{kT^2}\frac{\partial}{\partial \beta} \tag{27.4.5}$$

$$= (-k\beta^2)\left(\frac{\partial}{\partial \beta}\right) \tag{27.4.6}$$

Therefore:

$$\bar{C}_V = (-k\beta^2)\left(\frac{\partial \varepsilon_{vib}}{\partial \beta}\right)$$

and when the vibrational partition function (Equation 27.4.3) is introduced:

$$q_{\text{vib}} = -k\beta^2 \frac{\left[(1-e^{-hc\nu/kT})(-hc\tilde{\nu}) - e^{-hc\nu/kT}(+hc\tilde{\nu})\right] e^{-hc\nu/kT}}{(1-e^{-hc\nu/kT})^2} hv\tilde{\nu} \tag{27.4.7}$$

$$= k\left(\frac{\Theta_{\text{vib}}}{T}\right)^2 \frac{e^{-\Theta_{\text{vib}}/T}}{\left(1-e^{-\Theta_{\text{vib}}/T}\right)^2} \tag{27.4.8}$$

For large T, the $\bar{C}_V$ becomes:

$$N_A k = R$$

and for small T, $\bar{C}_V$ goes to zero as demonstrated in Figure 18.4.1 .

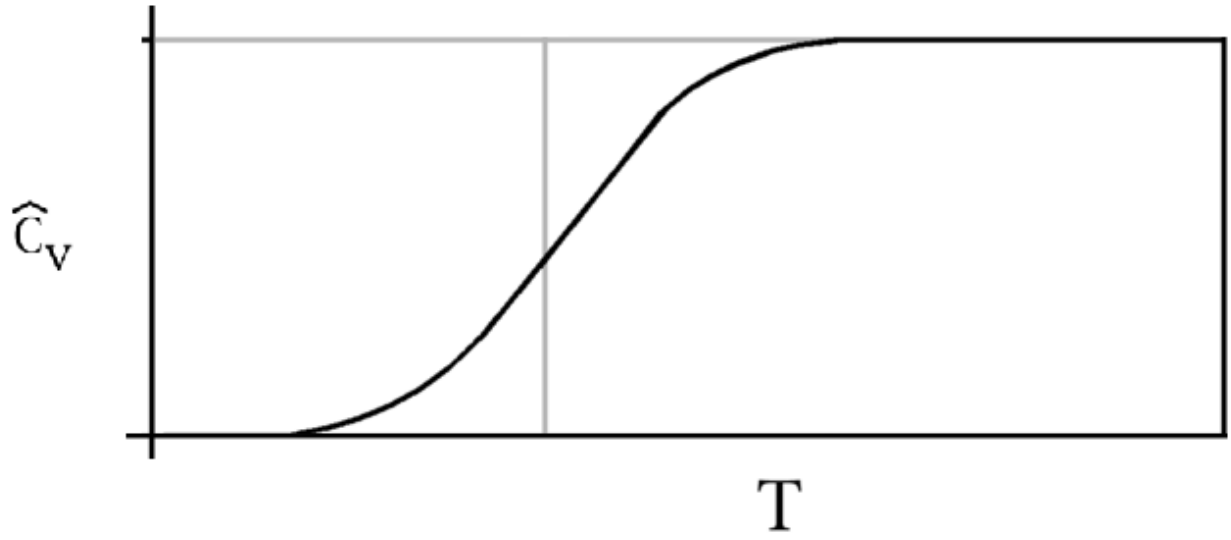


Figure 18.4.1 : Vibrational heat capacity of a diatomic

The vibrational heat capacity is shown as function of the reduced temperature T/Θ to get a general picture valid for all diatomic gases. Compare the parameters on Table 18.4.1 to see on what different absolute scales we have to think for different gases. Clearly the vibrational contribution to the heat capacity *depends on temperature*. For many molecules (especially light ones), the vibrational contribution only kicks in at quite high temperatures.

The value of Θ_{vib} is determined mostly by

1. the strength of a bond (the stronger the higher Θ_{vib})
2. the (effective) mass of the molecule (the lighter the higher Θ_{vib})

Molecules with low Θ_{vib} often dissociate at lower temperatures, although the *harmonic* oscillator model is not sufficient to describe that phenomenon.

Vibrational Populations

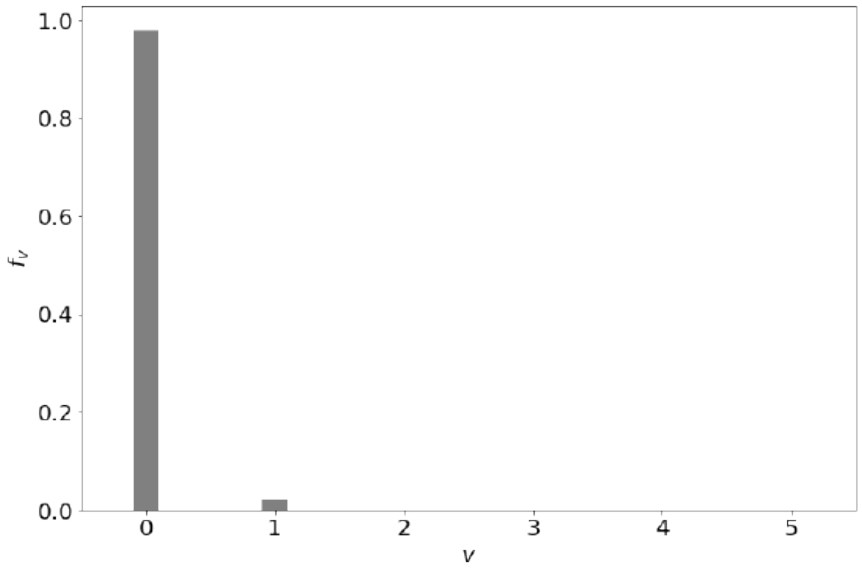
We can calculate the fraction of molecules in each vibrational state. The fraction of molecules in the vth vibrational state is given by:

$$f_v = \frac{e^{-h\nu(v+\frac{1}{2})/kT}}{q_{\text{vib}}}$$

Substituting in Equation 27.4.2, we get:

$$\begin{aligned} f_v &= \left(1-e^{-h\nu/kT}\right) e^{-h\nu v/kT} \\ &= \left(1-e^{-\Theta_{\text{vib}}/T}\right) e^{-\Theta_{\text{vib}} v/T} \end{aligned} \tag{27.4.9}$$

We can plot the fraction molecules in each vibrational state.



The vibrational population of Cl_2 at 300 K. Most of the molecules are in the ground vibrational state, $v = 0$.

From the figure, we can see that most of the Cl_2 molecules are in the ground vibrational state at room temperature (300 K). This is true for most molecules. Only molecules with very weak bonds and low vibrational temperatures will populate a significant fraction of molecules in excited vibrational states.

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27.5: Most Molecules Are in Excited Rotational States at Ordinary Temperatures

The rotational quantum number is J and the energy of the rotations is:

$$E(J) = \tilde{B}J(J+1)$$

Where $\tilde{B}$ is in units of cm^{-1} and is equivalent to:

$$\frac{h}{8\pi^2 Ic}$$

Where c is the speed of light in units of cm^{-1}. However, with the exception of the ground state (i.e., $J = 0$), multiple eigenstates exist for a given value of J. This is a form of **degeneracy**, (g), and the number of levels per energy goes as 1, 3, 5, 7, 9 etc or:

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

Therefore, the summation to find the partition function $q_{\text{rot}}(T)$ contains an extra factor $g = 2J + 1$. This factor is mathematically very handy, because it is the derivative of:

$$g(J) = J(J+1)$$

This makes it possible to change variables to $X = J(J+1)$ and the integration becomes very easy. Notice that just like in the translation partition function, we approximate the summation with an integral. However, because we are dealing with far fewer levels, this is less justified in the rotational case. How justified it is depends on the gas and the temperature we consider. Roughly speaking we should be at a temperature $T >> \Theta_{\text{rot}}$.

Exercise 18.5.1

Look at table 18.2. When do we need to actually work out the (discrete) summation instead of making a (continuous) integration out of it?

Answer available at the end of this section.

The rotational constant B is directly linked to the moment of inertia:

$$I = \mu r^2$$

Where μ is the reduced mass of the molecule:

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$$

and r is the bond length. Again we can scale the behavior of different systems to one and the same picture by introducing a characteristic temperature:

$$\Theta_{rot} = \frac{hb}{k} = \frac{\hbar^2}{2Ik_b}$$

As we did for the translations, we can calculate the moment $\langle\epsilon\rangle$. For vibrations we get a relatively complicated function of temperature. However, for rotations, the moment is simply equal to NkT and this means that the rotational contribution to the molar C_v of a diatomic is simply R. As the vibrational and electronic contributions to the heat capacity are typically negligible at room temperature, we get:

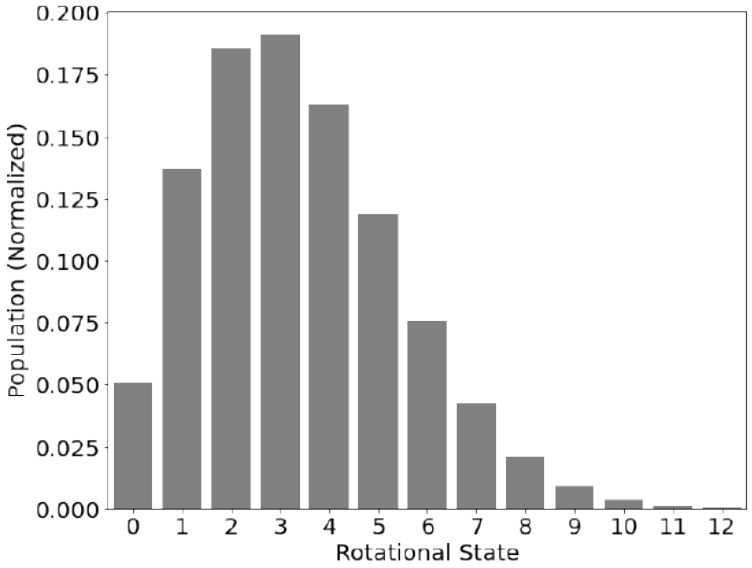
- monatomic gas

$$C_v = C_v^{trans} = \frac{3}{2}nR$$

- diatomic

$$C_v = C_v^{trans} + C_v^{rot} \tag{27.5.1}$$
$$= \frac{3}{2}nR + nR \tag{27.5.2}$$
$$= \frac{5}{2}nR \tag{27.5.3}$$

Rotational energies are less than vibrational and electronic energies and, at room temperature, many rotational states will be populated.



The normalized rotational population of HCl at room temperature.

Answers

Only for the lightest gases like He and $\mathrm{H_2}$ do we need to worry and then only at pretty low cryogenic circumstances. At room temperature, we can take the rotational levels as a continuous set and use an integral. Notice that the vibrational Θ values are much larger! At $T = 300\ \mathrm{K}$, usually only a single level is occupied and we are in the discrete limit. On the surface of the sun that would be a different matter of course.

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27.6: Rotational Partition Functions Contain a Symmetry Number

The rotational energy levels of a **diatomic molecule** are given by:

$$E_{\text{rot}}(J) = \tilde{B}J(J+1) \tag{27.6.1}$$

where:

$$\tilde{B} = \frac{h}{8\pi^2 Ic}$$

Here, $\tilde{B}$ is the rotational constant expressed in cm^{-1}. The rotational energy levels are given by:

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

where I is the moment of inertia of the molecule given by μr^2 for a diatomic, and μ is the reduced mass, and r the bond length (assuming rigid rotor approximation). The energies can be also expressed in terms of the rotational temperature, Θ_{rot}, defined as:

$$\Theta_{\text{rot}} = \frac{r^2}{8\pi^2 Ik} \tag{27.6.2}$$

The interpretation of θ_{rot} is as an estimate of the temperature at which thermal energy ($\approx kT$) is comparable to the spacing between rotational energy levels. At about this temperature the population of excited rotational levels becomes important. See Table 1.

Table 1: Select Rotational Temperatures. In each case the value refers to the most common isotopic species.

Molecule	H_2	N_2	O_2	F_2	HF	HCl	CO_2	HBr	CO
Θ_{rot}	87.6	2.88	2.08	1.27	30.2	15.2	0.561	12.2	2.78

In the summation for the expression for rotational partition function (q_{rot}), Equation 27.6.3, we can do an explicit summation:

$$q_{\text{rot}} = \sum_{j=0}(2J+1)e^{-E_J/kT} \tag{27.6.3}$$

if only a finite number of terms contribute. The factor $(2J+1)$ for each term in the expansion accounts for the degeneracy of a rotational state J. For each allowed energy E_J from Equation 27.6.1 there are $(2J+1)$ eigenstates. The Boltzmann factor must be multiplied by $(2J+1)$ to properly account for the degeneracy these states:

$$(2J+1)e^{-E_J/kT}$$

If the rotational energy levels are lying very close to one another, we can integrate similar to what we did for q_{trans} previously to get:

$$q_{\text{rot}} = \int_0^\infty (2J+1)R^{-\tilde{B}J(J+1)/kT}dJ$$

This integration can easily be done by substituting $x = J(J+1)$ and $dx = (2J+1)dJ$:

$$q_{\text{rot}} = \frac{kT}{\tilde{B}} \tag{27.6.4}$$

For a homonuclear diatomic molecule, rotating the molecule by 180° brings the molecule into a configuration which is *indistinguishable* from the original configuration. This leads to an overcounting of the accessible states. To correct for this, we divide the partition function by σ, which is called the **symmetry number** and is equal to the distinct number of ways by which a

molecule can be brought into identical configurations by rotations. The rotational partition function becomes:

$$q_{\text{rot}} = \frac{kT}{\tilde{B}\sigma} \tag{27.6.5}$$

or commonly expressed in terms of Θ_{rot}:

$$q_{\text{rot}} = \frac{T}{\Theta_{\text{rot}}\sigma} \tag{27.6.6}$$

Example 18.6.1

What is the rotational partition function of H_2 at 300 K?

Solution

The value of $\tilde{B}$ for H_2 is 60.864 cm^{-1}. The value of kT in cm^{-1} can be obtained by dividing it by hc, i.e., which is $kT/hc = 209.7\ cm^{-1}$ at 300 K. $\sigma = 2$ for a homonuclear molecule. Therefore from Equation 27.6.5,

$$\begin{aligned} q_{\text{rot}} &= \frac{kT}{\tilde{B}\sigma} \\ &= \frac{209.7\ cm^{-1}}{(2)(60.864\ cm^{-1})} \\ &= 1.723 \end{aligned}$$

Since the rotational frequency of H_2 is quite large, only the first few rotational states are accessible at 300 K

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27.7: The Vibrational Partition Function

As with diatomic molecules, the energies of polyatomic molecules can be approximated by the sum of its individual degrees of freedom. Therefore, we can write the partition function as:

$$Q(N,V,T) = \frac{[q(V,T)]^2}{N!}$$

We can write the polyatomic analog to diatomic molecules:

$$Q(N,V,T) = \frac{(q_{\text{trans}}q_{\text{rot}}q_{\text{vib}}q_{\text{elec}})^N}{N!}$$

When derived for diatomic molecules, we assumed the rigid rotor model for rotations and the harmonic oscillator for vibrations. This allowed us to separate the rotational motion from the vibrational motion of the molecule. Polyatomic molecules are a bit more complicated, but we will still make use of these approximations.

The number of translational states available to any given molecule is far greater than the number of molecules in the system. q_{trans} is given by:

$$q_{\text{trans}} = \left[\frac{2\pi MkT}{h^2}\right]^{3/2} V$$

where M is the mass of the particle. Moving to the electronic partition function:

$$q_{\text{elec}} = \sum_i g_i e^{-E_i/kT}$$

where E_i is the energy of the electronic state i and {g_i} is its degeneracy. Electronic states are typically spaced far apart from each other. The probability of the system being in any state but the ground state is extremely small. We can therefore simplify the electronic partition function to include only the ground electronic state:

$$q_{\text{elec}} = g_{e1}e^{D_e/kT}$$

where $-D_e$ is the energy of the ground electronic state. To complete the polyatomic partition function, we still need q_{vib} and q_{rot}. We will finish this section with q_{vib} and talk about q_{rot} in the next.

The vibrational motion of diatomic molecules can be expressed as a set of independent harmonic oscillators. For polyatomic molecules, the independent vibrational motions are referred to as normal modes of vibration. The vibrational energy is then the sum of the energies for each normal mode:

$$E_{\text{vib}} = \sum_i^{\alpha} \left(v_i + \frac{1}{2}\right) h\nu$$

where ν_i is the vibrational frequency for the ith normal mode and α is the number of vibration degrees of freedom. A linear molecule has $3n-5$ vibrational degrees of freedom and a nonlinear molecule has $3n-6$ vibrational degrees of freedom. Because the normal modes are independent of each other, we can take out results from previous sections:

$$q_{\text{vib}} = \prod_i^{\alpha} \frac{e^{-\theta_{\text{vib},i}/2T}}{1-e^{-\theta_{\text{vib},i}/T}}$$

$$E_{\text{vib}} = Nk\sum_i^{\alpha}\left(\frac{\theta_{\text{vib},i}}{2} + \theta_{\text{vib},i}\frac{e^{-\theta_{\text{vib},i}/T}}{1-e^{-\theta_{\text{vib},i}/T}}\right)$$

$$C_{V,\text{vib}} = Nk\sum_i^{\alpha}\left(\left(\frac{\theta_{\text{vib},i}}{2}\right)^2 + \frac{e^{-\theta_{\text{vib},i}/T}}{(1-e^{-\theta_{\text{vib},i}/T})^2}\right)$$

where $\theta_{\text{vib},i}$ is the characteristic vibrational temperature defined by:

$$\theta_{\text{vib},i} = \frac{h\nu_i}{k}$$

Vibrational Entropy

There is a great deal of utility for thermodynamic functions calculated from the vibrational normal modes of a molecule. The vibrational energy and entropy depend on the shape a multidimensional potential energy surface. If one performs a conformational search of macromolecule it is one obtains energies and structures but little direct information concerning the shape of the potential energy surface for each conformation. The vibrational entropy gives a means determining whether there are significant entropic differences in the structures and therefore whether certain conformations will be favored based on the entropy.

However, it is possible to take appropriate linear combinations of the coordinates so that the cross terms are eliminated and the classical Hamiltonian as well as the operator corresponding to it contains no cross terms and in terms of the new coordinates, the Hamiltonian can be written as,

$$H = \sum_{i=1}^{f} \frac{h^2}{2\mu_i} \frac{\partial}{\partial q_i^2} + \sum_{i=1}^{f} \frac{k_i}{2} q_i^2 \tag{27.7.1}$$

Here, the degrees of freedom f is $3N-5$ for a linear molecule and $3N-6$ for a nonlinear molecule. Here, k_i is the force constant and μ_i is the reduced mass for that particular vibrational mode which is referred to as a **normal mode**.

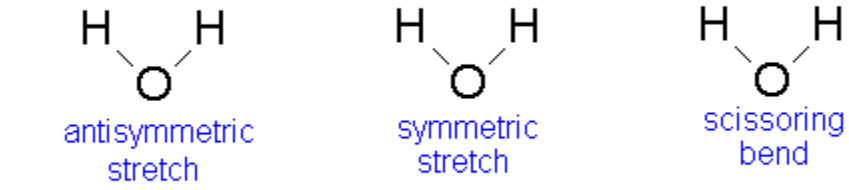


Figure 18.7.1 : The three vibrational modes of water, the symmetric stretch (3656.7 cm^{-1}, 5160 K), the asymmetric stretch (3755.8 cm^{-1} , 5360 K) and the bending mode (1594.8 cm^{-1} ,2290 K) are shown. The vibrational frequencies and the characteristic temperature for each mode are shown in parenthesis. Although not shown in the animation, the oxygen atom also moves with each of these normal modes.

The Equation 27.7.1 represents f linearly independent harmonic oscillators and the total energy for such a system is

$$\epsilon_{vib} = \sum_{i=1}^{f} \left(v_i + \frac{1}{2} \right) h\nu_i$$

The vibrational frequencies are given by

$$\nu_i = \frac{1}{2\pi} \sqrt{\frac{k_i}{\mu_i}}$$

The vibrational partition function is given by the product of f vibrational functions for each frequency.

$$q_{vib} = \prod_{i=1}^{f} \frac{e^{-\Theta_{vib,i}/2T}}{1 - e^{-\Theta_{vib,i}/T}} \tag{27.7.2}$$

with

$$\Theta_{vib,i} = \frac{h\nu_i}{k_B}$$

As with the previous discussion regarding simple diatomics, $\Theta_{vib,i}$ is called the **characteristic vibrational temperature**. The molar energies and the heat capacities are given by

$$\langle E_{vib} \rangle = Nk \sum_{i=1}^{f} \left[\frac{\Theta_{vib,i}}{2} + \frac{\Theta_{vib,i} e^{-\Theta_{vib,i}/T}}{1 - e^{-\Theta_{vib,i}/T}} \right]$$

and

$$\bar{C}_V = Nk_B \sum_{i=1}^{f} \left(\frac{\Theta_{vib,i}}{T} \right)^2 \frac{e^{-\Theta_{vib,i}/T}}{\left(1 - e^{-\Theta_{vib,i}/T}\right)^2}$$

NO_2Exam

The three characteristic vibrational temperatures for NO_2 are 1900 K, 1980 K and 2330 K. Calculate the vibrational partition function at 300 K.

Solution

The vibrational partition is (Equation 27.7.2)

$$q_{vib} = \prod_{i=1}^{f} \frac{e^{-\Theta_{vib,i}/2T}}{1 - e^{-\Theta_{vib,i}/T}}$$

If we calculate q_{vib} by taking the zero point energies as the reference points with respect to which the other energies are measured

$$\begin{aligned} q_{vib} &= \prod_{i=1}^{f} \frac{1}{1 - e^{-\Theta_{vib,i}/T}} = \left(\frac{1}{1 - e^{-1900/300}} \right) \left(\frac{1}{1 - e^{-1980/300}} \right) \left(\frac{1}{1 - e^{-2330/300}} \right) \\ &= (1.0018)(1.0014)(1.0004) = 1.0035 \end{aligned}$$

The implication is that very few vibrational states of NO_2 (other than the ground vibrational state) are accessible at 300 K. This is standard of the vibrations of most molecules.

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- 18.7: Vibrational Partition Functions of Polyatomic Molecules Include the Partition Function for Each Normal Coordinate is licensed CC BY-NC-SA 4.0.

27.8: The Rotational Partition Function Depends on the Shape of the Molecule

For a polyatomic molecule containing N atoms, the total number of degrees of freedom is $3N$. Out of these, three degrees of freedom are taken up for the translational motion of the molecule as a whole. For nonlinear molecules, there are three rotational degrees of freedom and the $3N–6$ vibrational degrees. For linear molecules, the rotational motion along the molecular axis is quantum mechanically not meaningful as the rotated configuration is indistinguishable from the original configuration. Therefore, linear molecules have two rotational degrees of freedom and $3N–5$ vibrational degrees of freedom.

To investigate the rotational motion, we need to fix the center of mass of the molecule and calculate the three principal moments of inertia I_A, I_B, and I_C of the ellipsoid of inertia. The center of mass is defined as the point for which the following identities hold:

$$\sum_i m_i x_i = \sum_i m_i y_i = \sum_i m_i z_i$$

The inertia products are defined by:

$$I_{xx} = \sum_i m_i \left(y_i^2 + z_i^2\right)$$

$$I_{xy} = \sum_i m_i \left(x_i y_i\right)$$

The other components I_{yy}, I_{xz},.. are defined analogously. To find the direction cosines $\alpha_i, \beta_o, \gamma_i$ of the three principle moments of inertia, we need to solve the following matrix equations:

$$\alpha(I_{xx} - \eta) - \beta I_{xy} - \gamma I_{xz} = 0$$

$$\alpha I_{xy} - \beta(I_{yy} - \eta) - \gamma I_{yz} = 0$$

$$-\alpha I_{xz} - \beta I_{yz} + \gamma(I_{zz} - \eta) = 0$$

If the off diagonal terms I_{xy} are zero in the above equations, then the x, y, z axis will be the principal axis. The energy of a rotor with the three moments of inertia I_A, I_B. and I_C is given by:

$$\begin{aligned}\epsilon &= \frac{1}{2} I_A \omega_A^2 + \frac{1}{2} I_B \omega_B^2 + \frac{1}{2} I_C \omega_C^2 \\ &= \frac{L_A^2}{2I_A} + \frac{L_B^2}{2I_B} + \frac{L_C^2}{2I_C}\end{aligned}$$

Each of the rotational degrees of freedom will have a characteristic rotational temperature in terms of the moment of inertia:

$$\Theta_{rot,i} = \frac{hbar^2}{2I_i k} \qquad i = A, B, C$$

There are many different shapes of molecules and these shapes affect the rotational behavior of the molecules. Molecules are therefore classified according to symmetry into different groups called tops. The three different tops are:

$$\begin{aligned}&\text{Spherical top} && \Theta_{rot,A} = \Theta_{rot,B} = \Theta_{rot,C} \\ &\text{Symmetric top} && \Theta_{rot,A} = \Theta_{rot,B} \neq \Theta_{rot,C} \\ &\text{Asymmetric top} && \Theta_{rot,A} \neq \Theta_{rot,B} \neq \Theta_{rot,C}\end{aligned}$$

Spherical Tops

The spherical top can be solved exactly to give:

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

$$g_J = (2J + 1^2) \qquad J = 0, 1, 2, ...$$

The rotational partition function is:

$$\begin{aligned} q_{\text{rot}} &= \sum_{J=0}^{\infty} (2J+1)^2 e^{h^2 J(J+1)/2IkT} \\ &= \sum_{J=0}^{\infty} (2J+1)^2 e^{\Theta_{\text{rot}} J(J+1)/T} \end{aligned}$$

For almost all spherical top molecules:

$$\Theta_{\text{rot}} \gg T$$

Therefore, we can convert the sum to an integral:

$$q_{\text{rot}} = \frac{1}{\sigma} \int_0^{\infty} (2J+1)^2 e^{\Theta_{\text{rot}} J(J+1)/T}$$

where we have now included the symmetry term, σ. Solving for this integral, we get:

$$q_{\text{rot}} = \frac{\pi^{1/2}}{\sigma} \left(\frac{T}{q_{\text{rot}}} \right)^{3/2}$$

Symmetric Tops

Here, ω_A, ω_B, and ω_C are the three angular speeds and L_A, L_B, and L_C are the three angular momenta. For a symmetric top molecule such as ammonia, or chloromethane, two components of the moments of inertia are equal, i.e., $I_B = I_C$. The rotational energy levels of such a molecule are specified by two quantum numbers J and K. The total angular momentum is determined by J and the component of this angular momentum along the unique molecular axis is determined by K. The energy levels are given by:

$$\epsilon_{J,K} = \tilde{B}J(J+1) + (\tilde{A} - \tilde{B})K^2$$

with rotational constants in units of wavenumbers:

$$\tilde{B} = \frac{h}{8\pi^2 c I_B}$$

and:

$$\tilde{A} = \frac{h}{8\pi^2 c I_A}$$

where

- J takes on values $0, 1, 2, ...\infty$ and
- $K = -J, -J+1, -J+2, ...0, 1, 2, ...J$.

The rotational partition function is given by:

$$q_{rot} = \frac{1}{\sigma} \sum_{J=0}^{\infty} (2J+1) e^{-\tilde{B}J(J+1)/kT} \sum_{K=-J}^{J} (2J+1) e^{\tilde{A}-\tilde{B})K^2/kT}$$

This can be converted to an integral and the result is:

$$q_{rot} = \frac{\sqrt{\pi}}{\sigma}\left(\frac{8\pi I_B kT}{h^2}\right)\left(\frac{8\pi I_A kT}{h^2}\right)^{1/2}$$

Asymmetric Tops

For asymmetric tops, the expressions for rotational energies are more complex and the conversions to integrations are not easy. One can actually calculate the sum of terms using a computer. An intuitive answer can be obtained by integrating over the angular momenta L_A, L_B and L_C as:

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} e^{H(p,q)/kT}\, dL_A\, dL_B\, dL_C = \sqrt{2\pi I_A kT}\sqrt{2\pi I_B kT}\sqrt{2\pi I_C kT}$$

And then multiplying by a factor of $8\pi^2/\sigma h^3$, we get the rotational partition function. The factor of $8\pi^2$ accounts for the angular integration. For any axis chosen in a molecule, a complete rotation contributes a factor of 2π. Integration over all possible orientations of this axis contribute another factor of 4π. The factor of h^3 is for the conversion from the classical phase space to the quantum mechanical phase space.

Symmetry Number

As discussed previously, the **symmetry number** σ corrects for overcounting of rotational configurations. If the molecule has no center of symmetry (e.g. HCN) $\sigma = 1$ whereas if the molecule has a center of symmetry (e.g. $\mathrm{CO_2}$) then $\sigma = 2$.

The final result is:

$$q_{rot} = \frac{\pi^2}{\sigma}\sqrt{\frac{8\pi I_A kT}{h^2}}\sqrt{\frac{8\pi I_B kT}{h^2}}\sqrt{\frac{8\pi I_C kT}{h^2}} \tag{27.8.1}$$

Classical Derivation (Optional)

We can explicitly obtain the classical rotational partition function of an asymmetric top by writing the classical expression for the rotational energy in terms of the Euler angles. The orientation of a rigid rotor can be specified by there Euler angles θ, φ, and ψ with the ranges of angles 0 to π, 0 to 2π and 0 to 2π respectively. The rotational Hamiltonian for the kinetic energy can be written in terms of the angles and their conjugate momenta (p_θ, p_ϕ, p_ψ)

$$H = \frac{\sin^2\psi}{2I_A}\left(p_\theta - \frac{\cos\psi}{\sin\theta\sin\psi}(p_\phi - \cos\theta p_\psi)\right)^2$$

$$+\frac{\cos^2\psi}{2I_B}\left(p_\theta - \frac{\sin\psi}{\cos\theta\cos\psi}(p_\phi - \cos\theta p_\psi)\right)^2 + \frac{1}{2I_C}p_\psi^2$$

The classical rotational partition function is given by

$$q_{rot} = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_0^{\pi}\int_0^{2\pi}\int_0^{2\pi}\frac{1}{h^3}e^{-H(p,q)/kT}dp_\theta\, dp_\phi\, dp_\psi\, d\theta\, d\phi\, d\psi$$

The integrations can be simplified by rewriting $H(p,q)/kT$ as

$$\frac{H}{kT} = \frac{1}{2I_A kT}\left(\frac{\sin^2\psi}{I_A} + \frac{\cos^2\psi}{I_B}\right)\left(p_\theta + \left(\frac{1}{I_B} - \frac{1}{I_A}\right)\frac{\sin\psi\cos\psi}{\sin\theta\left(\frac{\sin^\psi}{I_A} + \frac{\cos^2\psi}{I_B}\right)}(p_\phi - \cos\theta p_\psi)\right)^2$$

$$+\frac{1}{2kTI_AI_B\sin^2\theta}\left(\frac{1}{\sin\theta\left(\frac{\sin^{\psi}}{I_A}+\frac{\cos^2\psi}{I_B}\right)}(p_\phi-\cos\theta p_\psi)\right)^2+\frac{1}{2KTI_c}p_\psi^2$$

Using the following integral,

$$\int_{-\infty}^{\infty}e^{-a(x+b)^2}dx=\int_{-\infty}^{\infty}e^{-ax^2}dx=\sqrt{\frac{\pi}{a}}$$

Integration over p_θ gives using the above expression

$$\sqrt{2\pi kT}\left(\frac{\sin^2\psi}{I_A}+\frac{\cos^2\psi}{I_B}\right)^{-1/2} \tag{27.8.2}$$

Integration over p_φ gives the factor,

$$\sqrt{2\pi kTI_AI_B}\sin\theta\left(\frac{\sin^2\psi}{I_A}+\frac{\cos^2\psi}{I_B}\right)^{1/2}$$

This cancels partly the second square root in Equation 27.8.2. Integration over p_ψ gives the factor

$$\sqrt{2\pi kTI_c}$$

Integration over θ, φ and ψ gives a factor of $8\pi^2$.

$$\int_0^{\pi}\sin\theta\,d\theta=2$$

$$\int_0^{2\pi}d\phi=2\pi$$

$$\int_0^{2\pi}d\psi=2\pi$$

Combining all the integrals, we finally get Equation 27.8.1 after reintroduced the symmetry number σ as before with diatomic molecular rotation.

We can simplify calculations by defining **characteristic rotational temperatures** for each axis of rotational:

$$\Theta_A=\frac{h^2}{8\pi^2I_Ak}$$

$$\Theta_B=\frac{h^2}{8\pi^2I_Bk}$$

$$\Theta_C=\frac{h^2}{8\pi^2I_Ck}$$

The polyatomic rotational partition function expressed in Equation 27.8.1 can then be re-expressed as:

$$q_{rot}=\frac{\sqrt{\pi}}{\sigma}\sqrt{\frac{T^3}{\Theta_A\Theta_B\Theta_C}} \tag{27.8.3}$$

or alternatively:

$$\ln q_{rot}=\frac{1}{2}\ln\frac{\pi T}{\Theta_A\Theta_B\Theta_C\sigma^2}$$

Example: Nitrogen Dioxide

The three characteristic rotational temperatures for NO_2 are $111.5\ K$, $0.624\ K$ and $0.590\ K$. Calculate the rotational partition function at 300 K.

Solution

The rotational temperature is given by Equation 27.8.3:

$$q_{rot} = \frac{\sqrt{\pi}}{\sigma}\sqrt{\frac{T^3}{\Theta_A\Theta_B\Theta_C}}$$

The rotational partition function becomes,

$$q_{rot} = \frac{1.772}{2}\sqrt{\frac{300\ K}{(11.5\ K)(0.624\,K)(22.55\ K)}} = 2242.4$$

Thermodynamics Properties

The molar thermodynamic functions can be readily calculated including average rotation energy and molar heat capacity:

$$E_{rot} = \frac{3}{2}RT$$

and:

$$\bar{C_V} = \frac{3}{2}R$$

Improvements over the classical approximation for the rotational partition function derived above have been obtained. One of the improved versions (with no derivation) is:

$$q_{rot} = q^0_{rot}\left[1 + \frac{h^2}{96\pi^2 kT}\left(\frac{2}{I_A} + \frac{2}{I_C} + \frac{2}{I_C} + \frac{I_C}{I_B I_B} - \frac{I_A}{I_B I_C} - \frac{I_B}{I_A I_C}\right)\right]$$

where q^0_{rot} is the classical approximation in Equation 27.8.1.

Comparing this result with the vibrational partition function calculation before ($q_{vib} = 1.0035$), give the implication that while multiple rotational states are accessible at room temperature, very few vibrational states (other than the ground vibrational state) are accessible.

Contributors and Attributions

- www.chem.iitb.ac.in/~bltembe/pdfs/ch_3.pdf

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27.9: Molar Heat Capacities

Learning Objectives

- **Goal**: Specific heat capacity data for a wide range of elements are used to assess the accuracy and limitations of the Dulong-Petit Law.
- **Prerequisites**: An introductory knowledge of statistical thermodynamics including the derivation of the vibrational (harmonic oscillator) contributions to the heat capacity are recommended.
- **Resources you will need**: This exercise should be carried out within a data analysis software environment which is capable of graphing and generating a best-fit line for an x-y data set.

The heat capacity (C) of a substance is a measure of how much heat is required to raise the temperature of that substance by one degree Kelvin. For a simple molecular gas, the molecules can simultaneously store kinetic energy in the translational, vibrational, and rotational motions associated with the individual molecules. In this case, the heat capacity of the substance can be broken down into translational, vibrational, and rotational contributions;

$$C = C_{trans} + C_{vib} + C_{rot} \tag{27.9.1}$$

Monoatomic crystalline solids represent a much simpler case. Einstein proposed a simple model for such substances whereby the atoms only have vibrational energy (each atom can vibrate in three perpendicular directions around its lattice position). Specifically, the 'Einstein Solid Model' assumes that the atoms act like three-dimensional harmonic oscillators (with the vibrational motion of each atom in each perpendicular dimension entirely independent). Statistical mechanics provides a relatively simple expression for the constant volume molar heat capacity ($C_{V,m}$) of a one-dimensional harmonic oscillator

$$C_{V,m}^{1-D} = R\left(\frac{\Theta_v}{T}\right)^2\left(\frac{e^{-\Theta_v/2T}}{1-e^{-\Theta_v/T}}\right)^2 \tag{27.9.2}$$

where R is the universal gas constant, T is absolute temperature, and Θ_v is called the 'characteristic vibrational temperature' of the oscillator and depends on the vibrational frequency (ν) according to

$$\Theta_v = \frac{hv}{k} \tag{27.9.3}$$

with h representing Plank's constant and k representing Boltzmann's constant.

Since the vibrations in each dimension are assumed to be independent, the expression for the constant volume molar heat capacity of a 'three-dimensional' Einstein Solid is obtained by simply multiplying Equation 27.9.2 by three;

$$C_{V,m}^{3-D} = 3R\left(\frac{\Theta_v}{T}\right)^2\left(\frac{e^{-\Theta_v/2T}}{1-e^{-\Theta_v/T}}\right)^2 \tag{27.9.4}$$

The temperature variation of the heat capacity of most metallic solids is well described by Equation 27.9.4. Furthermore, plots of Equation 27.9.4 as a function of temperature for metals with widely varying vibrational frequencies reveal that the heat capacity always approaches the same asymptotic limit of $3R$ at high temperatures. Stated another way, at high temperatures

$$\lim_{T\to\infty}\left[\left(\frac{\Theta_v}{T}\right)^2\left(\frac{e^{-\Theta_v/2T}}{1-e^{-\Theta_v/T}}\right)^2\right] = 1 \tag{27.9.5}$$

and Equation 27.9.4 reduces to

$$\lim_{T\to\infty}\left[C_{V,m}^{3D}\right] = 3R \tag{27.9.6}$$

(You will be asked to verify this result in the exercise below). According to Equation 27.9.6, the molar heat capacities of metallic solids should approach 24.9 J/(K mol) at high temperatures, regardless of the identity of the metal.

The vibrational frequencies of most metallic solids are usually small enough so that Θ_v lies considerably below room temperature ($\Theta_v \ll 298\ K$). For these substances, the limits implied by Equations 27.9.5 and 27.9.6 are well approximated even at room temperature, leading to the result that $C_{v,m} = 24.9\ J/(K \cdot mol)$ for most metals at room temperature.

In the early 1800s, two French scientists by the names of Pierre Louis Dulong and Alexis Therese Petit empirically discovered the same remarkable result. The Dulong-Petit Law is normally expressed in terms of the specific heat capacity (C_s) and the molar mass (M) of the metal

$$C_s M = C_{V,m} \approx 25(J\,K^{-1}\,mol^{-1}) \tag{27.9.7}$$

where C_s represents how much heat is required to raise the temperature of 'one gram' of that substance by one degree Kelvin. Dulong and Petit, as well as other scientists of their time, used this famous relationship as a means of establishing more accurate values for the atomic weight of metallic elements (by instead measuring the specific heat capacity of the element and using the Dulong-Petit relationship, which is a relatively simple method of establishing weights in comparison to the more disputable gravimetric methods that were being used at the time to establish the equivalent weights of elements).

In the exercise below, you will look up the specific heat capacities of a number of elements that exist as simple monoatomic solids at room temperature and assess the accuracy of the Dulong-Petit law.

Experimental Data

Consult the CRC Handbook of Chemistry and Physics (CRC Press: Boca Raton, FL) and compile a table of specific heat capacities for a large number of elements that are known to exist as monoatomic solids at room temperature. Also look up and record the molar mass of these elements. The elements that you consider should be restricted to those appearing in groups 1-14 of the periodic table. Make sure you generate a fairly large list which includes a number of elements that are normally considered as metallic in character (such as copper, iron, sodium, lithium, gold, platinum, barium, and aluminum), but also some non-metallic elements that are nonetheless monoatomic isotropic solids (such as carbon-diamond, beryllium, boron, and silicon). Heat capacities that are usually reported in the literature are not actual constant volume heat capacities (C_v), but are instead constant pressure heat capacities (C_p). Fortunately, C_p and C_v are essentially equal for simple solids (within the level of precision that we consider in this exercise), and you can assume that the values from the CRC Handbook represent C_s.

Exercises

1. Enter the element name, the specific heat capacity, and the molar mass of each element in a spreadsheet. Calculate the product of specific heat and molar mass for each element and calculate how much this product differs from the Dulong-Petit prediction (express your result as a percent difference relative to $3R$).
2. Assess the generality of the Dulong-Petit law in an alternate way by generating a plot of specific heat as a function of reciprocal Molar Mass (C_s versus $1/M$), which should be linear with a slope equal to 3R if the data behave according to Equation 27.9.7.
3. Inspect your results from 1 and 2 above and identify any elements that significantly deviate from the Dulong-Petit law. When they occur, do deviations tend to be smaller or larger than 3R? Does the degree of deviation from the Dulong-Petit law seem to correlate with periodic trends in metallic (or covalent) bonding for these elements? Do deviations tend to occur more readily for elements of smaller or higher atomic weight? Explain how the type of bonding and the magnitude of the atomic weight can lead to deviations from the arguments made in Equations 27.9.5-27.9.7 above.
4. Use the plotting method that you employed in step 2 above as a means of determining a value for the universal gas constant (R) - but make sure you throw-out any specific heat data for elements that you suspect do not fall within the limit $\Theta_v \ll 298\ K$. Calculate the percent error in the value of R that you determine.
5. Verify that the limit expressed in Equation 27.9.5 above is true (HINT: expand each of the exponential terms in a power series and note that higher-order terms are negligible in the limit $T \gg \Theta_v$).

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27.E: Partition Functions and Ideal Gases (Exercises)

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28: MANY-ELECTRON ATOMS

When two or more electrons are present in a system, the TISEq equation cannot be solved analytically. Thus for the vast majority of chemical applications, we must rely on approximate methods. We will explore some of these approximations in this and further chapter, starting from the many-electron atoms (all atoms other than hydrogen). It is important to stress that because of the nature of approximations, this is still a very active field of scientific research, and improved methods are developed every year.

The electronic Hamiltonian for a many-electron atom can be written as:

$$\hat{H}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \sum_{i=1}^{N} \left(-\frac{\hbar^2}{2m_e} \nabla_i^2 - \frac{Ze^2}{4\pi\varepsilon_0 r_i} \right) + \frac{e^2}{4\pi\epsilon_0} \sum_{i<j} \frac{1}{r_{ij}}, \tag{10.1}$$

where Z is the nuclear charge, m_e and e are respectively the mass and charge of an electron, $\mathbf{r}_i$ and ∇_i^2 are the spatial coordinates and the Laplacian of each electron, $r_i = |\mathbf{r}_i|$, and $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ is the distance between two electrons (all other symbols have been explained in previous chapters). The TISEq is easily written using Equation 22.3.1.

28.1: Many-Electron Wave Functions

28.2: Approximated Hamiltonians

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28.1: Many-Electron Wave Functions

When we have more than one electron, the sixth postulate that we discussed in chapter 24 comes into place. In other words, we need to account for the spin of the electrons and we need the wave function to be antisymmetric with respect to exchange of the coordinates of any two electrons. In order to do so, we can define a new variable $\mathbf{x}$ which represents the set of all four coordinates associated with an electron: three spatial coordinates $\mathbf{r}$, and one spin coordinate $\mathbf{s}$, i.e., $\mathbf{x} = \{\mathbf{r}, \mathbf{s}\}$. We can then write the electronic wave function as $\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)$, and we require the sixth postulate to hold by writing:

$$\Psi\left(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N\right) = -\Psi\left(\mathbf{x}_2, \mathbf{x}_1, \dots, \mathbf{x}_N\right) \tag{28.1.1}$$

A very important step in simplifying $\Psi(\mathbf{x})$ is to expand it in terms of a set of one-electron functions. Since we need to take into account the spin coordinate as well, we can define a new function, called **spin-orbital**, by multiplying a spatial orbital by one of the two spin functions:

$$\begin{aligned} \chi(\mathbf{x}) &= \psi(\mathbf{r})\phi_{\uparrow}(\mathbf{s}), \\ \chi(\mathbf{x}) &= \psi(\mathbf{r})\phi_{\downarrow}(\mathbf{s}). \end{aligned} \tag{28.1.2}$$

Notice that for a given spatial orbital $\psi(\mathbf{r})$, we can form two spin orbitals, one with $\uparrow$ spin, and one with $\downarrow$ spin (since the spin coordinate $\mathbf{s}$ has only two possible values, as already discussed in chapter 23). For the spatial orbitals we can use the same one-particle functions that solve the TISEq for the hydrogen atom, $\psi_{n\ell m_\ell}(\mathbf{r})$(eq. 21.7 in chapter 21). Notice how each spin-orbital now depends on four quantum numbers, the three for the spatial part, n, ℓ, m_ℓ, plus the spin quantum number m_s. We need to keep in mind, however, that the spin-orbitals, $\chi_{n\ell m_\ell m_s}$, *are not* analytic solutions to the TISEq, so the resulting wave function is *not* the exact wave function of the system, but just an approximation.

Once we have defined one-electron spin-orbitals for each electron in the system, we can use them as the basis for our many-electron wave function. While doing so, we need to make sure to enforce the antisymmetry property of the overall wave function. We will start from the simplest case of an atom with two electrons with coordinates $\mathbf{x}_1$ and $\mathbf{x}_2$, which we put in two spin-orbitals χ_1 and χ_2. We can write the total wave function as a linear combination of the two spin-orbitals as:

$$\begin{aligned} \Psi(\mathbf{x}_1, \mathbf{x}_2) =& b_{11}\chi_1(\mathbf{x}_1)\chi_1(\mathbf{x}_2) + b_{12}\chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2) + \\ & b_{21}\chi_2(\mathbf{x}_1)\chi_1(\mathbf{x}_2) + b_{22}\chi_2(\mathbf{x}_1)\chi_2(\mathbf{x}_2). \end{aligned} \tag{28.1.3}$$

We then notice that in order for the antisymmetry principle to be obeyed, we need $b_{12} = -b_{21}$ and $b_{11} = b_{22} = 0$, which give:

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = b_{12}\left[\chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2) - \chi_2(\mathbf{x}_1)\chi_1(\mathbf{x}_2)\right]. \tag{28.1.4}$$

This wave function is sufficient to describe two-electron atoms and ions, such as helium. The numerical coefficient can be determined imposing the normalization condition, and is equal to $b_{12} = \dfrac{1}{\sqrt{2}}$. For the ground state of helium, we can replace the spatial component of each spin-orbital with the $1s$ hydrogenic orbital, ψ_{100}, resulting in:

$$\begin{aligned} \Psi(\mathbf{x}_1, \mathbf{x}_2) &= \frac{1}{\sqrt{2}}\left[\psi_{100}(\mathbf{r}_1)\phi_{\uparrow}\,\psi_{100}(\mathbf{r}_2)\phi_{\downarrow} - \psi_{100}(\mathbf{r}_1)\phi_{\downarrow}\,\psi_{100}(\mathbf{r}_2)\phi_{\uparrow}\right] \\ &= \psi_{100}(\mathbf{r}_1)\psi_{100}(\mathbf{r}_2)\frac{1}{\sqrt{2}}\left[\phi_{\uparrow}\phi_{\downarrow} - \phi_{\downarrow}\phi_{\uparrow}\right], \end{aligned} \tag{28.1.5}$$

which clearly shows how we need just one spatial orbital, ψ_{100}, to describe the system, while the antisymmetry is taken care by a suitable combination of spin functions, $\dfrac{1}{\sqrt{2}}\left[\phi_{\uparrow}\phi_{\downarrow} - \phi_{\downarrow}\phi_{\uparrow}\right]$. Notice also that we commit a small inaccuracy when we say: "two electron occupies one spin-orbital, one electron has spin up, and the other electron has spin down, with configuration: $[\uparrow\downarrow]$", as is typically found in general chemistry textbooks. The reality of the spin configuration is indeed more complicated, and the ground state of helium should be represented as $\dfrac{1}{\sqrt{2}}\left[\uparrow\downarrow - \downarrow\uparrow\right]$.

In order to generalize from two electrons to N, we can first observe how Equation (26.1.4) could be easily constructed by placing the spin-orbitals into a 2×2 matrix and calculating its determinant:

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \chi_1(\mathbf{x}_1) & \chi_2(\mathbf{x}_1) \\ \chi_1(\mathbf{x}_2) & \chi_2(\mathbf{x}_2) \end{vmatrix}, \tag{28.1.6}$$

where each column contains one spin-orbital, each row contains the coordinates of a single electron, and the vertical bars around the matrix mean that we need to calculate its determinant. This notation is called the **Slater determinant**, and it is the preferred way of building any N-electron wave function. Slater determinants are useful because they can be easily bult for any case of N electrons in N spin-orbitals, and they also automatically enforce the antisymmetry of the resulting wave function. A general Slater determinant is written:

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(\mathbf{x}_1) & \chi_2(\mathbf{x}_1) & \cdots & \chi_N(\mathbf{x}_1) \\ \chi_1(\mathbf{x}_2) & \chi_2(\mathbf{x}_2) & \cdots & \chi_N(\mathbf{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(\mathbf{x}_N) & \chi_2(\mathbf{x}_N) & \cdots & \chi_N(\mathbf{x}_N) \end{vmatrix} = |\chi_1, \chi_2, \cdots, \chi_N\rangle, \tag{28.1.7}$$

where the notation $|\cdots\rangle$ is a shorthand to indicate the Slater determinant where only the diagonal elements are reported.

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28.2: Approximated Hamiltonians

In order to solve the TISEq for a many-electron atom we also need to approximate the Hamiltonian, since analytic solution using the full Hamiltonian as in Equation 26.1 are impossible to find. The most significant approximation used in chemistry is called the *variational method*.

Variational method

The basic idea of the variational method is to guess a "trial" wave function for the problem consisting of some adjustable parameters called "variational parameters". These parameters are adjusted until the energy of the trial wave function is minimized. The resulting trial wave function and its corresponding energy are variational method approximations to the exact wave function and energy.

Why would it make sense that the best approximate trial wave function is the one with the lowest energy? This results from the Variational Theorem, which states that the energy of any trial wave function E is always an upper bound to the exact ground state energy $\mathcal{E}_0$. This can be proven easily. Let the trial wave function be denoted Φ. Any trial function can formally be expanded as a linear combination of the exact eigenfunctions Ψ_i. Of course, in practice, we don't know the Ψ_i, since we are applying the variational method to a problem we can't solve analytically. Nevertheless, that doesn't prevent us from using the exact eigenfunctions in our proof, since they certainly exist and form a complete set, even if we don't happen to know them. So, the trial wave function can be written:

$$\Phi = \sum_i c_i \Psi_i, \tag{28.2.1}$$

and the approximate energy corresponding to this wave function is:

$$E[\Phi] = \frac{\int \Phi^* \hat{H} \Phi d\tau}{\int \Phi^* \Phi d\tau}, \tag{28.2.2}$$

where $\tau = (\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$ is the ensemble of the spatial coordinates of each electron and the integral symbol is assumed as a $3N$ -dimensional integration. Replacing the expansion over the exact wave functions, we obtain:

$$E[\Phi] = \frac{\sum_{ij} c_i^* c_j \int \Psi_i^* \hat{H} \Psi_j d\tau}{\sum_{ij} c_i^* c_j \int \Psi_i^* \Psi_j d\tau}. \tag{28.2.3}$$

Since the functions Ψ_j are the exact eigenfunctions of $\hat{H}$, we can use $\hat{H}\Psi_j = \mathcal{E}_j \Psi_j$ to obtain:

$$E[\Phi] = \frac{\sum_{ij} c_i^* c_j \mathcal{E}_j \int \Psi_i^* \Psi_j d\tau}{\sum_{ij} c_i^* c_j \int \Psi_i^* \Psi_j d\tau}. \tag{28.2.4}$$

Now using the fact that eigenfunctions of a Hermitian operator form an orthonormal set (or can be made to do so), we can write:

$$E[\Phi] = \frac{\sum_i c_i^* c_i \mathcal{E}_i}{\sum_i c_i^* c_i}. \tag{28.2.5}$$

We now subtract the exact ground state energy $\mathcal{E}_0$ from both sides to obtain

$$E[\Phi] - \mathcal{E}_0 = \frac{\sum_i c_i^* c_i (\mathcal{E}_i - \mathcal{E}_0)}{\sum_i c_i^* c_i}. \tag{28.2.6}$$

Since every term on the right-hand side is greater than or equal to zero, the left-hand side must also be greater than or equal to zero:

$$E[\Phi] \geq \mathcal{E}_0. \tag{28.2.7}$$

In other words, the energy of any approximate wave function is always greater than or equal to the exact ground state energy $\mathcal{E}_0$.

This explains the strategy of the variational method: since the energy of any approximate trial function is always above the true energy, then any variations in the trial function which lower its energy are necessarily making the approximate energy closer to the exact answer. (The trial wave function is also a better approximation to the true ground state wave function as the energy is lowered, although not necessarily in every possible sense unless the limit $\Phi = \Psi_0$ is reached).

Approximated solution for the helium atom

We now have all the ingredients to attempt the simplest approximated solution to the TISEq of a many-electron atom. We can start by writing the total wave function using the Slater determinant of Equation 26.1.7 in terms of spin-orbitals:

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = |\chi_1, \chi_2, \cdots, \chi_N\rangle = |\psi_1\phi_\uparrow, \psi_1\phi_\downarrow, \cdots, \psi_{\frac{N}{2}}\phi_\uparrow, \psi_{\frac{N}{2}}\phi_\downarrow\rangle, \tag{28.2.8}$$

and then we can replace it into the TISEq for an N-electron system. This results into a set of N one-electron equations, one for each electron. When we attempt to solve each individual equation, however, we end up with a problem, since the potential energy in the Hamiltonian of Equation 26.1 does not have spherical symmetry because of the electron-electron repulsion term. As such, the one-electron TISEq cannot be simply solved in spherical polar coordinates, as we did for the hydrogen atom in chapter 21. The simplest way of circumventing the problem is to neglect the electron-electron repulsion term (i.e., assume that the electrons are not correlated and do not interact with each other). For a 2-electron atom this procedure is straightforward, since the Hamiltonian can be written as a sum of one-electron Hamiltonians:

$$\hat{H} = \hat{H}_1 + \hat{H}_2, \tag{28.2.9}$$

with $\hat{H}_1$ and $\hat{H}_2$ looking identical to those used in the TISEq of the hydrogen atom. This one-particle Hamiltonian does not depend on the spin of the electron, and therefore, we can neglect the spin component of the Slater determinant and write the total wave function for the ground state of helium, Equation 26.1.4, simply as:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \psi_{100}(\mathbf{r}_1)\psi_{100}(\mathbf{r}_2). \tag{28.2.10}$$

The overall TISEq reduces to a set of two single-particle equations:

$$\begin{aligned} \hat{H}_1\psi_{100}(\mathbf{r}_1) &= E_1\psi_{100}(\mathbf{r}_1) \\ \hat{H}_2\psi_{100}(\mathbf{r}_2) &= E_2\psi_{100}(\mathbf{r}_2), \end{aligned} \tag{28.2.11}$$

which can then be solved similarly to those for the hydrogen atom, and the solution be combined to give:

$$E = E_1 + E_2. \tag{28.2.12}$$

In other words, the resulting energy eigenvalue for the ground state of the helium atom in this approximation is equal to twice the energy of a ψ_{100}, $1s$, orbital. The resulting approximated value for the energy of the helium atom is $7,217\ \mathrm{kJ/mol}$, compared with the exact value of $7,620\ \mathrm{kJ/mol}$.

The nuclear charge Z in the ψ_{100} orbital can be used as a variational parameter in the variational method to obtain a more accurate value of the energy. This method provides a result for the ground-state energy of the helium atom of $7,478\ \mathrm{kJ/mol}$ (only $142\ \mathrm{kJ/mol}$ lower than the exact value), with the nuclear charge parameter minimized at $Z_{\min} = 1.6875$. This new value of the nuclear charge can be interpreted as the effective nuclear charge that is felt by one electron when a second electron is present in the atom. This value is lower than the real nuclear charge ($Z = 2$) because the interaction between the electron and the nuclei is shielded by presence of the second electron.

This procedure can be extended to atoms with more than two electrons, resulting in the so-called Hartree-Fock method. The procedure, however, is not straightforward. We will explain it in more details in the next chapter, since it is the simplest approximation that also describes the chemical bond.

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29: INTRODUCTION TO MOLECULES

29.1: The Molecular Hamiltonian
29.2: The Born-Oppenheimer Approximation
29.3: Solving the Electronic Eigenvalue Problem

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29.1: The Molecular Hamiltonian

For a molecule, we can decompose the Hamiltonian operator as:

$$\hat{H} = \hat{K}_N + \hat{K}_e + \hat{V}_{NN} + \hat{V}_{eN} + \hat{K}_{ee} \tag{29.1.1}$$

where we have decomposed the kinetic energy operator into nuclear and electronic terms, $\hat{K}_N$ and $\hat{K}_e$, as well as the potential energy operator into terms representing the interactions between nuclei, $\hat{V}_{NN}$, between electrons, $\hat{V}_{ee}$, and between electrons and nuclei, $\hat{V}_{eN}$. Each term can then be calculated using:

$$\begin{aligned}
\hat{K}_N &= -\sum_{i}^{\text{nuclei}} \frac{\hbar^2}{2M_i}\nabla^2_{\mathbf{R}_i} \\
\hat{K}_e &= -\sum_{i}^{\text{electrons}} \frac{\hbar^2}{2m_e}\nabla^2_{\mathbf{r}_i} \\
\hat{V}_{NN} &= \sum_i \sum_{j>i} \frac{Z_i Z_j e^2}{4\pi\varepsilon_0 \left|\mathbf{R}_i - \mathbf{R}_j\right|} \\
\hat{V}_{eN} &= -\sum_i \sum_j \frac{Z_i e^2}{4\pi\varepsilon_0 \left|\mathbf{R}_i - \mathbf{r}_j\right|} \\
\hat{V}_{ee} &= \sum_i \sum_{i<j} \frac{e^2}{4\pi\varepsilon_0 \left|\mathbf{r}_i - \mathbf{r}_j\right|}
\end{aligned} \tag{29.1.2}$$

where M_i, Z_i, and $\mathbf{R}_i$ are the mass, atomic number, and coordinates of nucleus i, respectively, and all other symbols are the same as those used in Equation 26.1 for the many-electron atom Hamiltonian.

Small terms in the molecular Hamiltonian

The operator in Equation 29.1.1 is known as the "exact" nonrelativistic Hamiltonian in field-free space. However, it is important to remember that it neglects at least two effects. Firstly, although the speed of an electron in a hydrogen atom is less than 1% of the speed of light, relativistic mass corrections can become appreciable for the inner electrons of heavier atoms. Secondly, we have neglected the spin-orbit effects, which is explained as follows. From the point of view of an electron, it is being orbited by a nucleus which produces a magnetic field (proportional to $\mathbf{L}$); this field interacts with the electron's magnetic moment (proportional to $\mathbf{S}$), giving rise to a spin-orbit interaction (proportional to $\mathbf{L} \cdot \mathbf{S}$ for a diatomic.) Although spin-orbit effects can be important, they are generally neglected in quantum chemical calculations, and we will neglect them in the remainder of this textbook as well.

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29.2: The Born-Oppenheimer Approximation

As we already saw in the previous chapter, if a Hamiltonian is separable into two or more terms, then the total eigenfunctions are products of the individual eigenfunctions of the separated Hamiltonian terms. The total eigenvalues are then sums of individual eigenvalues of the separated Hamiltonian terms.

For example. let's consider a Hamiltonian that is separable into two terms, one involving coordinate q_1 and the other involving coordinate q_2:

$$\hat{H} = \hat{H}_1(q_1) + \hat{H}_2(q_2) \tag{29.2.1}$$

with the overall Schrödinger equation being:

$$\hat{H}\psi(q_1, q_2) = E\psi(q_1, q_2). \tag{29.2.2}$$

If we assume that the total wave function can be written in the form:

$$\psi(q_1, q_2) = \psi_1(q_1)\psi_2(q_2), \tag{29.2.3}$$

where $\psi_1(q_1)$ and $\psi_2(q_2)$ are eigenfunctions of $\hat{H}_1$ and $\hat{H}_2$ with eigenvalues E_1 and E_2, then:

$$\begin{aligned} \hat{H}\psi(q_1, q_2) &= (\hat{H}_1 + \hat{H}_2)\psi_1(q_1)\psi_2(q_2) \\ &= \hat{H}_1\psi_1(q_1)\psi_2(q_2) + \hat{H}_2\psi_1(q_1)\psi_2(q_2) \\ &= E_1\psi_1(q_1)\psi_2(q_2) + E_2\psi_1(q_1)\psi_2(q_2) \\ &= (E_1 + E_2)\psi_1(q_1)\psi_2(q_2) \\ &= E\psi(q_1, q_2) \end{aligned} \tag{29.2.4}$$

Thus the eigenfunctions of $\hat{H}$ are products of the eigenfunctions of $\hat{H}_1$ and $\hat{H}_2$, and the eigenvalues are the sums of eigenvalues of $\hat{H}_1$ and $\hat{H}_2$.

If we examine the nonrelativistic Hamiltonian in Equation 27.1.1, we see that the $\hat{V}_{en}$ terms prevents us from cleanly separating the electronic and nuclear coordinates and writing the total wave function. If we neglect these terms, we can write the total wave function as:

$$\psi(\mathbf{r}, \mathbf{R}) = \psi_e(\mathbf{r})\psi_N(\mathbf{R}), \tag{29.2.5}$$

This approximation is called the **Born-Oppenheimer approximation**, and allows us to treat the nuclei as nearly fixed with respect to electron motion. The Born-Oppenheimer approximation is almost always quantitatively correct, since the nuclei are much heavier than the electrons and the (fast) motion of the latter does not affect the (slow) motion of the former. Using this approximation, we can fix the nuclear configuration at some value, $\mathbf{R_a}$, and solve for the electronic portion of the the wave function, which is dependent only parametrically on $\mathbf{R}$ (we write this wave function as $\psi_e(\mathbf{r}; \mathbf{R_a})$, where the semicolon indicate the parametric dependence on the nuclear configuration). To solve the TISEq we can then write the electronic Hamiltonian as:

$$\hat{H}_e = \hat{K}_e(\mathbf{r}) + \hat{V}_{eN}(\mathbf{r}; \mathbf{R_a}) + \hat{V}_{ee}(\mathbf{r}) \tag{29.2.6}$$

where we have also factored out the nuclear kinetic energy, $\hat{K}_N$ (since it is smaller than $\hat{K}_e$ by a factor of $\frac{M_i}{m_e}$), as well as $\hat{V}_{NN}(\mathbf{R})$. This latter approximation is justified, since in the Born-Oppenheimer approximation $\mathbf{R}$ is just a parameter, and $\hat{V}_{NN}(\mathbf{R_a})$ is a constant that shifts the eigenvalues only by some fixed amount. This electronic Hamiltonian results in the following TISEq:

$$\hat{H}_e\psi_e(\mathbf{r}; \mathbf{R_a}) = E_e\psi_e(\mathbf{r}; \mathbf{R_a}), \tag{29.2.7}$$

which is the equation that is used to explain the chemical bond in the next section. Notice that Equation 29.2.7 is not the total TISEq of the system, since the nuclear eigenfunction and its eigenvalues (which can be obtained solving the Schrödinger equation with the nuclear Hamiltonian) are neglected. As a final note, in the remainder of this textbook we will confuse the term "total energy" with "total energy at fixed geometry", as is customary in many other quantum chemistry textbooks (i.e., we are neglecting the nuclear kinetic energy). This is just E_e of Equation 29.2.7, plus the constant shift,$\hat{V}_{NN}(\mathbf{R_a})$, given by the nuclear-

nuclear repulsion.

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29.3: Solving the Electronic Eigenvalue Problem

Once we have invoked the Born-Oppenheimer approximation, we can attempt to solve the electronic TISEq in Equation 27.2.7. However, for molecules with more than one electron, we need to—once again—keep in mind the antisymmetry of the wave function. This obviously means that we need to write the electronic wave function as a Slater determinant (i.e., all molecules but H_2^+ and a few related highly exotic ions). Once this is done, we can work on approximating the Hamiltonian, a task that is necessary because the presence of the electron-electron repulsion term forbids its analytic treatment. Similarly to the many-electron atom case, the simplest approximation to solve the molecular electronic TISEq is to use the variational method and to neglect the electron-electron repulsion. As we noticed in the previous chapter, this approximation is called the Hartree-Fock method.

The Hartree-Fock Method

The main difference when we apply the variational principle to a molecular Slater determinant is that we need to build orbitals (one-electron wave functions) that encompass the entire molecule. This can be done by assuming that the atomic contributions to the molecular orbitals will closely resemble the orbitals that we obtained for the hydrogen atom. The total molecular orbital can then be built by linearly combine these atomic contributions. This method is called **linear combination of atomic orbitals (LCAO)**. A consequence of the LCAO method is that the atomic orbitals on two different atomic centers are not necessarily orthogonal, and Equation 26.2.4 cannot be simplified easily. If we replace each atomic orbital $\psi(\mathbf{r})$ with a linear combination of suitable basis functions $f_i(\mathbf{r})$:

$$\psi(\mathbf{r}) = \sum_i^m c_i f_i(\mathbf{r}), \tag{29.3.1}$$

we can then use the following notation:

$$H_{ij} = \int \phi_i^* \hat{H} \phi_j d\tau \, , \qquad S_{ij} = \int \phi_i^* \phi_j d\tau, \tag{29.3.2}$$

to simplify Equation 26.2.4 to:

$$E[\Phi] = \frac{\sum_{ij} c_i^* c_j H_{ij}}{\sum_{ij} c_i^* c_j S_{ij}}. \tag{29.3.3}$$

Differentiating this energy with respect to the expansion coefficients c_i yields a non-trivial solution only if the following "secular determinant" equals zero:

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} & \cdots & H_{1m} - ES_{1m} \\ H_{21} - ES_{21} & H_{22} - ES_{22} & \cdots & H_{2m} - ES_{2m} \\ \vdots & \vdots & \ddots & \vdots \\ H_{m1} - ES_{m1} & H_{m2} - ES_{m2} & \cdots & H_{mm} - ES_{mm} \end{vmatrix} = 0 \tag{29.3.4}$$

where m is the number of basis functions used to expand the atomic orbitals. Solving this set of equations with a Hamiltonian where the electron-electron correlation is neglected results is non-trivial, but possible. The reason for the complications comes from the fact that even if we are neglecting the direct interaction between electrons, each of them interact with the nuclei through an interaction that is screened by the average field of all other electrons, similarly to what we saw for the helium atom. This means that the Hamiltonian itself and the value of the coefficients c_i in the wave function mutually depend on each other. A solution to this problem can be achieved numerically using specialized computer programs that use a cycle called the **self-consistent-field (SCF) procedure**. Starting from an initial guess of the coefficients, an approximated Hamiltonian operator is built from them and used to solve Equation 29.3.4. This solution gives updated values of the coefficients, which can then be used to create an improved version of the approximated Hamiltonian. This procedure is repeated until both the coefficients and the operator do not change anymore. From this final solution, the energy of the molecule is then calculated.

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30: THE CHEMICAL BOND IN DIATOMIC MOLECULES

In this chapter we will see a couple of examples of how the concept and mathematics of quantum mechanics can be applied to understand the chemical bond in molecules. We will start from the simplest molecule, the H_2^+ molecular ion, and then we will move on to the simplest two-electron bond in the hydrogen molecule. To simplify the notation in this chapter, we will move away from S.I. units and use a set tailored for molecules, called *atomic units (a.u.)*. This set of units is built by setting $\hbar = e = m_e = a_0 = 1$. As an example of the simplification that a.u. allows, the energy eigenvalues of the hydrogen atom, Equation 21.8, simply becomes $E_n = -\frac{1}{2n^2}$ in the a.u. of energy, which are called Hartrees.

30.1: The Chemical Bond in the Hydrogen Molecular Cation

30.2: The Chemical Bond in the Hydrogen Molecule

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30.1: The Chemical Bond in the Hydrogen Molecular Cation

This system has only one electron, but since its geometry is not spherical (figure 30.1.1), the TISEq cannot be solved analytically as for the hydrogen atom.

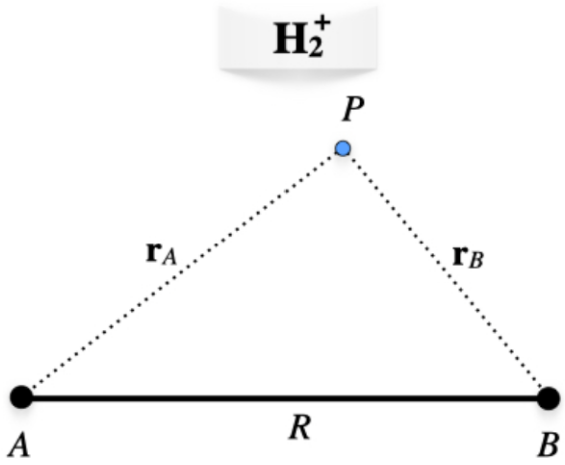


Figure 30.1.1: Geometry of the hydrogen molecular cation.

The electron is at point P, while the two protons are at position A and B at a fixed distance R. Using the Born-Oppenheimer approximation we can write the one-electron molecular Hamiltonian in a.u. as:

$$\hat{H} = \hat{H}_e + \frac{1}{R} = \left(-\frac{1}{2}\nabla^2 - \frac{1}{\mathbf{r}_A} - \frac{1}{\mathbf{r}_B}\right) + \frac{1}{R} \tag{30.1.1}$$

As a first approximation to the variational wave function, we can build the one-electron molecular orbital (MO) by linearly combine two $1s$ hydrogenic orbitals centered at A and B, respectively:

$$\varphi = c_1 a + c_2 b, \tag{30.1.2}$$

with:

$$\begin{aligned} a &= 1s_A = (\psi_{100})_A \\ b &= 1s_B = (\psi_{100})_B . \end{aligned} \tag{30.1.3}$$

Using Equation 27.3.2 and considering that the nuclei are identical, we can define the integrals $H_{aa} = H_{bb}, H_{ab} = H_{ba}$ and $S_{ab} = S$ (while $S_{aa} = 1$ because the hydrogen atom orbitals are normalized). The secular equation, Equation 27.3.4 can then be written:

$$\begin{vmatrix} H_{aa} - E & H_{ab} - ES \\ H_{ab} - ES & H_{aa} - E \end{vmatrix} = 0 \tag{30.1.4}$$

The expansion of the determinant results into:

$$\begin{aligned} (H_{aa} - E)^2 &= (H_{ab} - ES)^2 \\ H_{aa} - E &= \pm(H_{ab} - ES), \end{aligned} \tag{30.1.5}$$

with roots:

$$E_+ = \frac{H_{aa} + H_{ab}}{1+S} = H_{aa} + \frac{H_{ba} - SH_{aa}}{1+S},$$
$$E_- = \frac{H_{aa} - H_{ab}}{1-S} = H_{aa} - \frac{H_{ba} - SH_{aa}}{1-S}, \tag{30.1.6}$$

the first corresponding to the ground state, the second to the first excited state. Solving for the best value for the coefficients of the linear combination for the ground state E_+, we obtain:

$$c_1 = c_2 = \frac{1}{\sqrt{2+2S}}, \tag{30.1.7}$$

which gives the bonding MO:

$$\varphi_+ = \frac{a+b}{\sqrt{2+2S}}. \tag{30.1.8}$$

Proceeding similarly for the excited state, we obtain:

$$c_1 = \frac{1}{\sqrt{2-2S}} \quad c_2 = -\frac{1}{\sqrt{2-2S}}, \tag{30.1.9}$$

which gives the antibonding MO:

$$\varphi_- = \frac{b-a}{\sqrt{2-2S}}. \tag{30.1.10}$$

These results can be summarized in the molecular orbital diagram of figure 30.1.2 We notice that the splitting of the doubly degenerate atomic level under the interaction is non-symmetric for $S \neq 0$, the antibonding level being more repulsive and the bonding less attractive than the symmetric case occurring for $S = 0$.

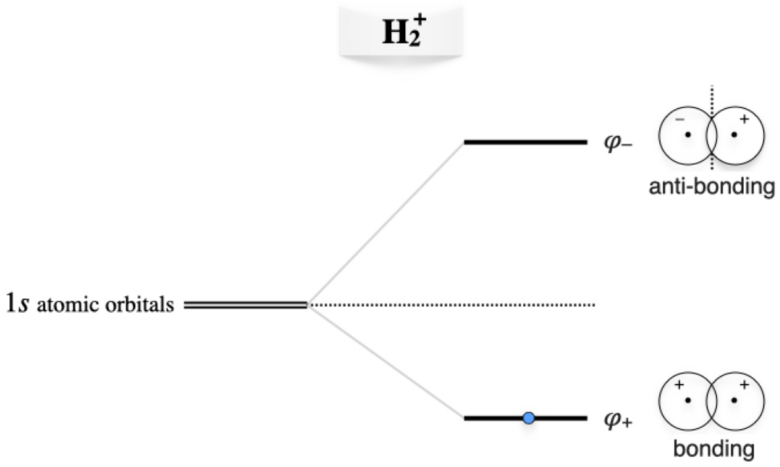


Figure 30.1.2: Molecular orbitals diagram for the hydrogen molecular cation.

Calculating the values for the integrals and repeating these calculations for different internuclear distances, R, results in the plot of figure 30.1.3 As we see from the plots, the ground state solution is negative for a vast portion of the plot. The energy is negative because the electronic energy calculated with the bonding orbital is lower than the nuclear repulsion. In other words, the creation of the molecular orbital stabilizes the molecular configuration versus the isolated fragments (one hydrogen atom and one proton).

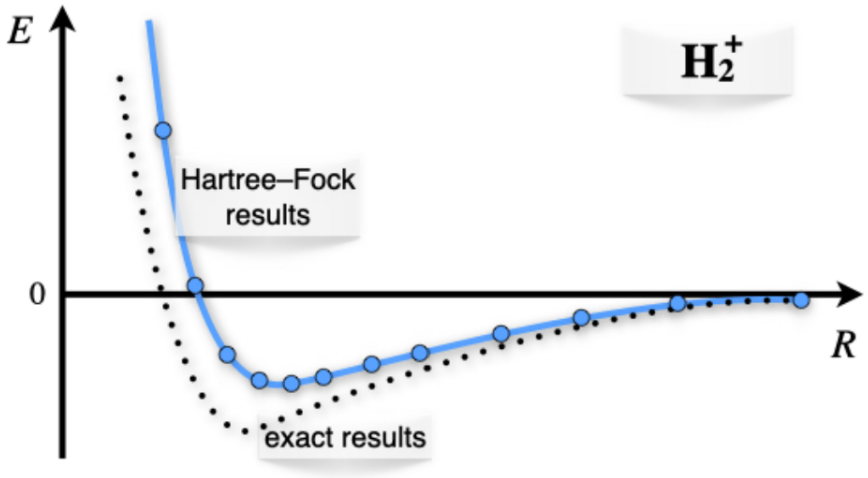


Figure 30.1.3: Born-Oppenheimer energy landscape for the hydrogen molecular cation.

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30.2: The Chemical Bond in the Hydrogen Molecule

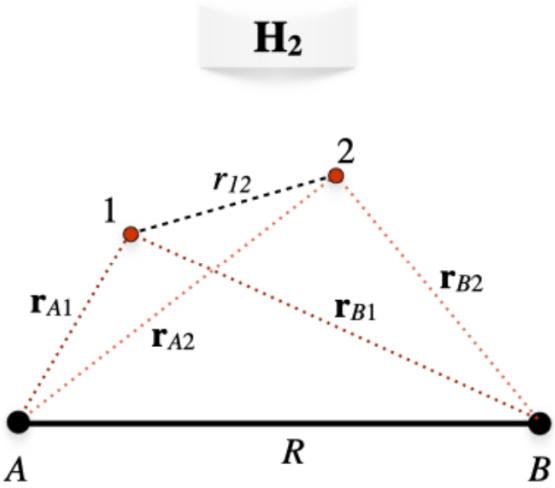


Figure 30.2.1: Geometry of the hydrogen molecule.

We can now examine the formation of the two-electron chemical bond in the H_2 molecule. With reference to figure 30.2.1, the molecular Hamiltonian for H_2 in a.u. in the Born-Oppenheimer approximation will be:

$$\begin{aligned}\hat{H} &= \hat{H}_e + \frac{1}{R} \\ &= \left(-\frac{1}{2}\nabla_1^2 - \frac{1}{\mathbf{r}_{A1}} - \frac{1}{\mathbf{r}_{B1}}\right) + \left(-\frac{1}{2}\nabla_2^2 - \frac{1}{\mathbf{r}_{A2}} - \frac{1}{\mathbf{r}_{B2}}\right) + \frac{1}{r_{12}} + \frac{1}{R} \\ &= \hat{h}_1 + \hat{h}_2 + \frac{1}{r_{12}} + \frac{1}{R},\end{aligned} \tag{30.2.1}$$

where $\hat{h}$ is the one-electron Hamiltonian. As for the previous case, we can build the first approximation to the molecular wave function by considering two $1s$ atomic orbitals $a(\mathbf{r}_1)$ and $b(\mathbf{r}_2)$ centered at A and B, respectively, having an overlap S. If we Neglect the electron-electron repulsion term, $\frac{1}{r_{12}}$, the resulting Hartree-Fock equations are exactly the same as in the previous case. The most important difference, though, is that in this case we need to consider the spin of the two electrons. Proceeding similarly to what we have done for the many-electron atom in chapter 26, we can build an antisymmetric wave function for H_2 using a Slater determinant of doubly occupied MOs. For the ground state, we can use the lowest energy orbital obtained from the solution of the Hartree-Fock equations, which we already obtained in Equation 28.1.8. Using a notation that is based on the symmetry of the molecule, this bonding orbital in H_2 is usually called σ_g, where σ refers to the σ bond that forms between the two atoms. The Slater determinant for the ground state is therefore:[1]

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = |\sigma_g\phi_\uparrow, \sigma_g\phi_\downarrow\rangle, = \sigma_g(\mathbf{r}_1)\sigma_g(\mathbf{r}_2)\frac{1}{\sqrt{2}}\left[\phi_\uparrow\phi_\downarrow - \phi_\downarrow\phi_\uparrow\right], \tag{30.2.2}$$

where:

$$\sigma_g = \varphi_+ = \frac{(\psi_{100})_A + (\psi_{100})_B}{\sqrt{2+2S}}. \tag{30.2.3}$$

The energies and the resulting MO diagram is similar to that for H_2^+, with the only difference that two electron will be described by the same σ_g MO (figure 30.2.2).

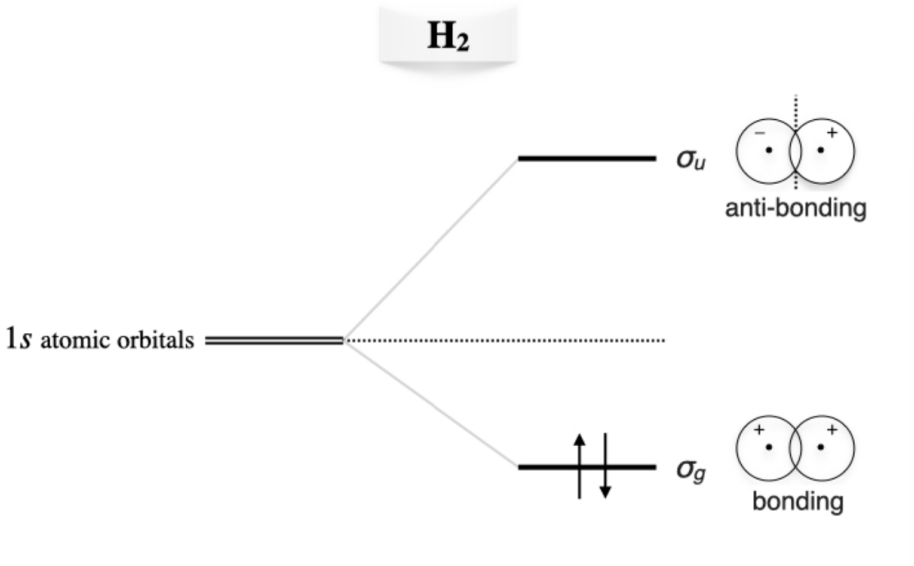


Figure \(\
PageIndex
{2}\):
Molecular orbitals diagram for the hydrogen molecule.

As for the many-electron atoms, the Hartree-Fock method is just an approximation to the exact solution. The accurate theoretical value for the bond energy at the bond distance of $R_e = 1.4\ \ a_0$ is $E = -0.17447\ \ E_h$. The variational result obtained with the wave function in Equation 30.2.2 is $E = -0.12778\ \ E_h$, which is $\sim 73\%$ of the exact value. The variational coefficient (i.e., the orbital exponent, c_0, that enters the $1s$ orbital formula $\psi_{100} = \frac{1}{\pi}\exp[c_0 r]$) is optimized at $c_0 = 1.1695$, a value that shows how the orbitals significantly contract due to spherical polarization.

If we scan the Born-Oppenheimer energy landscape using the wave function in Equation 30.2.2 as we have done for H_2^+, we obtain the plot in figure 30.2.3.

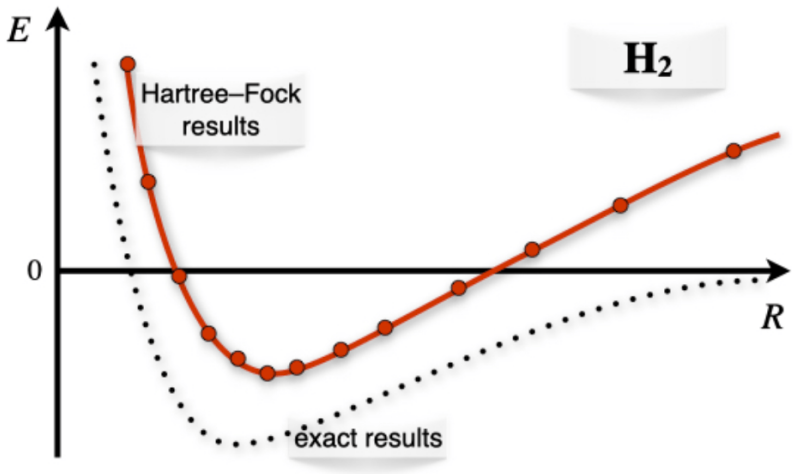


Figure 30.2.3: Born-Oppenheimer energy landscape for the hydrogen molecule.

As we can see, the Hartree-Fock results for H_2 describes the formation of the bond qualitatively around the bond distance (minimum of the curve), but they fail to describe the molecule at dissociation. This happens because in Equation 30.2.2 both electrons are in the same orbital with opposite spin (electrons are coupled), and the orbital is shared among both centers. At dissociation, this corresponds to an erroneous ionic dissociation state where both electron are localized on either one of the

two centers (this center is therefore negatively charged), with the other proton left without electrons. This is in contrast with the correct dissociation, where each electron should be localized around each center (and therefore, it should be uncoupled from the other electron). This error is once again the result of the approximations that are necessary to treat the TISEq of a many-electron system. It is obviously not a failure of quantum mechanics, and it can be easily corrected using more accurate approximations on modern computers.

---

1. Compare this equation to (10.6) for the helium atom.

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31: THE CHEMICAL BOND IN POLYATOMIC MOLECULES

The structure in space of polyatomic molecules depends on the stereochemistry of their chemical bonds and can be determined by solving the (approximated) TISEq using the Born—Oppenheimer approximation using a method that uses a linear combination of atomic orbitals to form molecular orbitals (LCAO-MO).

31.1: The Chemical Bond in the Water Molecule Using a Minimal Basis

31.2: Hartree-Fock Calculation for Water

31.3: Shapes and Energies of Molecular Orbitals

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31.1: The Chemical Bond in the Water Molecule Using a Minimal Basis

For a minimal representation of the two hydrogen atoms, we need two $1s$ functions, one centered on each atom. Oxygen has electrons in the second principal quantum level, so we will need one $1s$, one $2s$, and three $2p$ functions (one each of p_x, p_y, and p_z). Summarizing, for a minimal representation of the water wave function we need five orbitals on oxygen, plus one each on the hydrogen atoms, for a total of 7 functions. From these atomic functions, we can build a total wave function using the LCAO method of chapter 27, and then we can use the variational principle, in conjunction with the Hartree—Fock (HF) method, to build and solve a secular determinant that looks is similar to that in Equation 27.3.4, with $m = 7$ being the total number of basis functions. The approximated Hamiltonian operator in the HF method is called the Fock operator, and it can be divided into one-electron integrals, comprising the kinetic and potential energy contributions:

$$\begin{aligned} K_{ij} &= \int \phi_i^* \hat{K} \phi_j \, d\tau = \int \phi_i^* \left(-\frac{1}{2} \nabla^2 \right) \phi_j \, d\tau \\ V_{ij} &= \int \phi_i^* \hat{V} \phi_j \, d\tau = \int \phi_i^* \left(-\sum_k^{\text{nuclei}} \frac{Z_k}{r_k} \right) \phi_j \, d\tau, \end{aligned} \tag{31.1.1}$$

as well as two-electron integrals describing the coulomb repulsion between electrons:

$$V_{ijkl} = \iint \phi_i^* \phi_j^* \hat{r}_{12} \phi_k \phi_l \, d\tau_1 d\tau_2 = \iint \phi_i^* \phi_j^* \left(\frac{1}{r_{12}} \right) \phi_k \phi_l \, d\tau_1 d\tau_2. \tag{31.1.2}$$

Despite the minimal basis set, the total number of integrals that need to be calculated for water is large, since i, j, k, and l can be any one of the 7 basis functions. Hence there are $7 \times 7 = 49$ kinetic energy integrals, and the same number of potential energy integrals for each nucleus, resulting in $7 \times 7 \times 3 = 147$. The grand total of one-electron integrals is thus 196. For the two-electron integrals, we have $7 \times 7 \times 7 \times 7 = 2{,}401$ integrals to calculate. Overall for this simple calculation on water, we need almost $2{,}600$ integrals.[1]

All this to find 5 occupied molecular orbitals from which to form a final Slater determinant (10 electrons, two to an orbital, so 5 orbitals). The situation sounds horrible, but it should be recognized that the solutions to all of the integrals are known to be analytic formulae involving only interatomic distances, cartesian exponents, and the values of a single exponent in the atomic functions. If we use slightly simpler gaussian functions instead of the more complicated hydrogenic solutions, the total number of floating-point operations to solve the integrals is roughly $1{,}000{,}000$. In computer speak that's one megaflop (megaflop = million FLoating-point OPerations). A modern digital computer processor can achieve gigaflop per second performance, so the computer can accomplish all these calculations in under one second. An additional way in which things can be improved is to recognize that the molecule has symmetries that can be exploited to reduce the number of total integrals that needs to be calculated.

---

1. The numbers computed here involve the minimum amount of uncontracted "hydrogenic" functions that can be used for calculation on water. In real-life calculations a linear combination of simpler primitive functions (gaussians) is used to describe a single uncontracted function. For example in the simplest case, the STO-3G basis set, each uncontracted function is composed of 3 primitive gaussian functions. Thus, for any individual one-electron integral, there will be $3 \times 3 = 9$ separate integrals involving the primitives. There are thus $9 \times 196 = 1{,}764$ individual primitive one-electron integrals. As for the two-electron integrals, again, every individual integral will require considering every possible combination of constituent primitives which is $3 \times 3 \times 3 \times 3 = 81$. Thus, the total number of primitive two-electron integrals is $81 \times 2{,}401 = 194{,}481$ (gulp!) Notice that even for this small molecule the number of two-electron integrals totally dominates the number of one-electron integrals. The disparity only increases with molecular size. Notice: Portions of this section are based on Prof. C.J. Cramer's lecture notes available (here)[http://pollux.chem.umn.edu/4502/3502_lecture_29.pdf]

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31.2: Hartree-Fock Calculation for Water

To find the Hartree-Fock (HF) molecular orbitals (MOs) we need to solve the following secular determinant:

$$\begin{vmatrix} F_{11}-ES_{11} & F_{12}-ES_{12} & \cdots & F_{17}-ES_{17} \\ F_{21}-ES_{21} & F_{22}-ES_{22} & \cdots & F_{27}-ES_{27} \\ \vdots & \vdots & \ddots & \vdots \\ H_{71}-ES_{71} & F_{72}-ES_{72} & \cdots & F_{77}-ES_{77} \end{vmatrix} = 0 \tag{31.2.1}$$

with S_{ij} being the overlap integrals of Equation 27.3.2, and F_{ij} the matrix elements of the Fock operator, defined using the one- and two-electron integrals in Equation 29.1.1 and Equation 29.1.2 as:

$$F_{ij} = K_{ij} + V_{ij} + \sum_{kl} P_{kl}\left[V_{ijkl} - \frac{1}{2}V_{ikjl}\right], \tag{31.2.2}$$

with the density matrix elements P_{kl} defined as:

$$P_{kl} = 2\sum_{i}^{\text{occupied}} a_{ki}a_{li}, \tag{31.2.3}$$

where the a values are the coefficients of the basis functions in the occupied molecular orbitals. These values will be determined using the SCF procedure, which proceeds as follows: At the first step we simply guess what these are, then we iterate through solution of the secular determinant to derive new coefficients and we continue to do so until self-consistency is reached (i.e. the $N+1$ step provides coefficients and energies that are equal to those in the N step).

We can try to solve the SCF procedure for water using a fixed geometry of the nuclei close to the experimental structure: O-H bond lengths of $0.95\ \dot{A}$ and a valence bond angle at oxygen of 104.5°. To do so, we can use a minimal basis functions composed of the following seven orbitals: basis function #1 is an oxygen $1s$ orbital, #2 is an oxygen $2s$ orbital, #3 is an oxygen $2p_x$ orbital, #4 is an oxygen $2p_y$ orbital, #5 is an oxygen $2p_z$ orbital, #6 is one hydrogen $1s$ orbital, and #7 is the other hydrogen $1s$ orbital. The corresponding integrals introduced in the previous section can be calculated using a quantum chemistry code. The calculated overlap matrix elements are:

$$\mathbf{S} = \begin{bmatrix} \text{O } 1s & \text{O } 2s & \text{O } 2p_x & \text{O } 2p_y & \text{O } 2p_z & \text{H}_a\ 1s & \text{H}_b\ 1s & \\ 1.000 & & & & & & & \text{O } 1s \\ 0.237 & 1.000 & & & & & & \text{O } 2s \\ 0.000 & 0.000 & 1.000 & & & & & \text{O } 2p_x \\ 0.000 & 0.000 & 0.000 & 1.000 & & & & \text{O } 2p_y \\ 0.000 & 0.000 & 0.000 & 0.000 & 1.000 & & & \text{O } 2p_z \\ 0.055 & 0.479 & 0.000 & 0.313 & -0.242 & 1.000 & & \text{H}_a\ 1s \\ 0.055 & 0.479 & 0.000 & -0.313 & -0.242 & 0.256 & 1.000 & \text{H}_b\ 1s \end{bmatrix} \tag{31.2.4}$$

There are many noteworthy features in $\mathbf{S}$. First, it is shown in a lower packed triangular form because every element j,i is the same as the element i,j by symmetry, and every diagonal element is 1 because the basis functions are normalized. Note that, again by symmetry, every p orbital on oxygen is orthogonal (overlap = zero) with every s orbital and with each other, but the two s orbitals do overlap (this is due to the fact that they are not pure hydrogenic orbitals—which would indeed be orthogonal—but they have been optimized, so $S_{12} = 0.237$). Note also that the oxygen $1s$ orbital overlaps about an order of magnitude less with any hydrogen $1s$ orbital than does the oxygen $2s$ orbital, reflecting how much more rapidly the first quantum-level orbital decays compared to the second. Note that by symmetry the oxygen p_x cannot overlap with the hydrogen $1s$ functions (positive overlap below the plane exactly cancels negative overlap above the plane) and that the oxygen p_y overlaps with the two hydrogen $1s$ orbitals equally in magnitude but with different sign because the p orbital has different phase at its different ends. Finally, the overlap of the p_z is identical with each H $1s$ because it is not changing which lobe it uses to interact. The kinetic energy matrix (in a.u.) is:

$$\mathbf{K} = \begin{bmatrix} 29.003 & & & & & & \\ -0.168 & 0.808 & & & & & \\ 0.000 & 0.000 & 2.529 & & & & \\ 0.000 & 0.000 & 0.000 & 2.529 & & & \\ 0.000 & 0.000 & 0.000 & 0.000 & 2.529 & & \\ -0.002 & 0.132 & 0.000 & 0.229 & -0.177 & 0.760 & \\ -0.002 & 0.132 & 0.000 & -0.229 & -0.177 & 0.009 & 0.760 \end{bmatrix} \tag{31.2.5}$$

Notice that every diagonal term is much larger than any off-diagonal term. Recall that each each kinetic energy integral, Equation 29.1.1, involves the Laplacian operator, ∇^2. The Laplacian reports back the sum of second derivatives in all coordinate directions. That is, it is a measure of how fast the slope of the function is changing in various directions. If we take two atomic orbitals μ and ν far apart from each other, then since gaussians go to zero at least exponentially fast with distance, ν is likely to be very flat where μ is large. The second derivative of a flat function is zero. So, every point in the integration will be roughly the amplitude of μ times zero, and not much will accumulate. For the diagonal element, on the other hand, the interesting second derivatives will occur where the function has maximum amplitude (amongst other places) so the accumulation should be much larger. Notice also that off-diagonal terms can be negative. That is because there is no real physical meaning to a kinetic energy expectation value involving two different orbitals. It is just an integral that appears in the complete secular determinant. Symmetry again keeps p orbitals from mixing with s orbitals or with each other. The nuclear attraction matrix is:

$$\mathbf{V} = \begin{bmatrix} -61.733 & & & & & & \\ -7.447 & -10.151 & & & & & \\ 0.000 & 0.000 & -9.926 & & & & \\ 0.000 & 0.000 & 0.000 & -10.152 & & & \\ 0.000 & 0.000 & 0.000 & 0.000 & -10.088 & & \\ -1.778 & -3.920 & 0.000 & -0.228 & -0.184 & -5.867 & \\ -1.778 & -3.920 & 0.000 & 0.228 & 0.184 & -1.652 & -5.867 \end{bmatrix} \tag{31.2.6}$$

Again, diagonal elements are bigger than off-diagonal elements because the $1/r$ operator acting on a basis function ν will ensure that the largest contribution to the overall integral will come from the nucleus k on which basis function ν resides. Unless μ also has significant amplitude around that nucleus, it will multiply the result by roughly zero and the whole integral will be small. Again, positive values can arise when two different functions are involved even though electrons in a single orbital must always be attracted to nuclei and thus diagonal elements must always be negative. Note that the p orbitals all have different nuclear attractions. That is because, although they all have the same attraction to the O nucleus, they have different amplitudes at the H nuclei. The p_x orbital has the smallest amplitude at the H nuclei (zero, since they are in its nodal plane), so it has the smallest nuclear attraction integral. The p_z orbital has somewhat smaller amplitude at the H nuclei than the p_y orbital because the bond angle is greater than 90° (it is 104.5°; if it were 90° the O-H bonds would bisect the p_y and p_z orbitals and their amplitudes at the H nuclei would necessarily be the same). Thus, the nuclear attraction integral for the latter orbital is slightly smaller than for the former.

The sum of the kinetic and nuclear attraction integrals is usually called the one- electron or core part of the Fock matrix and abbreviated $\mathbf{h}$ (i.e., $\mathbf{h} = \mathbf{K} + \mathbf{V}$). One then writes $\mathbf{F} = \mathbf{h} + \mathbf{G}$ where $\mathbf{F}$ is the Fock matrix, $\mathbf{h}$ is the one-electron matrix, and $\mathbf{G}$ is the remaining part of the Fock matrix coming from the two-electron four-index integrals (cf Equation 31.2.2). To compute those two-electron integrals, however, we need the density matrix, which itself comes from the occupied MO coefficients. So, we need an initial guess at those coefficients. We can get such a guess many ways, but ultimately any guess is as good as any other. With these coefficients we can compute the density matrix using Equation 31.2.3:

$$\mathbf{P} = \begin{bmatrix} 2.108 & & & & & & \\ -0.456 & 2.010 & & & & & \\ 0.000 & 0.000 & 2.000 & & & & \\ 0.000 & 0.000 & 0.000 & 0.737 & & & \\ -0.104 & 0.618 & 0.000 & 0.000 & 1.215 & & \\ -0.022 & -0.059 & 0.000 & 0.539 & -0.482 & 0.606 & \\ -0.022 & -0.059 & 0.000 & -0.539 & -0.482 & -0.183 & 0.606 \end{bmatrix} \tag{31.2.7}$$

With $\mathbf{P}$, we can compute the remaining contribution of $\mathbf{G}$ to the Fock matrix. We will not list all 406 two-electron integrals here. Instead, we will simply write the total Fock matrix:

$$\mathbf{F} = \begin{bmatrix} -20.236 & & & & & & \\ -5.163 & -2.453 & & & & & \\ 0.000 & 0.000 & -0.395 & & & & \\ 0.000 & 0.000 & 0.000 & -0.327 & & & \\ 0.029 & 0.130 & 0.000 & 0.000 & -0.353 & & \\ -1.216 & -1.037 & 0.000 & -0.398 & 0.372 & -0.588 & \\ -1.216 & -1.037 & 0.000 & 0.398 & 0.372 & -0.403 & -0.588 \end{bmatrix} \tag{31.2.8}$$

So, we're finally ready to solve the secular determinant, since we have $\mathbf{F}$ and $\mathbf{S}$ fully formed. When we do that, and then solve for the MO coefficients for each root E, we get new occupied MOs. Then, we iterate again, and again, and again, until we are satisfied that further iterations will not change either our (i) energy, (ii) density matrix, or (iii) MO coefficients (it's up to the quantum chemist to decide what is considered satisfactory).

In our water calculation, if we monitor the energy at each step we find:

$$\begin{aligned} E(RHF) &= -74.893\,002\,803 && \text{a.u. after 1 cycles} \\ E(RHF) &= -74.961\,289\,145 && \text{a.u. after 2 cycles} \\ E(RHF) &= -74.961\,707\,247 && \text{a.u. after 3 cycles} \\ E(RHF) &= -74.961\,751\,946 && \text{a.u. after 4 cycles} \\ E(RHF) &= -74.961\,753\,962 && \text{a.u. after 5 cycles} \\ E(RHF) &= -74.961\,754\,063 && \text{a.u. after 6 cycles} \\ E(RHF) &= -74.961\,754\,063 && \text{a.u. after 7 cycles} \end{aligned} \tag{31.2.9}$$

Which means that our original guess was really not too bad—off by a bit less than 0.1 a.u. or roughly 60 kcal mol^{-1}. Our guess energy is too high, as the variational principle guarantees that it must be. Our first iteration through the secular determinant picks up nearly 0.07 a.u., our next iteration an additional $0.000\ 42$ or so, and by the end we are converged to within 1 nanohartree ($0.000\ 0006$ kcal mol^{-1}).

The final optimized MOs for water are:

	1	2	3	4	5	6	7
E	−20.24094	−1.27218	−.62173	−.45392	−.39176	.61293	.75095
1	.99411	−.23251	.00000	−.10356	.00000	−.13340	.00000
2	.02672	.83085	.00000	.53920	.00000	.89746	.00000
3	.00000	.00000	.00000	.00000	1.0000	.00000	.00000
4	.00000	.00000	.60677	.00000	.00000	.00000	.99474
5	−.00442	−.13216	.00000	.77828	.00000	−.74288	.00000
6	−.00605	.15919	.44453	−.27494	.00000	−.80246	−.84542
7	−.00605	.15919	−.44453	−.27494	.00000	−.80246	.84542

(31.2.10)

where the first row reports the eigenvalues of each MO, in E_h (i.e., the energy of one electron in the MO). The sum of all of the occupied MO energies should be an underestimation of the total electronic energy because electron-electron repulsion will have been double counted. So, if we sum the occupied orbital energies (times two, since there are two electrons in each orbital), we get $2(-20.24094\ -1.27218\ -0.62173\ -0.45392\ -0.39176) = -45.961\ 060$. If we now subtract the electron-electron repulsion energy $38.265\ 406$ we get $-84.226\ 466$. If we add the nuclear repulsion energy $9.264\ 701$ to this we get a total energy $-74.961\ 765$. The difference between this and the converged result above ($-74.961\ 754$) can be attributed to rounding in the MO energies, which are truncated after 5 places. Notice that the five occupied MOs all have negative energies. So, their electrons are bound within the molecule. The unoccupied MOs (called "virtual" MOs) all have positive energies, meaning that the molecule will not spontaneously accept an electron from another source.

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31.3: Shapes and Energies of Molecular Orbitals

If we analyze the optimized coefficients of the occupied MOs reported in Equation 29.2.10, we observe that the lowest energy orbital (by a lot!) is a nearly pure oxygen $1s$ orbital since the coefficient of the oxygen $1s$ basis function is very nearly 1 and all other coefficients are rather close to 0. Note, however, that the coefficient is not really a percentage measure. That's because the basis functions are not necessarily orthogonal to one another. Let's consider the next molecular orbital up, number 2. It has a dominant contribution from the oxygen $2s$ basis function, but non-trivial contributions from many other basis functions as well. In order to understand which kind of orbital it is, it is useful to try to visualize some of its properties. For example, recall that the square of the orbital at a particular point in space represents a probability density. As such, we can map values of the square of each orbital on a grid in 3-dimensional space, and then pick a value of probability density, say $0.04\ a_0^{-3}$, and plot that as a contour surface (remember that a probability density is a 4-dimensional quantity, so we need to take a slice at some constant density to be able to plot it in 3-D). That surface is called an "isodensity" surface. In addition to the square of the function, we can also regions where the wave function is positive blue and regions where it's negative red. The five occupied and two unoccupied MOs mapped from their one-electron wave functions are plotted in figuere 31.3.1.

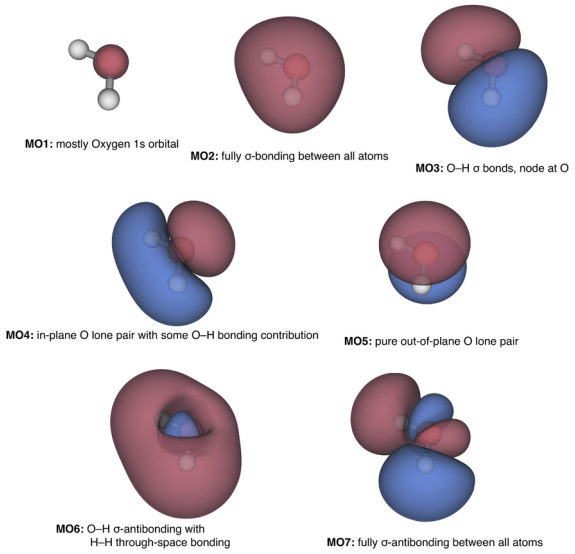


Figure 31.3.1: Isodensity maps of the Molecular Orbitals (MOs) of water.

Going back to the Lewis structure of water as taught in general chemistry courses, it says that there is one pair of electrons in one O–H σ bond, one pair in another identical such σ bond, and two equivalent pairs that constitute the lone pairs on oxygen. The two lone pairs and the O–H bonds should by pointing towards the apices of a tetrahedron because they are all considered to be sp^3 hybridized.

As you can see, the MOs look nothing like the Lewis picture. Instead, amongst other details, there is one lone pair that is pure p (not sp^3), another that is, if anything, sp^2-like, but also enjoys contribution from hydrogen $1s$ components. There is one orbital that looks like both O–H σ bonds are present, but another that has an odd "bonding-all-over" character to it.

Is it really possible that for something as simple as water all the things you've ever been told about the Lewis structure are wrong? Water must have two equivalent lone pairs, right?

It turns out that the molecular orbital results can be tested with spectroscopic experiments, and suffice to say, they agree perfectly.

But the sp^3-hybridized picture of water works well, for example, to explain its hydrogen-bonding behavior: In liquid water each water molecule makes two hydrogen bonds to other water molecules and accepts two more from different water molecules and the final structure has a net lattice-like form that is tetrahedral at each oxygen atom. How can the above MOs explain that? The key point to remember is that another molecule does not see the individual orbitals of water, it just sees the final effect of all of those electrons and nuclei **together**. To explain the tetrahedral H-bond lattice we can plot some constant level of electron

density (i.e. $0.02) and map onto this isodensity surface the values of the electrostatic potential. We can find these values by bringing a positive test charge onto that surface and recording how much would it find itself attracted (because of a net negative electrostatic potential) or repelled (because of a net positive electrostatic potential). This is done in figure 31.3.2. Notice how the negative potential is entirely on the oxygen side and the positive potential entirely on the hydrogens side. Moreover, the negative potential splays out to the tetrahedral points and the positive potential does too (those points for the purple region being roughly where the H atoms are).

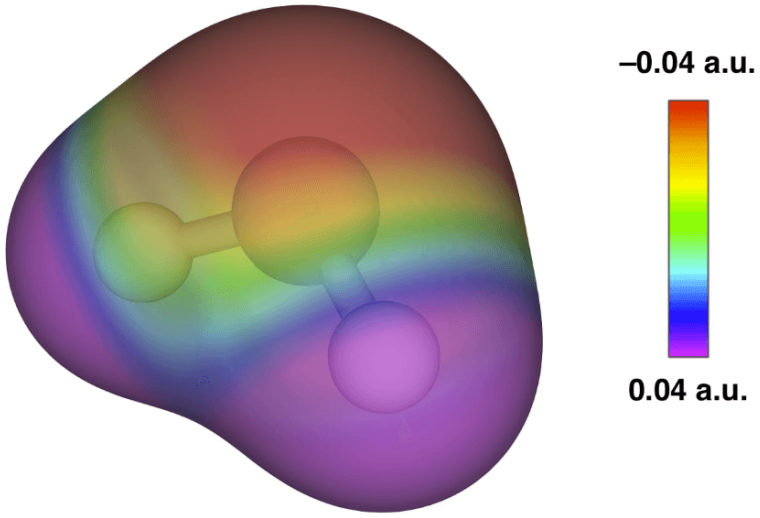


Figure 31.3.2: Molecular electrostatic potential of water plotted on a 0.02 a.u. isodensity surface.

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32: GROUP THEORY - EXPLOITING SYMMETRY

32.1: Using Symmetry to Simplify Calculations

32.2: The Symmetry of Molecules

32.3: Symmetry Operations Define Groups

32.4: Symmetry Operations can be Represented by Matrices

32.5: The C_3V Point Group Has a 2-D Irreducible Representation

32.6: Character Tables

32.7: Relations involving Characters

32.8: Using Symmetry to Predict Zero in a Secular Determinant

32.9: Generating Operators for Irreducible Representations

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32.1: Using Symmetry to Simplify Calculations

To a fully understand the math behind group theory one needs to take a look at the theory portion of the Group Theory topic or refer to one of the reference text listed at the bottom of the page. Never the less as Chemist the object in question we are examining is usually a molecule. Though we live in the 21st century and much is known about the physical aspects that give rise to molecular and atomic properties. The number of high level calculations that need to be performed can be both time consuming and tedious. To most experimentalist this task is takes away time and is usually not the integral part of their work. When one thinks of group theory applications one doesn't necessarily associated it with everyday life or a simple toy like a Rubik's cube. A Rubik's cube is an a cube that has a 3×3 array of different colored tiles on each of its six surfaces, for a total of 54 tiles. Since the cube exist in 3D space, the three axis are x, y, z. Since the rubik's cube only allows rotation which are called operations, there are three such operations around each of the x, y, z axis.

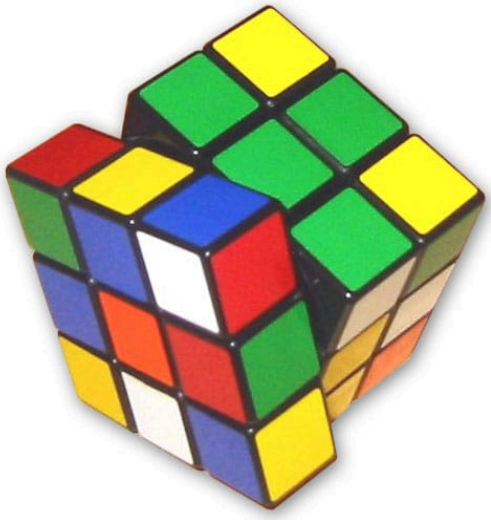


Figure: Reubik's cube. Use with permission from Wikipedia

Of course the ultimate challenge of a Rubik's cube is to place all six colors on each of the six faces. By performing a series of such operations on the Rubik's cube one can arrive at a solution (A link of a person solving a Rubik's cube[1] in 10.4s with operations performed noted, the operations performed will not translate to chemistry applications but it is a good example of how symmetry operations arrive at a solution). The operations shown in the Rubik's cube case are inherent to the make up of the cube, i.e., the only operations allowed are the rotations along the x, y, z axis. Therefore the Rubik's cube only has x,y,z rotation operations. Similarly the operations that are specific to a molecule are dependent on its symmetry.

Using group theory, we can exploit the symmetry of molecules to give us a rich amount of information on the molecular orbitals, rotations, and vibrations of bonds, to name a few. Making symmetry arguments, we can skip complicated quantum calculations to gain qualitatively accurate information.

In section 10.7, we used Hückel theory to explore the π bonding network of benzene by constructing linear combinations of $2p_x$ atomic orbitals on the carbon atoms. In doing so, the roots of the secular equations were found via solving the 6×6 secular determinant.

$$\begin{vmatrix} x & 1 & 0 & 0 & 0 & 1 \\ 1 & x & 1 & 0 & 0 & 0 \\ 0 & 1 & x & 1 & 0 & 0 \\ 0 & 0 & 1 & x & 1 & 0 \\ 0 & 0 & 0 & 1 & x & 1 \\ 1 & 0 & 0 & 0 & 1 & x \end{vmatrix} = 0 \tag{32.1.1}$$

Since the secular determinant is a 6×6 matrix, there are six solutions or values of x that can be determined after expanding the determinant into the resulting (6th-order) polynomial.

$$x^6 - 6x^4 + 9x^2 - 4 = 0 \tag{32.1.2}$$

Secular determinants are formulated in terms of a specific basis set; i.e., a set of functions that describe the wavefunctions. For the determinnat in Equation 32.1.1, that basis set is the the $\{|2p_z\rangle\}$ orbitals on the carbons. However, any basis set can be used to represent the determinant (long as it span the same space). For example, the following linear combination of $\{|2p_z\rangle\}$ orbitals could also be used:

$$\begin{aligned}
|\phi_1\rangle &= \frac{1}{\sqrt{6}}\left[|2p_{z1}\rangle + |2p_{z2}\rangle + |2p_{z3}\rangle + |2p_{z4}\rangle + |2p_{z5}\rangle + |2p_{z6}\rangle\right] \\
|\phi_2\rangle &= \frac{1}{\sqrt{4}}\left[|2p_{z2}\rangle + |2p_{z3}\rangle - |2p_{z4}\rangle - |2p_{z5}\rangle\right] \\
|\phi_3\rangle &= \frac{1}{\sqrt{3}}\left[|2p_{z1}\rangle + \frac{1}{2}|2p_{z2}\rangle - \frac{1}{2}|2p_{z3}\rangle - |2p_{z4}\rangle - \frac{1}{2}|2p_{z5}\rangle + \frac{1}{2}|2p_{z6}\rangle\right] \\
|\phi_4\rangle &= \frac{1}{\sqrt{4}}\left[|2p_{z2}\rangle - |2p_{z3}\rangle + |2p_{z4}\rangle - |2p_{z5}\rangle\right] \\
|\phi_5\rangle &= \frac{1}{\sqrt{3}}\left[|2p_{z1}\rangle - \frac{1}{2}|2p_{z2}\rangle - \frac{1}{2}|2p_{z3}\rangle + |2p_{z4}\rangle - \frac{1}{2}|2p_{z5}\rangle - \frac{1}{2}|2p_{z6}\rangle\right] \\
|\phi_6\rangle &= \frac{1}{\sqrt{6}}\left[|2p_{z1}\rangle - |2p_{z2}\rangle + |2p_{z3}\rangle - |2p_{z4}\rangle + |2p_{z5}\rangle - |2p_{z6}\rangle\right]
\end{aligned}$$

In this new basis set $\{\phi\rangle\}$, the secular determinant Equation 32.1.1 is represented as

$$\begin{vmatrix}
x+2 & 0 & 0 & 0 & 0 & 0 \\
0 & x-2 & 0 & 0 & 0 & 0 \\
0 & 0 & x+1 & \frac{x+1}{2} & 0 & 0 \\
0 & 0 & \frac{x+1}{2} & x+1 & 0 & 0 \\
0 & 0 & 0 & 0 & x-1 & \frac{x-1}{2} \\
0 & 0 & 0 & 0 & \frac{x-1}{2} & x-1
\end{vmatrix} = 0 \tag{32.1.3}$$

This is the determinant into a bock diagonal form; which can be expanded into a product of smaller determinants to give the polynomial

$$\frac{9}{16}(x+2)(x-2)(x+1)^2(x-1)^2 = 0$$

The roots to this equation are ± 2, ± 1 and ± 1. This is not surprising since these are the same roots obtained from expanding the determinant in the original basis set (Equation 32.1.2). You may remember that the selection of a specific basis set to represent a function does not change the fundamental nature of the function (e.g., a parabola in 2D space is the same curve if represented in terms of Cartesian coordinates (x and y) or polar coordinates (θ and r), which both span 2-D space).

As you recall, Hückel theory (irrespective of the basis set) was used to simplify the general secular determinant (e.g., for benzene)

$$\begin{vmatrix}
H_{11} - ES_{11} & H_{12} - ES_{12} & H_{13} - ES_{13} & H_{14} - ES_{14} & H_{15} - ES_{15} & H_{16} - ES_{16} \\
H_{21} - ES_{21} & H_{22} - ES_{22} & H_{23} - ES_{23} & H_{24} - ES_{24} & H_{25} - ES_{25} & H_{26} - ES_{26} \\
H_{31} - ES_{31} & H_{32} - ES_{32} & H_{33} - ES_{33} & H_{34} - ES_{34} & H_{35} - ES_{35} & H_{36} - ES_{36} \\
H_{41} - ES_{41} & H_{42} - ES_{42} & H_{43} - ES_{43} & H_{44} - ES_{44} & H_{45} - ES_{45} & H_{46} - ES_{46} \\
H_{51} - ES_{51} & H_{52} - ES_{52} & H_{53} - ES_{53} & H_{54} - ES_{54} & H_{55} - ES_{55} & H_{56} - ES_{56} \\
H_{61} - ES_{61} & H_{62} - ES_{62} & H_{63} - ES_{63} & H_{64} - ES_{64} & H_{65} - ES_{65} & H_{66} - ES_{6}
\end{vmatrix} = 0 \tag{32.1.4}$$

where H_{ij} are the Hamiltonian matrix elements

$$H_{ij} = \langle \phi_i | \hat{H} | \phi_j \rangle = \int \phi_i H \phi_j \mathrm{d}v$$

and S_{ij} are the overlap integrals.

$$S_{ij} = \langle \phi_i | \phi_j \rangle = \int \phi_i \phi_j \mathrm{d}v$$

In general, this involves solving 36 Hamiltonian matrix elements (H_{ij}) and 36 overlap integrals (S_{ij}), which can be a daunting task to do by hand without the assumptions of Hückel theory to help out. As with the application of Hückel theory, which was used to set most of these integrals to zero, solving for the energies from Equation 32.1.4 can be simplified by using the intrinsic symmetry of the benzene system to demonstrate (rigorously) that many of these integrals are zero. This is the subject of group theory. Group theory is used to exploit the symmetry of molecules to quickly gain insights into their properties, such as vibrations and molecular orbitals.

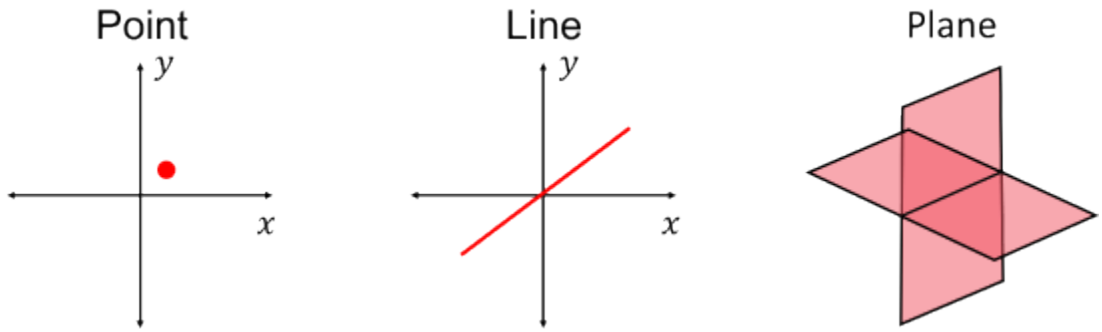
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32.2: The Symmetry of Molecules

Symmetry Elements

A *symmetry operation* is an action that leaves an object looking the same after it has been carried out. For example, if we take a molecule of water and rotate it by 180° about an axis passing through the central O atom (between the two H atoms) it will look the same as before. Each symmetry operation has a corresponding *symmetry element*, which is the axis, plane (2-dimensional), line (1-dimensional) or point (0-dimensional) with respect to which the symmetry operation is carried out:



The symmetry element consists of all the points that stay in the same place when the symmetry operation is performed. In a rotation, the line of points that stay in the same place constitute a *symmetry axis*; in a reflection the points that remain unchanged make up a *plane of symmetry*. The symmetry of a molecule or ion can be described in terms of the complete collection of symmetry operations it possesses. The symmetry elements that a molecule (and any other 3-D object) may possess are discussed below.

Symmetry Operations

The symmetry of a molecule or ion can be described in terms of the complete collection of symmetry operations it possesses. There are five types of operations:

1. Identity, E
2. Rotation, C_n
3. Reflection, σ
4. Inversion, i
5. Improper Rotation, S_n

Symmetry Operations

A symmetry operation is a permutation of atoms such that the molecule is transformed into a state **indistinguishable** from the starting state.

Identity Symmetry, E

The identity operator, E, consists of doing nothing, and the corresponding symmetry element is the entire molecule. Every molecule possesses at least this operation. For example, the $\mathrm{CHFClBr}$ molecule in Figure 12.2.1 . The identify symmetry operation is not indicated since all molecule exhibit this symmetry.

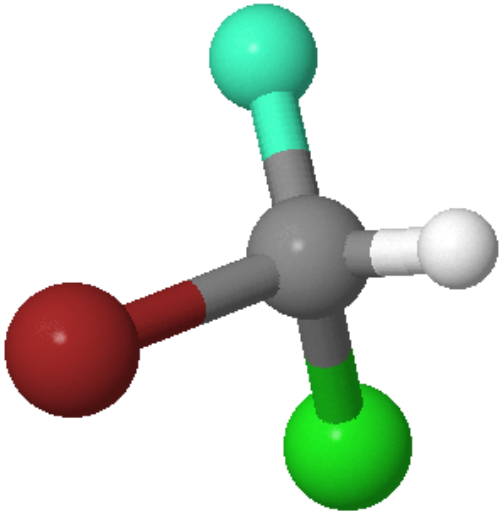


Figure 12.2.1 : Example of Identify Symmetry: The $\mathrm{CHFClBr}$ molecule contain no other symmetry other than identity. Image created via Symmetry @ Otterbein site by Dean Johnston et al.

n-fold Axis of Rotation, C_n

The rotation operation (sometimes called proper rotation), C_n, rotates an object about an axis by $2\pi/n$ radians or $360^\circ/n$. Rotation by C_n leaves the molecule unchanged. The H_2O molecule has a C_2 axis (Figure 12.2.2). Molecules can have more than one C_n axis, in which case the one with the highest value of n is called the *principal axis*. In some high symmetry systems, there may be more than one principal axis. Note that by convention, rotations are *counterclockwise* about the axis. C_n rotations are indicated via vectors with labels as indicated below.

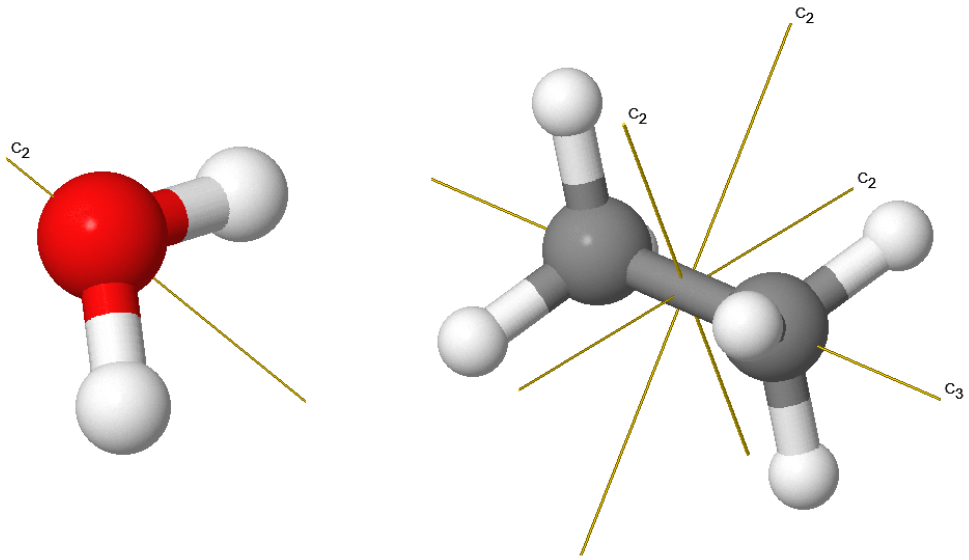


Figure 12.2.2 : Examples of n-fold Axis of Rotation: (left) The water molecule contains a C_2 axis. (right) Ethane contains both C_2 and C_3 axes. Image created via Symmetry @ Otterbein site by Dean Johnston et al.

We always want to express rotations in their simplest equivalent fractions of m/n:

$$C_4^2 = C_2$$

$$C_6^4 = C_3^2$$

$$C_8^6 = C_4^3$$

Rotating an object n times brings the object back to the original object and is equivalent to the identity operation, E:

$$C_n^n = E$$

Linear molecules have a very high rotational symmetry: C_∞. Examples include diatomics such as CO, NO, and $\mathrm{CO_2}$.

Reflection, σ

Reflection, σ, defines the bilateral symmetry about a plane (mirror plane / reflection plane). Reflection in the plane leaves the molecule looking the same. In a molecule that also has an axis of symmetry, a mirror plane that includes the axis is called a vertical mirror plane and is labeled σ_v, while one perpendicular to the axis is called a horizontal mirror plane and is labeled σ_h. A vertical mirror plane that bisects the angle between two C_2 axes is called a dihedral mirror plane, σ_d. If no principal axis exist, σ_h is defined as the plane of the molecule. σ symmetry is indicated as a plane on molecules; since they often bisect atoms, which should be clearly indicated.

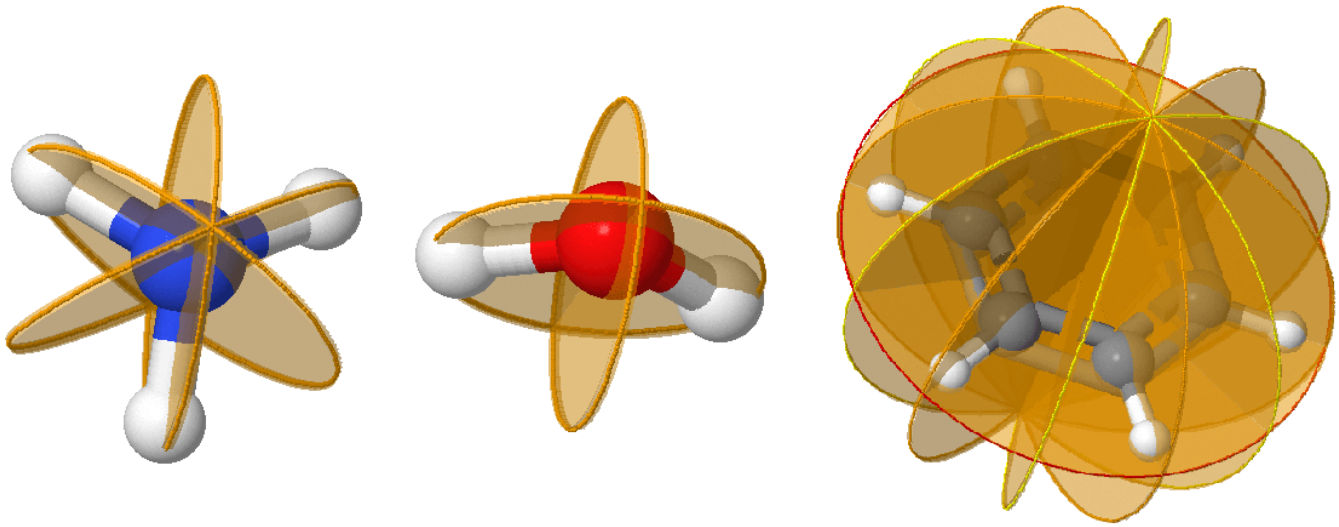


Figure 12.2.3 : Examples of reflection symmetry. (left) The ammonia molecule contains three identical reflection planes. All are designated as vertical symmetry planes (σ_v) because they contain the principle rotation axis.(middle) The water molecule contains two different reflection planes. (right) benzene contains a total of seven reflection planes, one horizontal plane (σ_h) and six vertical planes (σ_v and σ_d). Image created via Symmetry @ Otterbein site by Dean Johnston et al.

For any mirror plane, performing two successive reflections about the same plane brings objects back to their original configuration:

$$\sigma\sigma = \sigma^2 = E$$

Inversion, i

Inversion, i, through the center of symmetry leaves the molecule unchanged. Inversion consists of passing each point through the center of inversion and out to the same distance on the other side of the molecule. If inversion symmetry exists, a line drawn from any atom through the center will connect with an equivalent atom at an equivalent distance from the center. Examples of molecules with centers of inversion is shown in Figure 12.2.4 . Centers of inversion are indicated via a point, which may or may not overlap with an atoms. The inversion center is always located at the central point of the molecule and there can only be one inversion center in any system. The centers of inversion in the examples below do not overlap with atoms.

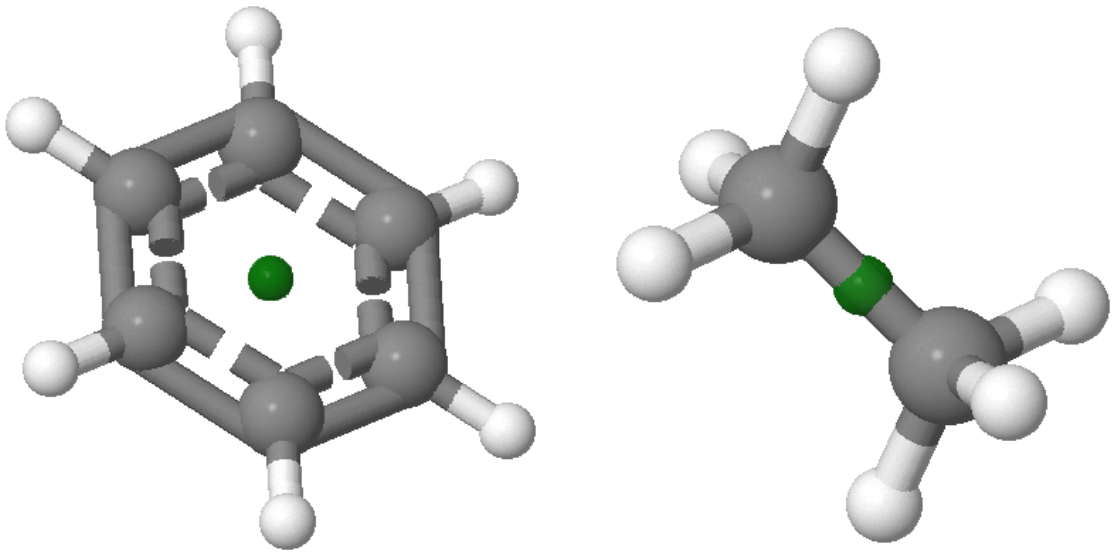


Figure 12.2.4 : Examples of Center of Inversion Symmetry. (left) Benzene and (right) staggard ethane have centers of inversion (green balls). Image created via Symmetry @ Otterbein site by Dean Johnston et al.

Performing inversion twice in succession brings every point back to its original position:

$$ii = i^2 = E$$

Molecules with no inversion symmetry are said to be centrosymmetric.

n-fold Axis of Improper Rotation, S_n

Improper rotations, S_n, are also called rotation-reflections. The rotation-reflection operation consists of rotating by C_n about an axis, followed by reflecting in a plane perpendicular to the same axis. Improper rotation symmetry is indicated with both an axis and a plan as demonstrated in the examples in Figure 12.2.5 .

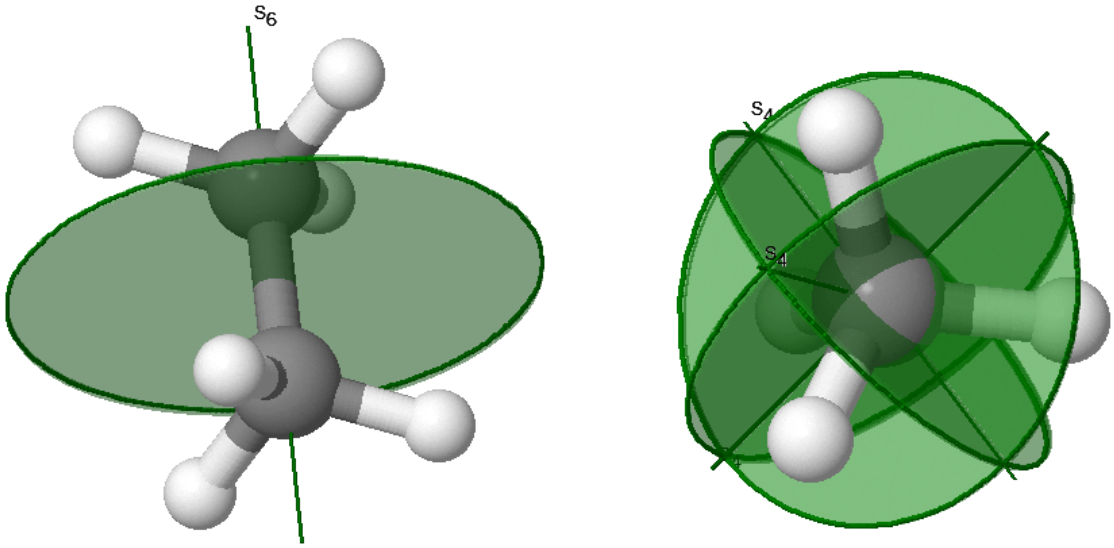


Figure 12.2.5 : Examples of Improper axis of rotation. (left) Staggered ethane contains an S_6 axis of improper rotation. (right) Methane contains three S_4 axes of improper rotation. Image created via Symmetry @ Otterbein site by Dean Johnston et al.

Note

S_1 is the same as reflection and S_2 is the same as inversion.

The lowest-order improper rotation that is not a simpler operation is S_3. The pattern of successive operations depends on if n is even or odd. The general relationships for S_n operations are:

- If n is even, $S_n^n = E$
  - Molecule returns to original orientation configuration after each full rotation
  - There are an even number of rotation operators and reflection operators
- If n is odd, $S_n^n = \sigma$ and $S_n^{2n} = E$
  - First full rotation:
    - Molecular does not return to original configuration after first rotation
    - There are an odd number of rotation operators and reflection operators
  - Second full rotation:
    - Molecule returns to original orientation configuration
    - There are an even number of rotation operators and reflection operators
- When m is even, there is always a corresponding proper rotation (C_n):
  - $S_n^m = C_n^m$ when $m < n$
  - $S_n^m = C_n^{m-n}$ when $m > n$ (2nd rotation)
- If S_n with even n exists, $C_{n/2}$ exists
- If S_n with odd n exists, then both C_n and σ perpendicular to C_n exist

Summary of Symmetry Operations

The identity E and rotations C_n are symmetry operations that could actually be carried out on a molecule. For this reason they are called *proper symmetry operations*. Reflections, inversions and improper rotations can only be imagined (it is not actually possible to turn a molecule into its mirror image or to invert it without some fairly drastic rearrangement of chemical bonds) and as such, are termed *improper symmetry operations*. These five symmetry operations are tabulated in Table 12.2.1 .

Table 12.2.1 : The five principal symmetry elements and their operators for 3D space

Symbol Elements	Description	Symbol Operator	Symbol
E	identity	$\hat{E}$	no change
C_n	n-fold axis of rotation	$\hat{C}_n$	Rotation by $360\,°/n$ leaves the molecule unchanged
σ	plane of symmetry	$\hat{\sigma}$	Reflection in the plane leaves the molecule unchanged
i	center of symmetry.	$\hat{i}$	Inversion through the center of symmetry leaves the molecule unchanged.
S_n	n-fold improper rotation	$\hat{S}_n$	The rotary reflection operation consists of rotating through an angle $360\,°/n$ about the axis, followed by reflecting in a plane perpendicular to the axis.

Defining the Coordinate System

Axis Definitions

Conventionally, when imposing a set of Cartesian axes on a molecule (as we will need to do later on in the course), the z axis lies along the principal axis of the molecule, the x axis lies in the plane of the molecule (or in a plane containing the largest number of atoms if the molecule is non-planar), and the y axis makes up a right handed axis system.

Generally, the following conventions are observed to define the coordinate system:

1. The origin of the coordinate system is located at the central atom or the center of the molecule.
2. The z-axis is collinear with the highest-order rotational axis (principal axis).
3. For planar molecules, if the z-axis is perpendicular to the molecular plane:
   - The x-axis lies in the plane of the molecule and passes through the greatest number of atoms.

   If the z-axis lies in the plane of the molecule:
   - The x-axis stands perpendicular to the plane
4. For non-planar molecules, once the z-axis has been defined, the x-axis is the usually chosen so that the xz plane contains as many atoms as possible.

Molecular Point Groups

It is only possible for certain combinations of symmetry elements to be present in a molecule (or any other object). As a result, we may group together molecules that possess the same symmetry elements and classify molecules according to their symmetry. These groups of symmetry elements are called *point groups* (due to the fact that there is at least one point in space that remains unchanged no matter which symmetry operation from the group is applied). There are two systems of notation for labeling symmetry groups, called the Schönflies and Hermann-Mauguin (or International) systems. Schönflies notation is used by chemists and spectroscopists, while Crystallographers prefer Hermann-Mauguin notation.The symmetry of individual molecules is usually described using the **Schönflies** notation, which is used below. The common point groups can be categorized into the following:

- Nonrotational groups
- Single-axis rotationa groups
- Dihedral groups
- Cubic groups

Shared Names

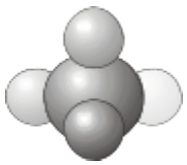
Some of the point groups share their names with symmetry operations, so be careful you do not mix up the two. It is usually clear from the context which one is being referred to.

Nonrotational groups

Nonrotational groups represent the lowest symmetry groups. They include:

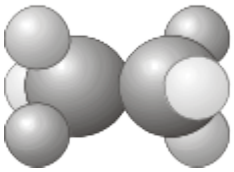
C_1 - Contains only the identity (a C_1 rotation is a rotation by 360° and is the same as the identity operation, E). Molecules that belongs to the C_1 group have no symmetry and are therefore asymmetric.

- Example: CHDFCl

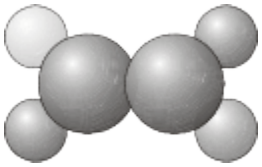


C_i - Contains the identity E and a center of inversion i.

- Example: $C_2H_2F_2Cl_2$



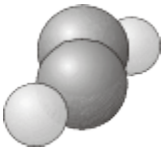
C_S - Contains the identity E and a plane of reflection σ.



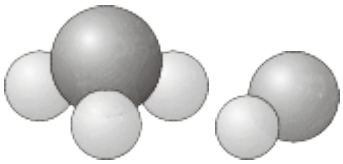
Single-axis rotation groups

Single-axis rotation groups are examples of cyclic groups. In cyclic groups, all of the operators commute (Abelian). In their multiplication tables, elements appear along right-to-left diagonals. Knowing this pattern makes it easy to construct multiplication tables! Single-axis rotational groups include:

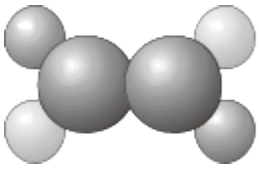
C_n - Contains the identity and an n-fold axis of rotation.



C_{nv} - Contains the identity, an n-fold axis of rotation, and n vertical mirror planes σ_v.



C_{nh} - Contains the identity, an n-fold axis of rotation, and a horizontal reflection plane σ_h (note that in C_{2h} this combination of symmetry elements automatically implies a center of inversion).



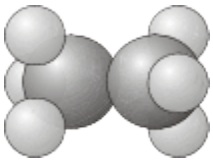
S_n - Contains the identity and *one* S_n axis. Note that molecules only belong to S_n if they have not already been classified in terms of one of the preceding point groups (e.g. S_2 is the same as C_i, and a molecule with this symmetry would already have been classified).

Dihedral groups

The dihedral groups have n two-fold axes perpendicular to the principal n-fold axis. These C_2 axis are called dihedral axes. Dihedral groups groups include:

D_n - Contains the identity, an n-fold axis of rotation, and n 2-fold rotations about axes perpendicular to the principal axis.

D_{nd} - Contains the same symmetry elements as D_n with the addition of n dihedral mirror planes.



D_{nh} - Contains the same symmetry elements as D_n with the addition of a horizontal mirror plane.

- There are n-fold vertical mirror places (σ_v)
- Includes n-fold improper axis when $n > 2$
- They are centrosymmetric when n is even

$D_{\infty h}$ - Same as D_{nh}, except the principal rotational axis is an infinite-fold C_∞.

- This is the point group for all linear centrosymmetric linear molecules (e.g. H_2, CO_2)

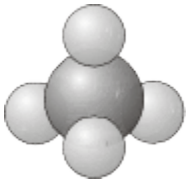


Cubic groups

The following groups are the cubic groups, which contain more than one principal axis. The cubic groups are associated with polyhedra that are geometrically related to the cube. All are characterized by the presence of multiple, intersecting, high-order rotational axes. They separate into the tetrahedral groups (T_d, T_h and T) and the octahedral groups (O and O_h).

T_d - Contains all the symmetry elements of a regular tetrahedron, including the identity, 4 C_3 axes, 3 C_2 axes, 6 dihedral mirror planes, and 3 S_4 axes e.g. $\mathrm{CH_4}$.

- Example: Methane, $\mathrm{C_4}$

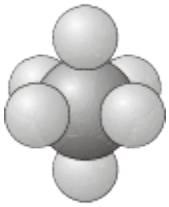


T - Same as for T_d but no planes of reflection.

T_h - Same as for T but contains a center of inversion.

O_h - The group of the regular octahedron.

- Example: Sulfur hexafluoride, $\mathrm{SF_6}$



O - Same as for O_h, but with no planes of reflection.

I_h - Icoshedral, a geometric shape with 20 faces.

- Example: Buckminsterfullerene, (C_{60})

Summary of groups

The final group is the full rotation group R_3, which consists of an infinite number of C_n axes with all possible values of n and describes the symmetry of a sphere. Atoms (but no molecules) belong to R_3, and the group has important applications in atomic quantum mechanics. However, we won't be treating it any further here.

Table 12.2.2 : Common Point Groups for Molecules

Nonaxial groups	C_1	C_s	C_i	-	-	-	-	-	-
C_n groups	C_2	C_3	C_4	C_5	C_6	C_7	C_8	-	-
D_n groups	D_2	D_3	D_4	D_5	D_6	D_7	D_8	-	-
C_{nv} groups	C_{2v}	C_{3v}	C_{4v}	C_{5v}	C_{6v}	C_{7v}	C_{8v}	-	-
C_{nh} groups	C_{2h}	C_{3h}	C_{4h}	C_{5h}	C_{6h}	-	-	-	-
D_{nh} groups	D_{2h}	D_{3h}	D_{4h}	D_{5h}	D_{6h}	D_{7h}	D_{8h}	-	-
D_{nd} groups	D_{2d}	D_{3d}	D_{4d}	D_{5d}	D_{6d}	D_{7d}	D_{8d}	-	-
S_n groups	S_2	-	S_4	-	S_6		S_8	S_{10}	S_{12}
Cubic groups	T	T_h	T_d	O	O_h	I	I_h	-	-
Linear groups	$C_{\infty v}$	$D_{\infty h}$	-	-	-	-	-	-	-

Once you become more familiar with the symmetry elements and point groups described above, you will find it quite straightforward to classify a molecule in terms of its point group. In the meantime, the flowchart shown below provides a step-by-step approach to the problem.

alt

[1]Though the Hermann-Mauguin system can be used to label point groups, it is usually used in the discussion of crystal symmetry. In crystals, in addition to the symmetry elements described above, translational symmetry elements are very important. Translational symmetry operations leave no point unchanged, with the consequence that crystal symmetry is described in terms of *space groups* rather than *point groups*.

Symmetry and Physical Properties

Carrying out a symmetry operation on a molecule must not change any of its physical properties. It turns out that this has some interesting consequences, allowing us to predict whether or not a molecule may be chiral or polar on the basis of its point group.

For a molecule to have a permanent dipole moment, it must have an asymmetric charge distribution. The point group of the molecule not only determines whether the molecule may have a dipole moment, but also in which direction(s) it may point. If a molecule has a C_n axis with $n > 1$, it **cannot** have a dipole moment perpendicular to the axis of rotation (for example, a C_2 rotation would interchange the ends of such a dipole moment and reverse the polarity, which is not allowed – rotations with higher values of n would also change the direction in which the dipole points). Any dipole must lie parallel to a C_n axis.

Also, if the point group of the molecule contains any symmetry operation that would interchange the two ends of the molecule, such as a σ_h mirror plane or a C_2 rotation perpendicular to the principal axis, then there cannot be a dipole moment along the axis. The only groups compatible with a dipole moment are C_n, C_{nv} and C_s. In molecules belonging to C_n or C_{nv} the dipole must lie along the axis of rotation.

One example of symmetry in chemistry that you will already have come across is found in the isomeric pairs of molecules called enantiomers. Enantiomers are non-superimposable mirror images of each other, and one consequence of this symmetrical

relationship is that they rotate the plane of polarized light passing through them in opposite directions. Such molecules are said to be chiral,[2] meaning that they cannot be superimposed on their mirror image. Formally, the symmetry element that precludes a molecule from being chiral is a rotation-reflection axis S_n. Such an axis is often implied by other symmetry elements present in a group.

For example, a point group that has C_n and σ_h as elements will also have S_n. Similarly, a center of inversion is equivalent to S_2. As a rule of thumb, a molecule definitely cannot have be chiral if it has a center of inversion or a mirror plane of any type (σ_h, σ_v or σ_d), but if these symmetry elements are absent the molecule should be checked carefully for an S_n axis before it is assumed to be chiral.

Chirality

The word chiral has its origins in the Greek word for hand ($\chi\epsilon\rho\iota$, pronounced 'cheri' with a soft ch as in 'loch'). A pair of hands is also a pair of non-superimposable mirror images, and you will often hear chirality referred to as 'handedness' for this reason.

Summary

All molecules can be described in terms of their symmetry or lack thereof, which may contain symmetry elements (point, line, plane). Identity, rotation, reflection, and inversion are symmetry operations (movement of the molecules such that after the movement, all the atoms of the molecules is coincidental with equivalent atom of the molecule in original).

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- 12.2: Symmetry Elements and Operations Define the Point Groups by Claire Vallance, Delmar Larsen, Jerry LaRue is licensed CC BY 4.0.

32.3: Symmetry Operations Define Groups

Now that we have explored some of the properties of symmetry operations and elements and their behavior within point groups, we are ready to introduce the formal mathematical definition of a group.

A mathematical group is defined as a set of elements (g_1, g_2, g_3...) together with a rule for forming combinations $g_i g_j$. The number of elements h is called the **order** of the group. For our purposes, the elements are the symmetry operations of a molecule and the rule for combining them is the sequential application of symmetry operations investigated in the previous section. The elements of the group and the rule for combining them must satisfy the following criteria.

1. The group must include the identity E, for which
$$Eg_i = g_i \tag{32.3.1}$$
for all the elements of the group.
2. The elements must satisfy the **group property** that the combination of any pair of elements is also an element of the group.
3. Each element g_i must have an inverse g_i^{-1}, which is also an element of the group, such that
$$g_i g_i^{-1} = g_i^{-1} g_i = E \tag{32.3.2}$$
(e.g. in C_{3v} the inverse of C_3^+ is C_3^-, the inverse of (σ_v is σ_v', the inverse g_i^{-1} effectively 'undoes' the effect of the symmetry operation g_i).
4. The rule of combination must be associative i.e.
$$(g_i g_j)(g_k) = g_i(g_j g_k) \tag{32.3.3}$$

The above definition **does not** require the elements to commute, which would require

$$g_i g_k = g_k g_i \tag{32.3.4}$$

As we discovered in the C_{3v} example above, in many groups the outcome of consecutive application of two symmetry operations depends on the order in which the operations are applied.

Note: Commuting is not a Requirement of Group Elements

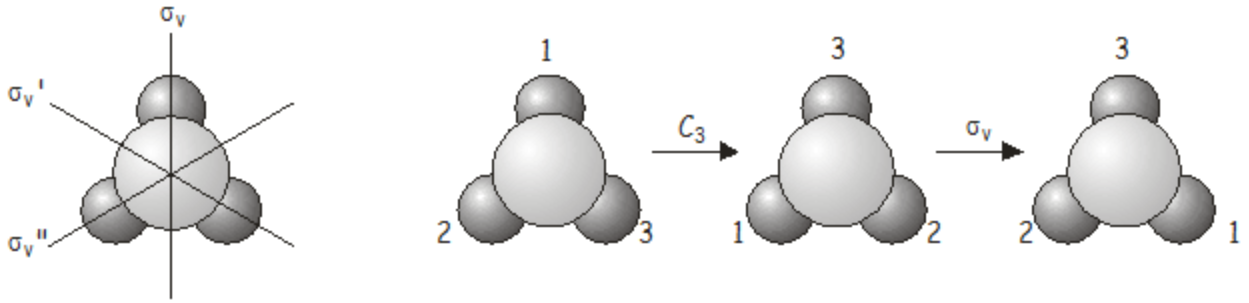
Groups for which the elements do not commute are called *non-Abelian* groups; those for which they elements do commute are *Abelian*.

Group theory is an important area in mathematics, and luckily for chemists the mathematicians have already done most of the work for us. Along with the formal definition of a group comes a comprehensive mathematical framework that allows us to carry out a rigorous treatment of symmetry in molecular systems and learn about its consequences.

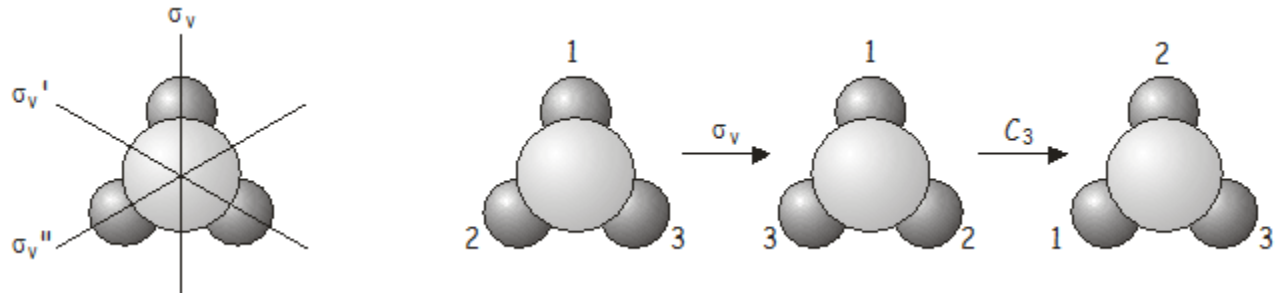
Many problems involving operators or operations (such as those found in quantum mechanics or group theory) may be reformulated in terms of matrices. Any of you who have come across transformation matrices before will know that symmetry operations such as rotations and reflections may be represented by matrices. It turns out that the set of matrices representing the symmetry operations in a group obey all the conditions laid out above in the mathematical definition of a group, and using matrix representations of symmetry operations simplifies carrying out calculations in group theory. Before we learn how to use matrices in group theory, it will probably be helpful to review some basic definitions and properties of matrices.

Group Multiplication

Now we will investigate what happens when we apply two symmetry operations in sequence. As an example, consider the NH_3 molecule, which belongs to the C_{3v} point group. Consider what happens if we apply a C_3rotation followed by a σ_v reflection. We write this combined operation $\sigma_v C_3$ (when written, symmetry operations operate on the thing directly to their right, just as operators do in quantum mechanics – we therefore have to work backwards from right to left from the notation to get the correct order in which the operators are applied). As we shall soon see, the order in which the operations are applied is important.



The combined operation $\sigma_v C_3$ is equivalent to σ_v'', which is also a symmetry operation of the C_{3v} point group. Now let's see what happens if we apply the operators in the reverse order i.e. $C_3\sigma_v$ (σ_v followed by C_3).



Again, the combined operation $C_3\sigma_v$ is equivalent to another operation of the point group, this time σ_v'.

There are two important points that are illustrated by this example:

1. The order in which two operations are applied is important. For two symmetry operations A and B, AB is not necessarily the same as BA, i.e. symmetry operations do not in general commute. In some groups the symmetry elements do commute; such groups are said to be *Abelian*.
2. If two operations from the same point group are applied in sequence, the result will be equivalent to another operation from the point group. Symmetry operations that are related to each other by other symmetry operations of the group are said to belong to the same *class*. In NH_3, the three mirror planes σ_v, σ_v' and σ_v'' belong to the same class (related to each other through a C_3 rotation), as do the rotations C_3^+ and C_3^- (anticlockwise and clockwise rotations about the principal axis, related to each other by a vertical mirror plane

The effects of applying two symmetry operations in sequence within a given point group are summarized in *group multiplication tables*. As an example, the complete group multiplication table for C_{3v} using the symmetry operations as defined in the figures above is shown below. The operations written along the first row of the table are carried out first, followed by those written in the first column (note that the table would change if we chose to name σ_v, σ_v' and σ_v'' in some different order).

$$\begin{array}{ccccccc}
C_{3v} & E & C_3^+ & C_3^- & \sigma_v & \sigma_v' & \sigma_v'' \\
E & E & C_3^+ & C_3^- & \sigma_v & \sigma_v' & \sigma_v'' \\
C_3^+ & C_3^+ & C_3^- & E & \sigma_v' & \sigma_v'' & \sigma_v \\
C_3^- & C_3^- & E & C_3^+ & \sigma_v'' & \sigma_v & \sigma_v' \\
\sigma_v & \sigma_v & \sigma_v'' & \sigma_v' & E & C_3^- & C_3^+ \\
\sigma_v' & \sigma_v' & \sigma_v & \sigma_v'' & C_3^+ & E & C_3^- \\
\sigma_v'' & \sigma_v'' & \sigma_v' & \sigma_v & C_3^- & C_3^+ & E
\end{array} \tag{32.3.5}$$

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32.4: Symmetry Operations can be Represented by Matrices

Matrices can be used to map one set of coordinates or functions onto another set. Matrices used for this purpose are called *transformation matrices*. In group theory, we can use transformation matrices to carry out the various symmetry operations discussed previously. As a simple example, we will investigate the matrices we would use to carry out some of these symmetry operations on a vector in 2D space (x, y).

The Identity Operation

The identity operation leaves the vector unchanged, and as you may already suspect, the appropriate matrix is the identity matrix.

$$(x, y)\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix} = (x, y) \tag{32.4.1}$$

Reflection in a plane

The simplest example of a reflection matrix corresponds to reflecting the vector (x, y) in either the x or y axes. Reflection in the x axis maps y to $-y$, while reflection in the y axis maps x to $-x$. The appropriate matrix is very like the identity matrix but with a change in sign for the appropriate element. Reflection in the x axis transforms the vector (x, y) to $(x, -y)$, and the appropriate matrix is

$$(x, y)\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix} = (x, -y) \tag{32.4.2}$$

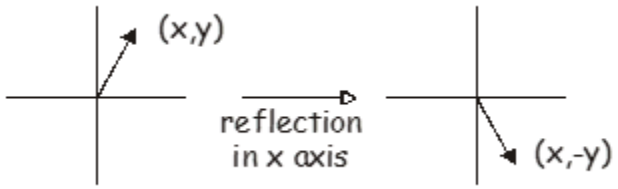


Figure 32.4.1: Reflection across the x-axis in 2D space.

Reflection in the y axis transforms the vector (x, y) to $(-x, y)$, and the appropriate matrix is

$$(x, y)\begin{pmatrix}-1 & 0\\ 0 & 1\end{pmatrix} = (-x, y) \tag{32.4.3}$$

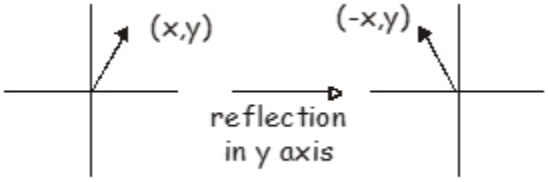


Figure 32.4.2: Reflection across the y-axis *in 2D space*.

More generally, matrices can be used to represent reflections in any plane (or line in 2D). For example, reflection in the 45° axis shown below maps (x, y) onto $(-y, -x)$.

$$(x, y)\begin{pmatrix}0 & -1\\ -1 & 0\end{pmatrix} = (-y, -x) \tag{32.4.4}$$

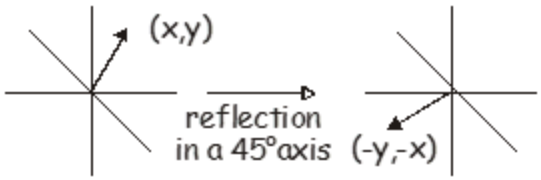


Figure 32.4.3: Reflection across the axis that is rotated 45° with with respect to x-axis *in 2D space*.

Rotation about an Axis

In two dimensions, the appropriate matrix to represent rotation by an angle θ about the origin is

$$R(\theta) = \begin{pmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{pmatrix} \tag{32.4.5}$$

In three dimensions, rotations about the x, y and z axes acting on a vector (x, y, z) are represented by the following matrices.

$$R_x(\theta) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\theta & -\sin\theta \\ 0 & \sin\theta & \cos\theta \end{pmatrix} \tag{32.4.6}$$

$$R_y(\theta) = \begin{pmatrix} \cos\theta & 0 & -\sin\theta \\ 0 & 1 & 0 \\ \sin\theta & 0 & \cos\theta \end{pmatrix} \tag{32.4.7}$$

$$R_z(\theta) = \begin{pmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{32.4.8}$$

Matrix Representation

The symmetry operations in a group may be represented by a set of transformation matrices $\Gamma(g)$, one for each symmetry element g. Each individual matrix is called a *representative* of the corresponding symmetry operation, and the complete set of matrices is called a *matrix representation* of the group. The matrix representatives act on some chosen *basis set* of functions, and the actual matrices making up a given representation will depend on the basis that has been chosen. The representation is then said to *span* the chosen basis. In the examples above we were looking at the effect of some simple transformation matrices on an arbitrary vector (x, y). The basis was therefore a pair of unit vectors pointing in the x and y directions. In most of the examples we will be considering in this course, we will use sets of atomic orbitals as basis functions for matrix representations. Before proceeding any further, we must check that a matrix representation of a group obeys all of the rules set out in the formal mathematical definition of a group.

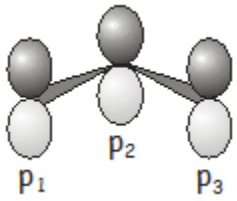
1. The first rule is that the group must include the identity operation E (the 'do nothing' operation). We showed above that the matrix representative of the identity operation is simply the identity matrix. As a consequence, every matrix representation includes the appropriate identity matrix.
2. The second rule is that the combination of any pair of elements must also be an element of the group (the *group property*). If we multiply together any two matrix representatives, we should get a new matrix which is a representative of another symmetry operation of the group. In fact, matrix representatives multiply together to give new representatives in exactly the same way as symmetry operations combine according to the group multiplication table. For example, in the C_{3v} point group, we showed that the combined symmetry operation $C_3\sigma_v$ is equivalent to σ_v''. In a matrix representation of the group, if the matrix representatives of C_3 and σ_v are multiplied together, the result will be the representative of σ_v''.
3. The third rule states that every operation must have an inverse, which is also a member of the group. The combined effect of carrying out an operation and its inverse is the same as the identity operation. It is fairly easy to show that matrix representatives satisfy this criterion. For example, the inverse of a reflection is another reflection, identical to the first. In matrix terms we would therefore expect that a reflection matrix was its own inverse, and that two identical reflection matrices multiplied together would give the identity matrix. This turns out to be true, and can be verified using any of the reflection

matrices in the examples above. The inverse of a rotation matrix is another rotation matrix corresponding to a rotation of the opposite sense to the first.

4. The final rule states that the rule of combination of symmetry elements in a group must be associative. This is automatically satisfied by the rules of matrix multiplication.

Example: a matrix representation of the C_{2v} point group (the allyl radical)

In this example, we'll take as our basis a p orbital on each carbon atom (p_1, p_2, p_3).



Note that the p orbitals are *perpendicular* to the plane of the carbon atoms (this may seem obvious, but if you're visualizing the basis incorrectly it will shortly cause you a not inconsiderable amount of confusion). The symmetry operations in the C_{2v} point group, and their effect on the three p orbitals, are as follows:

$$\begin{array}{ll} E & (p_1, p_2, p_3) \rightarrow (p_1, p_2, p_3) \\ C_2 & (p_1, p_2, p_3) \rightarrow (-p_3, -p_2, -p_1) \\ \sigma_v & (p_1, p_2, p_3) \rightarrow (-p_1, -p_2, -p_3) \\ \sigma_v' & (p_1, p_2, p_3) \rightarrow (p_3, p_2, p_1) \end{array} \tag{32.4.9}$$

The matrices that carry out the transformation are

$$\begin{array}{lll} \Gamma(E) & (p_1, p_2, p_3) \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = (p_1, p_2, p_3) \\ \Gamma(C_2) & (p_1, p_2, p_3) \begin{pmatrix} 0 & 0 & -1 \\ 0 & -1 & 0 \\ -1 & 0 & 0 \end{pmatrix} = (-p_3, -p_2, -p_1) \\ \Gamma(\sigma_v) & (p_1, p_2, p_3) \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} = (-p_1, -p_2, -p_3) \\ \Gamma(\sigma_v') & (p_1, p_2, p_3) \begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix} = (p_3, p_2, p_1) \end{array} \tag{32.4.10}$$

Note

We have written the vectors representing our basis as *row vectors*. This is important. If we had written them as column vectors, the corresponding transformation matrices would be the transposes of the matrices above, and would not reproduce the group multiplication table (try it as an exercise if you need to convince yourself).

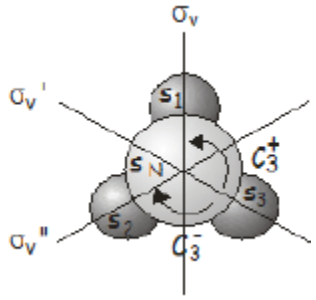
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32.5: The C_3V Point Group Has a 2-D Irreducible Representation

The first thing we need to do before we can construct a matrix representation is to choose a basis. For NH_3, we will select a basis (s_N, s_1, s_2, s_3) that consists of the valence s orbitals on the nitrogen and the three hydrogen atoms. We need to consider what happens to this basis when it is acted on by each of the symmetry operations in the C_{3v} point group, and determine the matrices that would be required to produce the same effect. The basis set and the symmetry operations in the C_{3v} point group are summarized in the figure below.



The effects of the symmetry operations on our chosen basis are as follows:

$$\begin{array}{ll} E & (s_N, s_1, s_2, s_3) \rightarrow (s_N, s_1, s_2, s_3) \\ C_3^+ & (s_N, s_1, s_2, s_3) \rightarrow (s_N, s_2, s_3, s_1) \\ C_3^- & (s_N, s_1, s_2, s_3) \rightarrow (s_N, s_3, s_1, s_2) \\ \sigma_v & (s_N, s_1, s_2, s_3) \rightarrow (s_N, s_1, s_3, s_2) \\ \sigma_v' & (s_N, s_1, s_2, s_3) \rightarrow (s_N, s_2, s_1, s_3) \\ \sigma_v'' & (s_N, s_1, s_2, s_3) \rightarrow (s_N, s_3, s_2, s_1) \end{array} \tag{32.5.1}$$

By inspection, the matrices that carry out the same transformations are:

$$
\begin{aligned}
\Gamma(E) \quad & (s_N, s_1, s_2, s_3) \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} = (s_N, s_1, s_2, s_3) \\
\Gamma(C_3^+) \quad & (s_N, s_1, s_2, s_3) \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix} = (s_N, s_2, s_3, s_1) \\
\Gamma(C_3^-) \quad & (s_N, s_1, s_2, s_3) \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \end{pmatrix} = (s_N, s_3, s_1, s_2) \\
\Gamma(\sigma_v) \quad & (s_N, s_1, s_2, s_3) \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix} = (s_N, s_1, s_3, s_2) \\
\Gamma(\sigma_v') \quad & (s_N, s_1, s_2, s_3) \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} = (s_N, s_2, s_1, s_3) \\
\Gamma(\sigma_v'') \quad & (s_N, s_1, s_2, s_3) \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix} = (s_N, s_3, s_2, s_1)
\end{aligned} \tag{32.5.2}
$$

These six matrices therefore form a representation for the C_{3v} point group in the (s_N, s_1, s_2, s_3) basis. They multiply together according to the group multiplication table and satisfy all the requirements for a mathematical group.

Reduced Representations

If we look at the matrices carefully we see that they all take the same block diagonal form (a square matrix is said to be **block diagonal** if all the elements are zero except for a set of submatrices lying along the diagonal).

$$
\begin{array}{cccccc}
\Gamma(E) & \Gamma(C_3^+) & \Gamma(C_3^-) & \Gamma(\sigma_v) & \Gamma(\sigma_v') & \Gamma(\sigma_v'') \\
\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} & \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \end{pmatrix} & \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix} & \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix} & \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} & \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix} \\
\chi(E) = 4 & \chi(C_3^+) = 1 & \chi(C_3^-) = 1 & \chi(\sigma_v) = 2 & \chi(\sigma_v') = 2 & \chi(\sigma_v'') = 2
\end{array} \tag{32.5.3}
$$

A block diagonal matrix can be written as the *direct sum* of the matrices that lie along the diagonal. In the case of the C_{3v} matrix representation, each of the matrix representatives may be written as the direct sum of a 1×1 matrix and a 3×3 matrix.

$$\Gamma^{(4)}(g) = \Gamma^{(1)}(g) \otimes \Gamma^{(3)}(g) \tag{32.5.4}$$

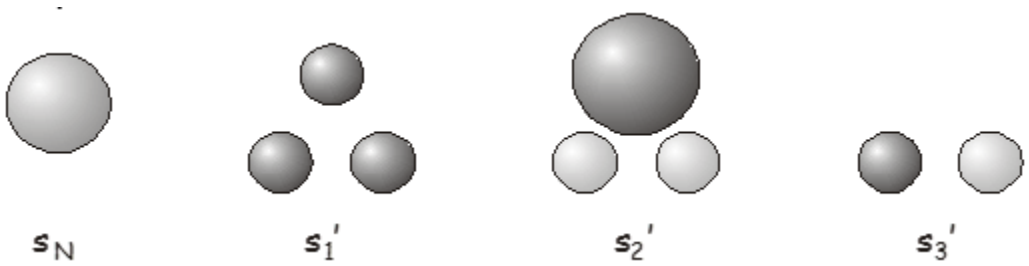
in which the bracketed superscripts denote the dimensionality of the matrices. Note that a direct sum is very different from ordinary matrix addition since it produces a matrix of higher dimensionality. A direct sum of two matrices of orders n and m is performed by placing the matrices to be summed along the diagonal of a matrix of order $n + m$ and filling in the remaining elements with zeroes.

The reason why this result is useful in group theory is that the two sets of matrices $\Gamma^{(1)}(g)$ and $\Gamma^{(3)}(g)$ also satisfy all of the requirements for a matrix representation. Each set contains the identity and an inverse for each member, and the members multiply together associatively according to the group multiplication table[3]. Recall that the basis for the original four-dimensional representation had the s orbitals (s_N, s_1, s_2, s_3) of ammonia as its basis. The first set of reduced matrices, $\Gamma^{(1)}(g)$, forms a one-dimensional representation with (s_N) as its basis. The second set, $\Gamma^{(3)}(g)$ forms a three-dimensional representation with the basis (s_1, s_2, s_3). Separation of the original representation into representations of lower dimensionality is called *reduction* of the representation. The two *reduced representations* are shown below.

$$\begin{array}{cccccccc} g & E & C_3^+ & C_3^- & \sigma_v & \sigma_v' & \sigma_v'' & \\ \Gamma^{(1)}(g) & (1) & (1) & (1) & (1) & (1) & (1) & \text{1D representation spanned by } (s_N) \\ \Gamma^{(3)}(g) & \begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix} & \begin{pmatrix}0&1&0\\0&0&1\\1&0&0\end{pmatrix} & \begin{pmatrix}0&0&1\\1&0&0\\0&1&0\end{pmatrix} & \begin{pmatrix}1&0&0\\0&0&1\\0&1&0\end{pmatrix} & \begin{pmatrix}0&1&0\\1&0&0\\0&0&1\end{pmatrix} & \begin{pmatrix}0&0&1\\0&1&0\\1&0&0\end{pmatrix} & \text{3D representation spanned by } (s_1, s_2, s_3) \end{array} \tag{32.5.5}$$

The logical next step is to investigate whether or not the three dimensional representation $\Gamma^{(3)}(g)$ can be reduced any further. As it stands, the matrices making up this representation are not in block diagonal form (some of you may have noted that the matrices representing E and σ_v are block diagonal, but in order for a representation to be reducible *all* of the matrix representatives must be in the *same* block diagonal form) so the representation is not reducible. However, we can carry out a similarity transformation (see 10.1) to a new representation spanned by a new set of basis functions (made up of linear combinations of (s_1, s_2, s_3)), which *is* reducible. In this case, the appropriate (normalized) linear combinations to use as our new basis functions are

$$\begin{aligned} s_1' &= \frac{1}{\sqrt{3}}(s_1 + s_2 + s_3) \\ s_2' &= \frac{1}{\sqrt{6}}(2s_1 - s_2 - s_3) \\ s_3' &= \frac{1}{\sqrt{2}}(s_2 - s_3) \end{aligned} \tag{32.5.6}$$



or in matrix form

$$\begin{array}{ccccc} (s_1', s_2', s_3') & = & (s_1, s_2, s_3) & \begin{pmatrix} \frac{1}{\sqrt{3}} & \frac{2}{\sqrt{6}} & 0 \\ \frac{1}{\sqrt{3}} & -\frac{1}{\sqrt{6}} & \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{3}} & -\frac{1}{\sqrt{6}} & -\frac{1}{\sqrt{2}} \end{pmatrix} \\ \mathbf{x'} & = & \mathbf{x} & C \end{array} \tag{32.5.7}$$

The matrices in the new representation are found from $\Gamma'(g) = C^{-1}\Gamma(g)C$ to be

$$\begin{array}{cccccccc} & E & & C_3^+ & & C_3^- & \sigma_v & \sigma_v' & \sigma_v'' \\ \Gamma^{(3),}(g) & \begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix} & \begin{pmatrix}1&0&0\\0&-\frac{1}{2}&\frac{\sqrt{3}}{2}\\0&-\frac{\sqrt{3}}{2}&-\frac{1}{2}\end{pmatrix} & & \begin{pmatrix}1&0&0\\0&-\frac{1}{2}&-\frac{\sqrt{3}}{2}\\0&\frac{\sqrt{3}}{2}&-\frac{1}{2}\end{pmatrix} & \begin{pmatrix}1&0&0\\0&1&0\\0&0&-1\end{pmatrix} & \begin{pmatrix}1&0&0\\0&-\frac{1}{2}&\frac{\sqrt{3}}{2}\\0&\frac{\sqrt{3}}{2}&\frac{1}{2}\end{pmatrix} & \begin{pmatrix}1&0&0\\0&-\frac{1}{2}&-\frac{\sqrt{3}}{2}\\0&-\frac{\sqrt{3}}{2}&\frac{1}{2}\end{pmatrix} \end{array} \tag{32.5.8}$$

We see that each matrix is now in block diagonal form, and the representation may be reduced into the direct sum of a 1 x 1 representation spanned by (s_1') and a 2x2 representation spanned by (s_2', s_3'). The complete set of reduced representations obtained from the original 4D representation is:

E	C_3^+	C_3^-	σ_v	σ_v'	σ_v''	
(1)	(1)	(1)	(1)	(1)	(1)	1D representation spanned by (s_N)
(1)	(1)	(1)	(1)	(1)	(1)	1D representation spanned by (s_1')
$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}$	2D representation spanned by (s_2', s_3')

(32.5.9)

This is as far as we can go in reducing this representation. None of the three representations above can be reduced any further, and they are therefore called *irreducible representations*, of the point group. Formally, a representation is an irreducible representation if there is no similarity transform that can simultaneously convert all of the representatives into block diagonal form. The linear combination of basis functions that converts a matrix representation into block diagonal form, allowing reduction of the representation, is called a *symmetry adapted linear combination (SALC)*.

Irreducible Representations

The two one-dimensional irreducible representations spanned by s_N and s_1' are seen to be identical. This means that s_N and s_1' have the 'same symmetry', transforming in the same way under all of the symmetry operations of the point group and forming bases for the same matrix representation. As such, they are said to belong to the same *symmetry species*. There are a limited number of ways in which an arbitrary function can transform under the symmetry operations of a group, giving rise to a limited number of symmetry species. Any function that forms a basis for a matrix representation of a group must transform as one of the symmetry species of the group. The irreducible representations of a point group are labeled according to their symmetry species as follows:

i. 1D representations are labeled A or B, depending on whether they are symmetric (character $+1$) or antisymmetric (character -1) under rotation about the principal axis.
ii. 2D representations are labeled E, 3D representations are labeled T.
iii. In groups containing a center of inversion, g and u labels (from the German *gerade* and *ungerade*, meaning symmetric and antisymmetric) denote the character of the irreducible representation under inversion ($+1$ for g, -1 for u)
iv. In groups with a horizontal mirror plane but no center of inversion, the irreducible representations are given prime and double prime labels to denote whether they are symmetric (character $+1$ or antisymmetric (character -1) under reflection in the plane.
v. If further distinction between irreducible representations is required, subscripts 1 and 2 are used to denote the character with respect to a C_2 rotation perpendicular to the principal axis, or with respect to a vertical reflection if there are no C_2 rotations.

The 1D irreducible representation in the C_{3v} point group is symmetric (has character $+1$) under all the symmetry operations of the group. It therefore belongs to the irreducible representation A_1. The 2D irreducible representation has character 2 under the identity operation, -1 under rotation, and 0 under reflection, and belongs to the irreducible representation E.

Note

Sometimes there is confusion over the relationship between a function f and its irreducible representation, but it is quite important that you understand the connection. There are several different ways of stating the relationship. For example, the following statements all mean the same thing:

- "f has A_2 symmetry"
- "f transforms as A_2"
- "f has the same symmetry

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32.6: Character Tables

Now that we've learnt how to create a matrix representation of a point group within a given basis, we will move on to look at some of the properties that make these representations so powerful in the treatment of molecular symmetry. The trace of a matrix representative $\Gamma(g)$ is usually referred to as the *character* of the representation under the symmetry operation g. We will soon come to see that the characters of a matrix representation are often more useful than the matrix representatives themselves. Characters have several important properties.

1. The character of a symmetry operation is invariant under a similarity transform
2. Symmetry operations belonging to the same class have the same character in a given representation. Note that the character for a given class may be different in different representations, and that more than one class may have the same character.

Proofs of the above two statements are given in the Appendix.

Character Tables

A character table summarizes the behavior of all of the possible irreducible representations of a group under each of the symmetry operations of the group. The character table for C_{3v} is shown below.

$C_{3v}, 3m$	E	$2C_3$	$3\sigma_v$	$h = 6$
A_1	1	1	1	$z, z^2, x^2 + y^2$
A_2	1	1	-1	R_z
E	2	-1	0	$(x, y), (xy, x^2 + y^2), (xz, yz), (R_x, R_y)$

(32.6.1)

The various sections of the table are as follows:

i. The first element in the table gives the name of the point group, usually in both Schoenflies (C_{3v}) and Hermann-Mauguin ($3m$) notation.
ii. Along the first row are the symmetry operations of the group, E, $2C_3$ and $3\sigma_v$, followed by the order of the group. Because operations in the same class have the same character, symmetry operations are grouped into classes in the character table and not listed separately.
iii. In the first column are the irreducible representations of the group. In C_{3v} the irreducible representations are A_1, A_2 and E (the representation we considered above spans $2A_1$ + E).
iv. The characters of the irreducible representations under each symmetry operation are given in the bulk of the table.
v. The final column of the table lists a number of functions that transform as the various irreducible representations of the group. These are the Cartesian axes (x, y, z), the Cartesian products $(z^2, x^2 + y^2, xy, yz)$, and the rotations (R_x, R_y, R_z).

The functions listed in the final column of the table are important in many chemical applications of group theory, particularly in spectroscopy. For example, by looking at the transformation properties of x, y and z (sometimes given in character tables as T_x, T_y , T_z) we can discover the symmetry of translations along the x, y, and z axes. Similarly, R_x, R_y and R_z represent rotations about the three Cartesian axes. As we shall see later, the transformation properties of x, y, and z can also be used to determine whether or not a molecule can absorb a photon of x-, y-, or z-polarized light and undergo a spectroscopic transition. The Cartesian products play a similar role in determining selection rules for Raman transitions, which involve two photons.

A simple way to determine the characters of a representation

In many applications of group theory, we only need to know the characters of the representative matrices, rather than the matrices themselves. Luckily, when each basis function transforms as a 1D irreducible representation (which is true in many cases of interest) there is a simple shortcut to determining the characters without having to construct the entire matrix representation. All we have to do is to look at the way the individual basis functions transform under each symmetry operation. For a given operation, step through the basis functions as follows:

i. Add 1 to the character if the basis function is unchanged by the symmetry operation (i.e. the basis function is mapped onto itself);

ii. Add -1 to the character if the basis function changes sign under the symmetry operation (i.e the basis function is mapped onto minus itself);
iii. Add 0 to the character if the basis function moves when the symmetry operation is applied (i.e the basis function is mapped onto something different from itself).

Try this for the s orbital basis we have been using for the C_{3v} group. You should find you get the same characters as we obtained from the traces of the matrix representatives.

We can also work out the characters fairly easily when two basis functions transform together as a 2D irreducible representation. For example, in the C_{3v} point group x and y axes transform together as E. If we carry out a rotation about z by an angle θ, our x and y axes are transformed onto new axes x' and y'. However, the new axes can each be written as a linear combination of our original x and y axes. Using the rotation matrices introduced in Section 9, we see that:

$$\begin{aligned} x' &= \cos\theta\, x + \sin\theta\, y \\ y' &= -\sin\theta\, x + \cos\theta\, y \end{aligned} \tag{32.6.2}$$

For one-dimensional irreducible representations we asked if a basis function/axis was mapped onto itself, minus itself, or something different. For two-dimensional irreducible representations we need to ask how much of the 'old' axis is contained in the new one. From the above we see that the x' axis contains a contribution $\cos\theta$ from the x axis, and the y' axis contains a contribution $\cos\theta$ from the y axis. The characters of the x and y axes under a rotation through θ are therefore $\cos\theta$, and the overall character of the E irreducible representation is therefore $\cos\theta + \cos\theta = 2\cos\theta$. For a C_3 rotation through 120 degrees, the character of the E irreducible representation is therefore $2\cos 120° = -1$.

In general, *when an axis is rotated by an angle θ by a symmetry operation, its contribution to the character for that operation is $\cos\theta$.*

In many cases, the characters for rotations C_n and improper rotations S_n are complex numbers, usually expressed in terms of the quantity $\epsilon = \exp(2\pi i/n)$. It is fairly straightforward to reconcile this with the fact that in chemistry we are generally using group theory to investigate physical problems in which all quantities are real. It turns out that whenever our basis spans an irreducible representation whose characters are complex, it will also span a second irreducible representation whose characters are the complex conjugates of the first irreducible representation i.e. complex irreducible representations occur in pairs. According to the strict mathematics of group theory, each irreducible representation in the pair should be considered as a separate representation. However, when applying such irreducible representations in physical problems, we add the characters for the two irreducible representations together to get a single irreducible representation whose characters are real.

As an example, the 'correct' character table for the group C_3 takes the form:

$$\begin{array}{cccc} C_3 & E & C_3 & C_3^2 \\ A & 1 & 1 & 1 \\ E & \begin{Bmatrix} 1 \\ 1 \end{Bmatrix} & \begin{matrix} \epsilon \\ \epsilon* \end{matrix} & \begin{Bmatrix} \epsilon* \\ \epsilon \end{Bmatrix} \end{array} \tag{32.6.3}$$

Where $\epsilon = \exp(2\pi i/3)$. However, as chemists we would usually combine the two parts of the E irreducible representation to give:

$$\begin{array}{cccc} C_3 & E & C_3 & C_3^2 \\ A & 1 & 1 & 1 \\ E & 2 & -1 & 1 \end{array} \tag{32.6.4}$$

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32.7: Relations involving Characters

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32.8: Using Symmetry to Predict Zero in a Secular Determinant

As we continue with this course, we will discover that there are many times when we would like to know whether a particular integral is necessarily zero, or whether there is a chance that it may be non-zero. We can often use group theory to differentiate these two cases.

You will have already used symmetry properties of functions to determine whether or not a one-dimensional integral is zero. For example, cos(x) is an 'even' function (symmetric with respect to reflection through the origin), and it follows from this that

$$\int_{-\infty}^{\infty} \cos(x) dx = 0$$

In general integral between these limits for any other even function will be also be zero.

In the general case we may have an integral of more than one dimension. The key to determining whether a general integral is necessarily zero lies in the fact that because an integral is just a number, it must be invariant to any symmetry operation. For example, bonding in a diatomic (see next section) depends on the presence of a non-zero overlap between atomic orbitals on adjacent atoms, which may be quantified by an *overlap integral*. You would not expect the bonding in a molecule to change if you rotated the molecule through some angle θ, so the integral must be invariant to rotation, and indeed to any other symmetry operation.

In group theoretical terms, for an integral to be non-zero, *the integrand must transform as the totally symmetric irreducible representation in the appropriate point group*. In practice, the integrand may not transform as a single irreducible representation, but it **must include** the totally symmetric irreducible representation. These ideas should become more clear in the next section.

> It should be noted that even when the irreducible representations spanned by the integrand do include the totally symmetric irreducible representation, it is still possible for the integral to be zero. All group theory allows us to do is identify integrals that are *necessarily* zero based on the symmetry (or lack thereof) of the integrand.

Secular Equations

As we have seen already, any set of linear equations may be rewritten as a matrix equation $A\mathbf{x} = \mathbf{b}$. Linear equations are classified as *simultaneous linear equations* or *homogeneous linear equations*, depending on whether the vector $\mathbf{b}$ is non-zero or zero. For a set of simultaneous linear equations (non-zero $\mathbf{b}$) it is fairly apparent that if a unique solution exists, it can be found by multiplying both sides by the inverse matrix A^{-1} (since $A^{-1}A$ on the left hand side is equal to the identity matrix, which has no effect on the vector $\mathbf{x}$)

$$\begin{aligned} A\mathbf{x} &= \mathbf{b} \\ A^{-1}A\mathbf{x} &= A^{-1}\mathbf{b} \\ \mathbf{x} &= A^{-1}\mathbf{b} \end{aligned} \tag{32.8.1}$$

In practice, there are easier matrix methods for solving simultaneous equations than finding the inverse matrix, but these need not concern us here. We previously argued that in order for a matrix to have an inverse, **it must have a non-zero determinant**. Since A^{-1} must exist in order for a set of simultaneous linear equations to have a solution, this means that the determinant of the matrix A must be non-zero for the equations to be solvable.

> For a matrix to have an inverse, it must have a non-zero determinant.

The reverse is true for homogeneous linear equations. In this case the set of equations only has a solution if the determinant of A *is* equal to zero. The secular equations we want to solve are homogeneous equations, and we will use this property of the determinant to determine the molecular orbital energies. An important property of homogeneous equations is that if a vector $\mathbf{x}$

is a solution, so is any multiple of $\mathbf{x}$, meaning that the solutions (the molecular orbitals) can be normalized without causing any problems.

Solving for the orbital energies and expansion coefficients

Recall the secular equations for the A_1 orbitals of NH_3 derived in the previous section

$$\begin{aligned} c_1(H_{11} - ES_{11}) + c_2(H_{12} - ES_{12}) &= 0 \\ c_1(H_{12} - ES_{12}) + c_2(H_{22} - ES_{22}) &= 0 \end{aligned} \tag{32.8.2}$$

where c_1 and c_2 are the coefficients in the linear combination of the SALCs $\phi_1 = s_N$ and $\phi_2 = \frac{1}{\sqrt{3}}(s_1 + s_2 + s_3)$ used to construct the molecular orbital. Writing this set of homogeneous linear equations in matrix form gives

$$\begin{pmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{12} - ES_{12} & H_{22} - ES_{22} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix} \tag{32.8.3}$$

In order for the equations to have a solution, the determinant of the matrix must be equal to zero. Writing out the determinant will give us a polynomial equation in E that we can solve to obtain the orbital energies in terms of the Hamiltonian matrix elements H_{ij} and overlap integrals S_{ij}. The number of energies obtained by 'solving the secular determinant' in this way is equal to the order of the matrix, in this case two.

The secular determinant for Equation (21.3) is (noting that $S_{11} = S_{22} = 1$ since the SALCs are normalized)

$$(H_{11} - E)(H_{22} - E) - (H_{12} - ES_{12})^2 = 0 \tag{32.8.4}$$

Expanding and collecting terms in E gives

$$E^2(1 - S_{12}^2) + E(2H_{12}S_{12} - H_{11} - H_{22}) + (H_{11}H_{22} - H_{12}^2) = 0 \tag{32.8.5}$$

which can be solved using the quadratic formula to give the energies of the two molecular orbitals.

$$E_{\pm} = \frac{-(2H_{12}S_{12} - H_{11} - H_{22}) \pm \sqrt{(2H_{12}S_{12} - H_{11} - H_{22})^2 - 4(1 - S_{12}^2)(H_{11}H_{22} - H_{12}^2)}}{2(1 - S_{12}^2)} \tag{32.8.6}$$

To obtain numerical values for the energies, we need to evaluate the integrals H_{11}, H_{22}, H_{12}, and S_{12}. This would be quite a challenge to do analytically, but luckily there are a number of computer programs that can be used to calculate the integrals. One such program gives the following values.

$$\begin{aligned} H_{11} &= -26.0000\ eV \\ H_{22} &= -22.2216\ eV \\ H_{12} &= -29.7670\ eV \\ S_{12} &= 0.8167\ eV \end{aligned} \tag{32.8.7}$$

When we substitute these into our equation for the energy levels, we get:

$$\begin{aligned} E_+ &= 29.8336\ eV \\ E_- &= -31.0063\ eV \end{aligned} \tag{32.8.8}$$

We now have the orbital energies and the next step is to find the orbital coefficients. The coefficients for an orbital of energy E are found by substituting the energy into the secular equations and solving for the coefficients c_i. Since the two secular equations are not linearly independent (i.e. they are effectively only one equation), when we solve them to find the coefficients what we will end up with is the *relative* values of the coefficients. This is true in general: in a system with N coefficients, solving the secular equations will allow all N of the coefficients c_i to be obtained in terms of, say, c_1. The absolute values of the coefficients are found by normalizing the wavefunction.

Since the secular equations for the orbitals of energy E_+ and E_- are not linearly independent, we can choose to solve either one of them to find the orbital coefficients. We will choose the first.

$$(H_{11} - E_{\pm})c_1 + (H_{12} - E_{\pm}S_{12})c_2 = 0 \tag{32.8.9}$$

For the orbital with energy E_- = -31.0063 eV, substituting numerical values into this equation gives

$$\begin{aligned} 5.0063c_1 - 4.4442c_2 &= 0 \\ c_2 &= 1.1265c_1 \end{aligned} \tag{32.8.10}$$

The molecular orbital is therefore

$$\Psi = c_1(\phi_1 + 1.1265\phi_2) \tag{32.8.11}$$

Normalizing to find the constant c_1 (by requiring $< \Psi|\Psi >$ = 1) gives

$$\begin{aligned} \Psi_1 &= 0.4933\phi_1 + 0.5557\phi_2 \\ &= 0.4933s_N + 0.3208(s_1 + s_2 + s_3) \quad \text{(substituting the SALCs for } \phi_1 \text{ and } \phi_2) \end{aligned} \tag{32.8.12}$$

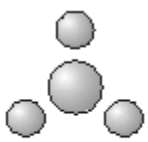
For the second orbital, with energy E_+ = 29.8336 eV, the secular equation is

$$\begin{aligned} -55.8336c_1 - 54.1321c_2 &= 0 \\ c_2 &= -1.0314c_1 \end{aligned} \tag{32.8.13}$$

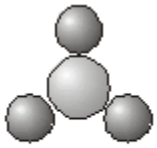
giving

$$\begin{aligned} \Psi_2 &= c_1(\phi_1 - 1.0314\phi_2) \\ &= 1.6242\phi_1 - 1.6752\phi_2 \qquad \text{(after normalization)} \\ &= 1.6242s_N - 0.9672(s_1 + s_2 + s_3) \end{aligned} \tag{32.8.14}$$

These two A_1 molecular orbitals Ψ_1 and Ψ_2, one bonding and one antibonding, are shown below.



Ψ_1



Ψ_2

The remaining two SALCs arising from the s orbitals of NH_3 ($\phi_3 = \frac{1}{\sqrt{6}}(2s_1 - s_2 - s_3)$ and $\phi_4 = \frac{1}{\sqrt{2}}(s_2 - s_3)$), form an orthogonal pair of molecular orbitals of E symmetry. We can show this by solving the secular determinant to find the orbital energies. The secular equations in this case are:

$$\begin{aligned} c_1(H_{33} - ES_{33}) + c_2(H_{34} - ES_{34}) &= 0 \\ c_1(H_{34} - ES_{34}) + c_2(H_{44} - ES_{44}) &= 0 \end{aligned} \tag{32.8.15}$$

Solving the secular determinant gives

$$E_{\pm} = \frac{-(2H_{34}S_{34} - H_{33} - H_{44}) \pm \sqrt{(2H_{34}S_{34} - H_{33} - H_{44})^2 - 4(1 - S_{34}^2)(H_{33}H_{44} - H_{34}^2)}}{2(1 - S_{34}^2)} \tag{32.8.16}$$

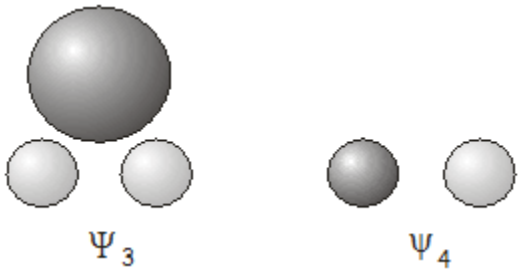
The integrals required are

$$\begin{aligned} H_{33} &= -9.2892\, eV \\ H_{44} &= -9.2892\, eV \\ H_{34} &= 0 \\ S_{34} &= 0 \end{aligned} \tag{32.8.17}$$

Using the fact that H_{34} = $S_{34} = 0$, the expression for the energies reduces to

$$E_{\pm} = \frac{(H_{33} + H_{44}) \pm (H_{33} - H_{44})}{2} \tag{32.8.18}$$

giving E_+ = H_{33} = -9.2892 eV and E_- = H_{44} = -9.2892 eV. Each SALC therefore forms a molecular orbital by itself, and the two orbitals have the same energy; the two SALCs form an orthogonal pair of degenerate orbitals. These two molecular orbitals of E symmetry are shown below.



Summary of the steps involved in constructing molecular orbitals

1. Choose a basis set of functions f_i consisting of the valence atomic orbitals on each atom in the system, or some chosen subset of these orbitals.
2. With the help of the appropriate character table, determine which irreducible representations are spanned by the basis set using Equation (15.20) to determine the number of times a_k that the kth irreducible representation appears in the representation.

$$a_k = \frac{1}{h} \sum_C n_C \chi(g) \chi_k(g) \tag{32.8.19}$$

3. Construct the SALCs ϕ_i that transform as each irreducible representation using Equation 16.1

$$\phi_i = \sum_g \chi_k(g) g f_i \tag{32.8.20}$$

4. Write down expressions for the molecular orbitals by taking linear combinations of all the irreducible representations of the same symmetry species.
5. Write down the secular equations for the system.
6. Solve the secular determinant to obtain the energies of the molecular orbitals.
7. Substitute each energy in turn back into the secular equations and solve to obtain the coefficients appearing in your molecular orbital expressions in step 4.
8. Normalize the orbitals.

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32.9: Generating Operators for Irreducible Representations

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33: SPECTROSCOPY

The primary method of measuring the energy levels of a material is through the use of electromagnetic radiation. Experiments involving electromagnetic radiation—matter interaction are called spectroscopies. Since the energy levels of atoms and molecules are discontinuous, they absorb or emit light only at specific energies. These specific values correspond to the energy level difference between the initial and final states and they can be measured as signals in spectroscopic experiments. The intensity of the experimental signals depends on the population of the initial state involved in the transition.

Depending on the type of radiation, as well as the shape of the molecules and the inner details of the instrument that is used, some transition might be visible by the experiment (allowed), while others might not be (forbidden). The analysis of allowed and forbidden transition for each type of spectroscopy results into some mathematical formula that are called **selection rules**.

To summarize, spectroscopy is mainly the result of the following three effects:

- The energy levels of the atoms or molecules (determining the position of the signals).
- The population of the energy levels (determining the intensity of the signals).
- The selection rules that account for the symmetry and the interaction with the instrument.

Spectroscopy is the most important experimental verification of quantum mechanics, since we can use it to validate its theoretical results on the energy levels of atoms and molecules.

33.1: Rotational Spectroscopy

33.2: Vibrational Spectroscopy

33.3: Electronic Spectroscopy

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33.1: Rotational Spectroscopy

Rotational spectroscopy is concerned with the measurement of the energies of transitions between quantized rotational states of molecules in the gas phase. Rotational transitions of molecules are usually measured in the range $1 - 10\ \mathrm{cm}^{-1}$ (microwave radiation) and rotational spectroscopy is therefore usually referred to as *microwave spectroscopy*.

Rotational spectroscopy is actively used by astrophysicists to explore the chemical composition of the interstellar medium using radio telescopes.

The rotational energies are derived theoretically by considering the molecules to be rigid rotors and applying the same treatment that we saw in chapter 20. Correction terms might be applied to account for deviation from the ideal rigid rotor case. As we saw in chapter 20, the quantized rotational energy levels of a rigid rotor depend on the angular moment of inertia, which in turn depends on the masses of the nuclei and the internuclear distance. Reversing the theoretical procedure of obtaining the energy levels from the distances, we can use the experimental energy levels to derive very precise values of molecular bond lengths (and in some complex case, also of angles). We will discuss below the simplest case of a diatomic molecule. For non-linear molecules, the moments of inertia are multiple, and only a few analytical method of solving the TISEq are available. For the most complicated cases, numerical methods can be used.

Rotation of diatomic molecules

Transitions between rotational states can be observed in molecules with a permanent electric dipole moment. The rigid rotor is a good starting point from which to construct a model of a rotating molecule. It is assumed that component atoms are point masses connected by rigid bonds. A linear molecule lies on a single axis and each atom moves on the surface of a sphere around the center of mass. The two degrees of rotational freedom correspond to the spherical coordinates, θ and φ, which describe the direction of the molecular axis. The quantum state is determined by two quantum numbers J and M. J defines the magnitude of the rotational angular momentum, and M its component about an axis fixed in space, such as an external electric or magnetic field. In the absence of external fields, the energy depends only on J. Under the rigid rotor model, the rotational energy levels, $F(J)$, of the molecule can be expressed as:

$$F\left(J\right) = BJ\left(J+1\right) \qquad J = 0, 1, 2, ... \tag{33.1.1}$$

where B is the rotational constant of the molecule and is related to its moment of inertia. In a diatomic molecule the moment of inertia about an axis perpendicular to the molecular axis is unique, so:

$$B = \frac{h}{8\pi^2 cI}, \tag{33.1.2}$$

with:

$$I = \frac{m_1 m_2}{m_1 + m_2} d^2, \tag{33.1.3}$$

where m_1 and m_2 are the masses of the atoms and d is the distance between them.

The selection rule for rotational spectroscopy dictate that during emission or absorption the rotational quantum number has to change by unity:

$$\Delta J = J' - J'' = \pm 1, \tag{33.1.4}$$

where J' denotes the lower level and J'' denotes the upper level involved in the transition. Thus, the locations of the lines in a rotational spectrum will be given by

$$\tilde{\nu}_{J'} \leftrightarrow J'' = F\left(J'\right) - F\left(J''\right) = 2B\left(J''+1\right) \qquad J'' = 0, 1, 2, ... \tag{33.1.5}$$

The diagram illustrates rotational transitions that obey the $\Delta J = 1$ selection rule is in figure 33.1.1.[1] The dashed lines show how these transitions map onto features that can be observed experimentally. Adjacent $J'' \leftarrow J'$ transitions are separated by $2B$ in the observed spectrum. Frequency or wavenumber units can also be used for the x axis of this plot.

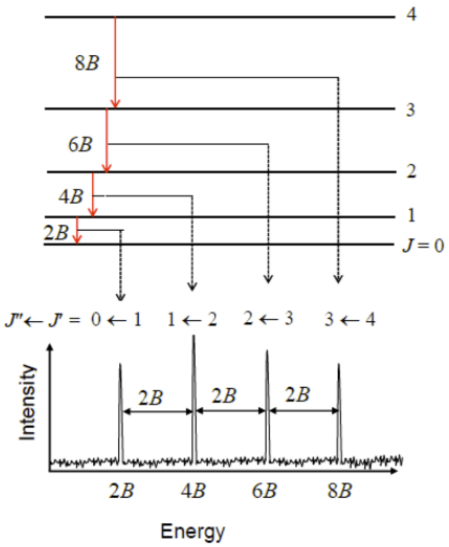


Figure 33.1.1: Rotational energy levels and line positions calculated in the rigid rotor approximation.

The probability of a transition taking place is the most important factor influencing the intensity of an observed rotational line. This probability is proportional to the population of the initial state involved in the transition. The population of a rotational state depends on two factors. The number of molecules in an excited state with quantum number J, relative to the number of molecules in the ground state, N_J/N_0 is given by the Boltzmann distribution:

$$\frac{N_J}{N_0} = e^{-\frac{E_J}{kT}} = \exp\left[-\frac{BhcJ(J+1)}{kT}\right], \tag{33.1.6}$$

where k is the Boltzmann constant and T is the absolute temperature. This factor decreases as J increases. The second factor is the degeneracy of the rotational state, which is equal to $2J+1$. This factor increases as J increases. Combining the two factors we obtain:

$$\text{population} \propto (2J+1)\exp\left[\frac{E_J}{kT}\right], \tag{33.1.7}$$

in agreement with the experimental shape of rotational spectra of diatomic molecules.

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33.2: Vibrational Spectroscopy

Vibrational spectroscopy is concerned with the measurement of the energies of transitions between quantized vibrational states of molecules in the gas phase. These transitions usually occur in the middle infrared (IR) region of the electromagnetic wave at approximately $4,000 - 400 \ \text{cm}^{-1}$ $(2.5 - 25 \ \mu\text{m})$. In the gas phase, vibrational transitions are almost always accompanied by changes in rotational energy. Transitions involving changes in both vibrational and rotational states are usually abbreviated as rovibrational transitions. Since changes in rotational energy levels are typically much smaller than changes in vibrational energy levels, changes in rotational state are said to give fine structure to the vibrational spectrum. For a given vibrational transition, the same theoretical treatment that we saw in the previous section for pure rotational spectroscopy gives the rotational quantum numbers, energy levels, and selection rules.

As we have done in the previous section, we will discuss below the simplest case of a diatomic molecule. For non-linear molecules the spectra becomes complicated to calculate, but their interpretation remains an important tool for the analysis of chemical structures.

Vibration of heteronuclear diatomic molecules

Diatomic molecules with the general formula AB have one normal mode of vibration involving stretching of the $\text{A} - \text{B}$ bond. The vibrational term values, $G(v)$ can be calculated with the harmonic approximation that we discussed in chapter 20. The resulting equidistant energy levels depend on one vibrational quantum number v:

$$G(v) = \omega_e \left(v + \frac{1}{2} \right), \tag{33.2.1}$$

where ω_e is the harmonic frequency around equilibrium. When the molecule is in the gas phase, it can rotate about an axis, perpendicular to the molecular axis, passing through the center of mass of the molecule. As we discussed in the previous section, the rotational energy is also quantized, and depend on the rotational quantum number J. The values of the ro-vibrational states are found (in wavenumbers) by combining the expressions for vibration and rotation:

$$G(v) + F_v(J) = \left[\omega_e \left(v + \frac{1}{2} \right) + B_v J(J+1) \right], \tag{33.2.2}$$

where $F_v(J)$ are the rotational levels at each vibrational state v.[1]

The selection rule for electric dipole allowed ro-vibrational transitions, in the case of a diamagnetic diatomic molecule is:

$$\Delta v = \pm 1 \ (\pm 2, \pm 3, ...), \ \Delta J = \pm 1. \tag{33.2.3}$$

The transition with $\Delta v = \pm 1$ is known as the *fundamental transition*, while the others are called *overtones*. The selection rule has two consequences:

1. Both the vibrational and rotational quantum numbers must change. The transition $\Delta v = \pm 1, \ \ \Delta J = 0$ (Q-branch) is forbidden.
2. The energy change of rotation can be either subtracted from or added to the energy change of vibration, giving the P- and R- branches of the spectrum, respectively.

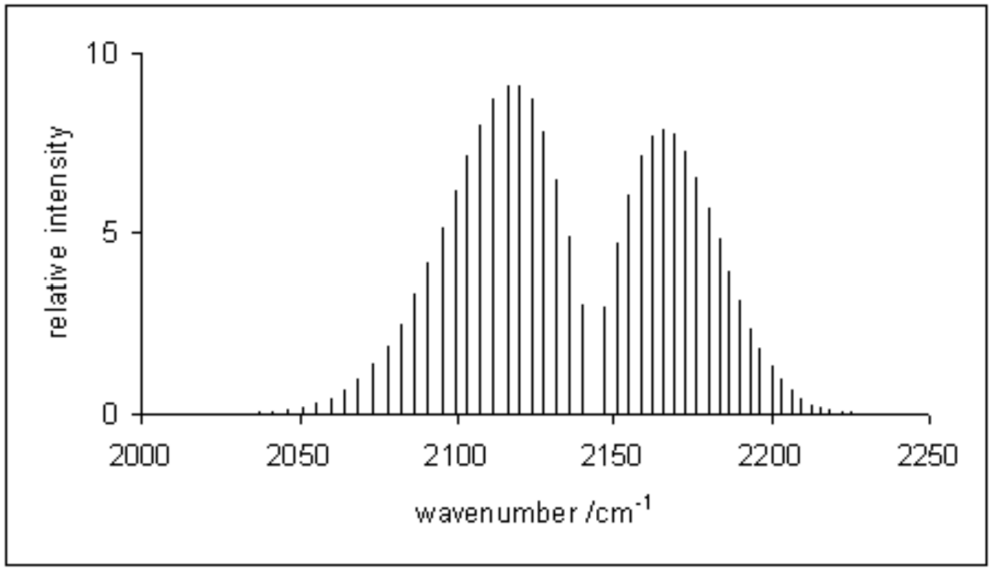


Figure 33.2.1: Simulated vibration-rotation line spectrum of carbon monoxide. The P-branch is to the left of the gap at 2140 1/cm, the R-branch on the right.

A typical rovibrational spectrum is reported in figure 33.2.1 for the CO molecule.[2] The intensity of the signals is—once again—proportional to the initial population of the levels. Notice how the signals in the spectrum are divided among two sides, the P-branch to the left, and the R-branch to the right. These signals correspond to the transitions reported in figure 33.2.2.[3] Notice how the transitions corresponding to the Q-branch are forbidden by the selection rules, and therefore not observed in the experimental spectrum. The position of the missing Q-branch, however, can be easily obtained from the experimental spectrum as the missing signal between the P- and R- branches. Since the Q-branch transitions do not involve changes in the rotational energy level, their value is directly proportional to ω_e. This fact makes rovibrational spectroscopy an important experimental tool in the determination of bond distances of diatomic molecules.

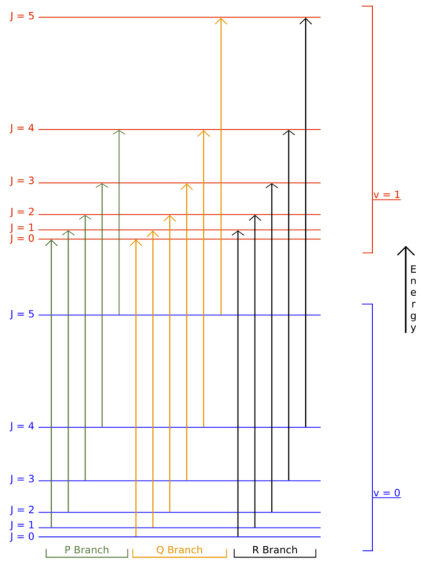


Figure 33.2.2: Schematic rovibrational energy level diagram for a linear molecule.

Vibration of homonuclear diatomic molecules

The quantum mechanics for homonuclear diatomic molecules is qualitatively the same as for heteronuclear diatomic molecules, but the selection rules governing transitions are different. Since the electric dipole moment of the homonuclear diatomics is zero, the fundamental vibrational transition is electric-dipole-forbidden and the molecules are infrared inactive.

The spectra of these molecules can be observed by a type of IR spectroscopy that is subject to different selection rules. This technique is called **Raman spectroscopy**, and allows identification of the rovibrational spectra of homonuclear diatomic molecules because their molecular vibration is Raman-allowed.

---

1. ⚠This is just a first approximation to rovibrational spectroscopy. Corrections for anharmonicity centrifugal distortion are necessary to closely match experimental spectra.
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33.3: Electronic Spectroscopy

Electronic spectroscopy is concerned with the measurement of the energies of transitions between quantized electronic states of molecules. Electronic transitions are always associated with simultaneous changes in vibrational levels. In the gas phase vibronic transitions are also accompanied by changes in rotational energy.

Electronic transitions are typically observed in the visible and ultraviolet regions, in the wavelength range approximately $200 - 700\ \text{nm}$ $(50,000 - 14,000\ \text{cm}^{-1})$. When the electronic and vibrational energy changes are drastically different, vibronic coupling (mixing of electronic and vibrational wave functions) can be neglected and the energy of a vibronic level can be taken as the sum of the electronic and vibrational (and rotational) energies; that is, the Born–Oppenheimer approximation applies. The overall molecular energy depends not only on the electronic state but also on the vibrational and rotational quantum numbers, v and J. In this context, it is conventional to add a double prime (v'', J'') for levels of the electronic ground state and a single prime (v', J') for electronically excited states.

Each electronic transition may show vibrational coarse structure, and for molecules in the gas phase, rotational fine structure. This is true even when the molecule has a zero dipole moment and therefore has no vibration-rotation infrared spectrum or pure rotational microwave spectrum.

It is necessary to distinguish between absorption and emission spectra. With absorption the molecule starts in the ground electronic state, and usually also in the vibrational ground state $v'' = 0$ because at ordinary temperatures the energy necessary for vibrational excitation is large compared to the average thermal energy. The molecule is excited to another electronic state and to many possible vibrational states $v' = 0, 1, 2, 3, \ldots$. With emission, the molecule can start in various populated vibrational states, and finishes in the electronic ground state in one of many populated vibrational levels. The emission spectrum is more complicated than the absorption spectrum of the same molecule because there are more changes in vibrational energy level.

As we did for the previous two cases, we will concentrate below on the electronic absorption spectroscopy of diatomic molecules.

Electronic spectroscopy of diatomic molecules

The vibronic spectra of diatomic molecules in the gas phase also show rotational fine structure. Each line in a vibrational progression will show P- and R- branches. For some electronic transitions there will also be a Q-branch. The transition energies of the lines for a particular vibronic transition are given (in wavenumbers) by:

$$G(J', J'') = \bar{\nu}_{v'-v''} + B'J'(J'+1) - B''J''(J''+1). \tag{33.3.1}$$

The values of the rotational constants, B' and B'' may differ appreciably because the bond length in the electronic excited state may be quite different from the bond length in the ground state. The rotational constant is inversely proportional to the square of the bond length. Usually $B' < B''$, as is true when an electron is promoted from a bonding orbital to an antibonding orbital, causing bond lengthening.

The treatment of rotational fine structure of vibronic transitions is similar to the treatment of rotation-vibration transitions and differs principally in the fact that the ground and excited states correspond to two different electronic states as well as to two different vibrational levels. For the P-branch $J' = J'' - 1$, so that:

$$\begin{aligned} \bar{\nu}_P &= \bar{\nu}_{v'-v''} + B'\left(J''-1\right)J'' - B''J''\left(J''+1\right) \\ &= \bar{\nu}_{v'-v''} - \left(B'+B''\right)J'' + \left(B'-B''\right)J'' \end{aligned} \tag{33.3.2}$$

Similarly, for the R-branch $J'' = J' - 1$, and:

$$\begin{aligned} \bar{\nu}_R &= \bar{\nu}_{v'-v''} + B'J'(J'+1) - B''J'(J'-1) \\ &= \bar{\nu}_{v'-v''} + (B'+B'')J' + (B'-B'')J'^2. \end{aligned} \tag{33.3.3}$$

Thus, the wavenumbers of transitions in both P- and R- branches are given, to a first approximation, by the single formula:

$$\bar{\nu}_{P,R} = \bar{\nu}_{v',v''} + (B'+B'')m + (B'-B'')m^2, \quad m = \pm 1, \pm 2 \ldots. \tag{33.3.4}$$

Here positive m values refer to the R-branch (with $m = +J' = J'' + 1$) and negative values refer to the P-branch (with $m = -J''$).

The intensity of allowed vibronic transitions is governed by the Franck-Condon principle, which states that during an electronic transition, a change from one vibrational energy level to another will be more likely to happen if the two vibrational wave functions overlap more significantly. A diagrammatic representation of electronic spectroscopy and the Frack-Condon principle for a diatomic molecule is presented in figure $33.3.1$.[1]

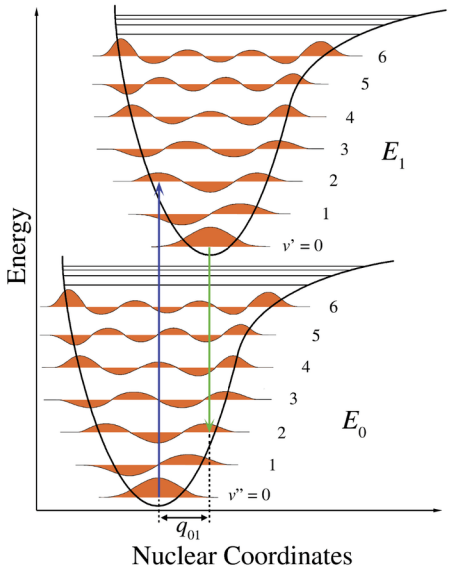


Figure $33.3.1$: Energy level diagram illustrating the Franck–Condon principle.

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