THERMODYNAMICS AND INTRODUCTION TO QUANTUM MECHANICS



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Thermodynamics and Introduction to Quantum Mechanics (Southern)

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Detailed Licensing

Licensing

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CHAPTER OVERVIEW

1: Fundamentals of Thermodynamics

1.1: Thermodynamic Definitions

1.2: Ideal Gas Equation of State

1.3: Equations of State for Real Gases

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1.1: Thermodynamic Definitions

Chemists are interested in systems containing matter—that which has mass and occupies physical space. Classical thermodynamics looks at *macroscopic* aspects of matter. It deals with the properties of aggregates of vast numbers of microscopic particles (molecules, atoms, and ions). The macroscopic viewpoint, in fact, treats matter as a *continuous* material medium rather than as the collection of discrete microscopic particles we know are actually present. Although this e-book is an exposition of classical thermodynamics, at times it will point out connections between macroscopic properties and molecular structure and behavior.

A thermodynamic **system** is any three-dimensional region of physical space on which we wish to focus our attention. Usually we consider only one system at a time and call it simply "the system." The rest of the physical universe constitutes the **surroundings** of the system.

The **boundary** is the closed three-dimensional surface that encloses the system and separates it from the surroundings. The boundary may (and usually does) coincide with real physical surfaces: the interface between two phases, the inner or outer surface of the wall of a flask or other vessel, and so on. Alternatively, part or all of the boundary may be an imagined intangible surface in space, unrelated to any physical structure. The size and shape of the system, as defined by its boundary, may change in time. In short, our choice of the three-dimensional region that constitutes the system is arbitrary—but it is essential that we know exactly what this choice is.

We usually think of the system as a part of the physical universe that we are able to influence only indirectly through its interaction with the surroundings, and the surroundings as the part of the universe that we are able to directly manipulate with various physical devices under our control. That is, we (the experimenters) are part of the surroundings, not the system.

For some purposes we may wish to treat the system as being divided into *subsystems*, or to treat the combination of two or more systems as a *supersystem*.

If over the course of time matter is transferred in either direction across the boundary, the system is **open**; otherwise it is **closed**. If the system is open, matter may pass through a stationary boundary, or the boundary may move through matter that is fixed in space.

If the boundary allows heat transfer between the system and surroundings, the boundary is **diathermal**. An **adiabatic** (Greek: *impassable*) boundary, on the other hand, is a boundary that does not allow heat transfer. We can, in principle, ensure that the boundary is adiabatic by surrounding the system with an adiabatic wall—one with perfect thermal insulation and a perfect radiation shield.

An **isolated** system is one that exchanges no matter, heat, or work with the surroundings, so that the mass and total energy of the system remain constant over time. (The energy in this definition of an isolated system is measured in a local reference frame, as will be explained in Sec. 2.6.2.) A closed system with an adiabatic boundary, constrained to do no work and to have no work done on it, is an isolated system.

> The constraints required to prevent work usually involve forces between the system and surroundings. In that sense a system may interact with the surroundings even though it is isolated. For instance, a gas contained within rigid, thermally-insulated walls is an isolated system; the gas exerts a force on each wall, and the wall exerts an equal and opposite force on the gas. An isolated system may also experience a constant external field, such as a gravitational field.

The term **body** usually implies a system, or part of a system, whose mass and chemical composition are constant over time.

2.1.1 Extensive and intensive properties

A quantitative *property* of a system describes some macroscopic feature that, although it may vary with time, has a particular value at any given instant of time.

Table 2.1 lists the symbols of some of the properties discussed in this chapter and the SI units in which they may be expressed. A much more complete table is found in Appendix C.

Most of the properties studied by thermodynamics may be classified as either extensive or intensive. We can distinguish these two types of properties by the following considerations.

If we imagine the system to be divided by an imaginary surface into two parts, any property of the system that is the sum of the property for the two parts is an **extensive property**. That is, an additive property is extensive. Examples are mass, volume, amount, energy, and the surface area of a solid.

> Sometimes a more restricted definition of an extensive property is used: The property must be not only additive, but also proportional to the mass or the amount when intensive properties remain constant. According to this definition, mass, volume, amount, and energy are extensive, but surface area is not.

If we imagine a homogeneous region of space to be divided into two or more parts of arbitrary size, any property that has the same value in each part and the whole is an **intensive property**; for example density, concentration, pressure (in a fluid), and temperature. The value of an intensive property is the same everywhere in a homogeneous region, but may vary from point to point in a heterogeneous region—it is a *local* property.

Since classical thermodynamics treats matter as a continuous medium, whereas matter actually contains discrete microscopic particles, the value of an intensive property at a point is a statistical average of the behavior of many particles. For instance, the density of a gas at one point in space is the average mass of a small volume element at that point, large enough to contain many molecules, divided by the volume of that element.

Some properties are defined as the ratio of two extensive quantities. If both extensive quantities refer to a homogeneous region of the system or to a small volume element, the ratio is an *intensive* property. For example concentration, defined as the ratio **amount/volume**, is intensive. A mathematical derivative of one such extensive quantity with respect to another is also intensive.

A special case is an extensive quantity divided by the mass, giving an intensive **specific quantity**; for example

$$\text{Specific volume} = \frac{V}{m} = \frac{1}{\rho} \tag{2.1.1}$$

If the symbol for the extensive quantity is a capital letter, it is customary to use the corresponding lower-case letter as the symbol for the specific quantity. Thus the symbol for specific volume is v.

Another special case encountered frequently in this e-book is an extensive property for a pure, homogeneous substance divided by the amount n. The resulting intensive property is called, in general, a **molar quantity** or molar property. To symbolize a molar quantity, this e-book follows the recommendation of the IUPAC: The symbol of the extensive quantity is followed by subscript m, and optionally the identity of the substance is indicated either by a subscript or a formula in parentheses. Examples are

$$\text{Molar volume} = \frac{V}{n} = V_{\mathrm{m}} \tag{2.1.2}$$

$$\text{Molar volume of substance } i = \frac{V}{n_i} = V_{\mathrm{m},i} \tag{2.1.3}$$

$$\text{Molar volume of } \mathrm{H_2O} \; = V_{\mathrm{m}}(\mathrm{H_2O}) \tag{2.1.4}$$

In the past, especially in the United States, molar quantities were commonly denoted with an overbar (e.g., $\overline{V}_i$).

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1.2: Ideal Gas Equation of State

In an ideal gas, there are no interactions between the particles, hence, the particles do not exert forces on each other. However, particles do experience a force when they collide with the walls of the container. Let us assume that each collision with a wall is elastic. Let us assume that the gas is in a cubic box of length a and that two of the walls are located at $x = 0$ and at $x = a$. Thus, a particle moving along the x direction will eventually collide with one of these walls and will exert a force on the wall when it strikes it, which we will denote as F_x. Since every action has an equal and opposite reaction, the wall exerts a force $-F_x$ on the particle. According to Newton's second law, the force $-F_x$ on the particle in this direction gives rise to an acceleration via

$$-F_x = ma_x = m\frac{\Delta v_x}{\Delta t} \tag{1.2.1}$$

Here, t represents the time interval between collisions with the same wall of the box. In an elastic collision, all that happens to the velocity is that it changes sign. Thus, if v_x is the velocity in the x direction before the collision, then $-v_x$ is the velocity after, and $\Delta v_x = -v_x - v_x = -2v_x$, so that

$$-F_x = -2m\frac{v_x}{\Delta t} \tag{1.2.2}$$

In order to find Δt, we recall that the particles move at constant speed. Thus, a collision between a particle and, say, the wall at $x = 0$ will not change the particle's speed. Before it strikes this wall again, it will proceed to the wall at $x = a$ first, bounce off that wall, and then return to the wall at $x = 0$. The total distance in the x direction traversed is $2a$, and since the speed in the x direction is always v_x, the interval $\Delta t = \frac{2a}{v_x}$. Consequently, the force is

$$-F_x = -\frac{mv_x^2}{a} \tag{1.2.3}$$

Thus, the force that the particle exerts on the wall is

$$F_x = \frac{mv_x^2}{a} \tag{1.2.4}$$

The mechanical definition of pressure is

$$P = \frac{\langle F \rangle}{A} \tag{1.2.5}$$

where $\langle F \rangle$ is the average force exerted by all N particles on a wall of the box of area A. Here $A = a^2$. If we use the wall at $x = 0$ we have been considering, then

$$P = \frac{N\langle F_x \rangle}{a^2} \tag{1.2.6}$$

because we have N particles hitting the wall. Hence,

$$P = \frac{Nm\langle v_x^2 \rangle}{a^3} \tag{1.2.7}$$

from our study of the Maxwell-Boltzmann distribution, we found that

$$\langle v_x^2 \rangle = \frac{k_B T}{m} \tag{1.2.8}$$

Hence, since $a^3 = V$,

$$P = \frac{Nk_B T}{V} = \frac{nRT}{V} \tag{1.2.9}$$

which is the ideal gas law.

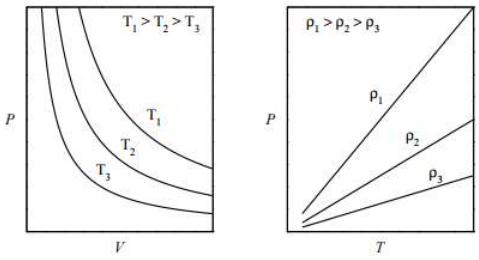


Figure 2.3.1: (Left) Pressure vs. volume for different temperatures (isotherms of the ideal-gas equation of state. (Right) Pressure vs. temperature for different densities $\rho = N/V$.

The ideal gas law is an example of an equation of state, which was introduced in Lecture 1. One way to visualize any equation of state is to plot the so-called *isotherms*, which are graphs of P vs. V at fixed values of T . For the ideal-gas equation of state $P = nRT/V$, some of the isotherms are shown in the figure below (left panel): If we plot P vs. T at fixed volume (called the *isochores*), we obtain the plot in the right panel. What is important to note, here, is that an ideal gas can exist *only* as a gas. It is not possible for an ideal gas to condense into some kind of "ideal liquid". In other words, a phase transition from gas to liquid can be modeled only if interparticle interactions are properly accounted for.

Note that the ideal-gas equation of state can be written in the form

$$\frac{PV}{nRT} = \frac{P\bar{V}}{RT} = \frac{P}{\rho RT} = 1 \tag{1.2.10}$$

where $\bar{V} = V/n$ is called the molar volume. Unlike V , which increases as the number of moles increases (an example of what is called an *extensive* quantity in thermodynamics), \(\bar{V}\) does not exhibit this dependence and, therefore, is called *intensive*. The quantity

$$Z = \frac{PV}{nRT} = \frac{P\bar{V}}{RT} = \frac{P}{\rho RT} \tag{1.2.11}$$

is called the *compressibility* of the gas. In an ideal gas, if we "compress" the gas by increasing P , the density ρ must increase as well so as to keep $Z = 1$. For a real gas, Z, therefore, gives us a measure of how much the gas deviates from ideal-gas behavior.

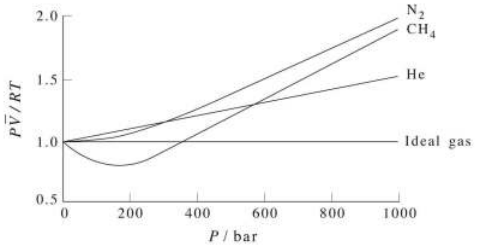


Figure 2.3.2: Plot of the compressibility Z vs. P for several gases, together with the ideal gas, where $Z = 1$.

Figure 2.2 shows a plot of Z vs. P for several real gases and for an ideal gas. The plot shows that for sufficiently low pressures (hence, low densities), each gas approaches ideal-gas behavior, as expected.

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1.3: Equations of State for Real Gases

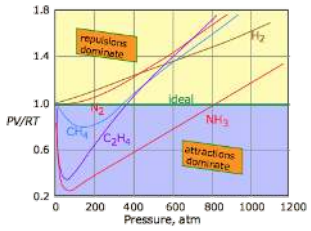
According to Boyle's law, the product PV is a constant at any given temperature, so a plot of PV as a function of the pressure of an ideal gas yields a horizontal straight line. This implies that any increase in the pressure of the gas is exactly counteracted by a decrease in the volume as the molecules are crowded closer together. But we know that the molecules themselves are finite objects having volumes of their own, and this must place a lower limit on the volume into which they can be squeezed. So we must reformulate the ideal gas equation of state as a relation that is true only in the limiting case of zero pressure:

$$\lim_{P \to 0} PV = nRT \tag{1.3.1}$$

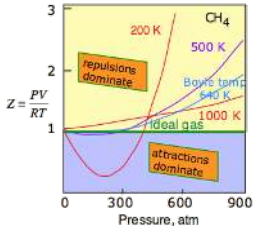
So what happens when a real gas is subjected to a very high pressure? The outcome varies with both the molar mass of the gas and its temperature, but in general we can see the the effects of both repulsive and attractive intermolecular forces:

- Repulsive forces: As a gas is compressed, the individual molecules begin to get in each other's way, giving rise to a very strong repulsive force acts to oppose any further volume decrease. We would therefore expect the PV vs P line to curve upward at high pressures, a nd this is in fact what is observed for all gases at sufficiently high pressures.
- Attractive forces: At very close distances, all molecules repel each other as their electron clouds come into contact. At greater distances, however, brief statistical fluctuations in the distribution these electron clouds give rise to a universal attractive force between all molecules. The more electrons in the molecule (and thus the greater the molecular weight), the greater is this attractive force. As long as the energy of thermal motion dominates this attractive force, the substance remains in the gaseous state, but at sufficiently low temperatures the attractions dominate and the substance condenses to a liquid or solid.

The universal attractive force described above is known as the *dispersion*, or *London* force. There may also be additional (and usually stronger) attractive forces related to charge imbalance in the molecule or to hydrogen bonding. These various attractive forces are often referred to collectively as *van der Waals forces*. A plot of PV/RT as a function of pressure is a very sensitive indicator of deviations from ideal behavior, since such a plot is just a horizontal line for an ideal gas. The two illustrations below show how these plots vary with the nature of the gas, and with temperature.



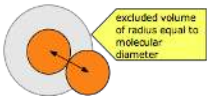
Intermolecular attractions, which generally increase with molecular weight, cause the PV product to decrease as higher pressures bring the molecules closer together and thus within the range of these attractive forces; the effect is to cause the volume to decrease more rapidly than it otherwise would. The repulsive forces always eventually win out. But as the molecules begin to intrude on each others' territory, the stronger repulsive forces cause the curve to bend upward.



The **temperature** makes a big difference! At higher temperatures, increased thermal motions overcome the effects of intermolecular attractions which normally dominate at lower pressures. So all gases behave more ideally at higher temperatures. For any gas, there is a special temperature (the *Boyle temperature*) at which attractive and repulsive forces exactly balance each other at zero pressure. As you can see in this plot for methane, this some of this balance does remain as the pressure is increased.

The van der Waals Equation of State

How might we modify the ideal gas equation of state to take into account the effects of intermolecular interactions? The first and most well known answer to this question was offered by the Dutch scientist J.D. van der Waals (1837-1923) in 1873. The ideal gas model assumes that the gas molecules are merely points that occupy no volume; the "V" term in the equation is the volume of the container and is independent of the nature of the gas.

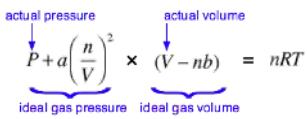


van der Waals recognized that the molecules themselves take up space that subtracts from the volume of the container, so that the "volume of the gas" V in the ideal gas equation should be replaced by the term $(V–b)$, in which b relates to the *excluded volume*, typically of the order of 20-100 cm^3 mol^{-1}. The excluded volume surrounding any molecule defines the closest possible approach of any two molecules during collision. Note that the excluded volume is greater then the volume of the molecule, its radius being half again as great as that of a spherical molecule.

The other effect that van der Waals needed to correct for are the intermolecular attractive forces. These are ignored in the ideal gas model, but in real gases they exert a small cohesive force between the molecules, thus helping to hold the gas together and reducing the pressure it exerts on the walls of the container.

Because this pressure depends on both the frequency *and* the intensity of collisions with the walls, the reduction in pressure is proportional to the *square* of the number of molecules per volume of space, and thus for a fixed number of molecules such as one mole, the reduction in pressure is inversely proportional to the square of the volume of the gas. The smaller the volume, the closer are the molecules and the greater will be the effect. The van der Waals equation replaces the P term in the ideal gas equation with $P + (a/V^2)$ in which the magnitude of the constant a increases with the strength of the intermolecular attractive forces.

The complete van der Waals equation of state can be written as



Although most students are not required to memorize this equation, you are expected to understand it and to explain the significance of the terms it contains. You should also understand that the van der Waals constants ***a*** and ***b*** must be determined empirically for every gas. This can be done by plotting the *P*-*V* behavior of the gas and adjusting the values of *a* and *b* until the van der Waals equation results in an identical plot. The constant ***a*** is related in a simple way to the molecular radius; thus the determination of ***a*** constitutes an indirect measurement of an important microscopic quantity.

Table **1.3.1** : van der Waals constants for some gases

Substance	molar mass, g	a (L^2-atm $mole^{-2}$)
hydrogen H_2	2	0.244
helium He	4	0.034
methane CH_4	16	2.25
water H_2O	18	5.46
nitrogen N_2	28	1.39
carbon dioxide CO_2	44	3.59
carbon tetrachloride CCl_4	154	20.4

The van der Waals equation is only one of many equations of state for real gases. More elaborate equations are required to describe the behavior of gases over wider pressure ranges. These generally take account of higher-order nonlinear attractive forces, and require the use of more empirical constants. Although we will make no use of them in this course, they are widely employed in chemical engineering work in which the behavior of gases at high pressures must be accurately predicted.

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CHAPTER OVERVIEW

2: The First Law of Thermodynamics

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2.1: Work and Heat

One of the pioneers in the field of modern thermodynamics was James P. Joule (1818 - 1889). Among the experiments Joule carried out, was an attempt to measure the effect on the temperature of a sample of water that was caused by doing work on the water. Using a clever apparatus to perform work on water by using a falling weight to turn paddles within an insulated canister filled with water, Joule was able to measure a temperature increase in the water.

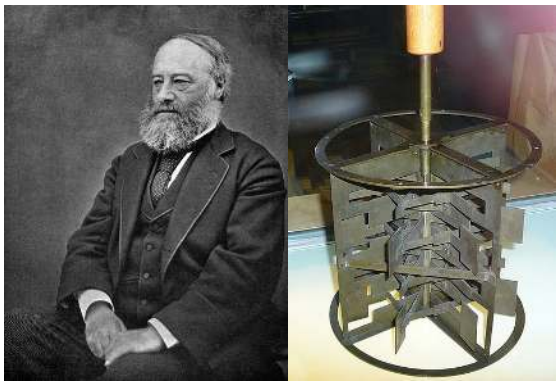


Figure **2.1.1**: (left) James Prescott Joule (1818 - 1889) (right) Joule's apparatus for measuring the work equivalent of heat. (CC BY-SA 3.0; Dr. Mirko Junge)

Thus, Joule was able to show that work and heat can have the same effect on matter – a change in temperature! It would then be reasonable to conclude that heating, as well as doing work on a system will increase its energy content, and thus it's ability to perform work in the surroundings. This leads to an important construct of the **First Law of Thermodynamics**:

> *The capacity of a system to do work is increased by heating the system or doing work on it.*

The **internal energy** (U) of a system is a measure of its capacity to supply energy that can do work within the surroundings, making U the ideal variable to keep track of the flow of heat and work energy into and out of a system. Changes in the internal energy of a system (ΔU) can be calculated by

$$\Delta U = U_f - U_i \tag{2.1.1}$$

where the subscripts i and f indicate initial and final states of the system. U as it turns out, is a state variable. In other words, the amount of energy available in a system to be supplied to the surroundings is independent on how that energy came to be available. That's important because the manner in which energy is transferred is path dependent.

There are two main methods energy can be transferred to or from a system. These are suggested in the previous statement of the first law of thermodynamics. Mathematically, we can restate the first law as

$$\Delta U = q + w$$

or

$$dU = dq + dw$$

where q is defined as the amount of energy that flows into a system in the form of **heat** and w is the amount of energy lost due to the system doing **work** on the surroundings.

Heat

Heat is the kind of energy that in the absence of other changes would have the effect of changing the temperature of the system. A process in which heat flows into a system is **endothermic** from the standpoint of the system ($q_{system} > 0$, $q_{surroundings} < 0$). Likewise, a process in which heat flows out of the system (into the surroundings) is called **exothermic** ($q_{system} < 0$, $q_{surroundings} > 0$). In the absence of any energy flow in the form or work, the flow of heat into or out of a system can be measured by a change in temperature. In cases where it is difficult to measure temperature changes of the system directly, the amount of heat energy

transferred in a process can be measured using a change in temperature of the soundings. (This concept will be used later in the discussion of calorimetry).

An infinitesimal amount of heat flow into or out of a system can be related to a change in temperature by

$$dq = C\,dT$$

where C is the **heat capacity** and has the definition

$$C = \frac{dq}{\partial T}$$

Heat capacities generally have units of (J mol^{-1} K^{-1}) and magnitudes equal to the number of J needed to raise the temperature of 1 mol of substance by 1 K. Similar to a heat capacity is a **specific heat** which is defined per unit mass rather than per mol. The specific heat of water, for example, has a value of 4.184 J g^{-1} K^{-1} (at constant pressure – a pathway distinction that will be discussed later.)

Example 2.1.1: Heat required to Raise Temperature

How much energy is needed to raise the temperature of 5.0 g of water from 21.0 °C to 25.0 °C?

Solution

$$\begin{aligned} q &= mC\Delta T \\ &= (5.0\ \cancel{g})(4.184\frac{J}{\cancel{g}\ \cancel{^\circ C}})(25.0\cancel{^\circ C} - 21.0\cancel{^\circ C}) \\ &= 84\,J \end{aligned}$$

What is a partial derivative?

A partial derivative, like a total derivative, is a slope. It gives a magnitude as to how quickly a function changes value when one of the dependent variables changes. Mathematically, a partial derivative is defined for a function $f(x_1, x_2, \ldots x_n)$ by

$$\left(\frac{\partial f}{\partial x_i}\right)_{x_j \neq i} = \lim_{\Delta_i \to 0}\left(\frac{f(x_1 + \Delta x_1, x_2 + \Delta x_2, \ldots, x_i + \Delta x_i, \ldots x_n + \Delta x_n) - f(x_1, x_2, \ldots x_i, \ldots x_n)}{\Delta x_i}\right)$$

Because it measures how much a function changes for a change in a given dependent variable, infinitesimal changes in the in the function can be described by

$$df = \sum_i \left(\frac{\partial f}{\partial x_i}\right)_{x_j \neq i}$$

So that each contribution to the total change in the function f can be considered separately.

For simplicity, consider an ideal gas. The pressure can be calculated for the gas using the ideal gas law. In this expression, pressure is a function of temperature and molar volume.

$$p(V,T) = \frac{RT}{V}$$

The partial derivatives of p can be expressed in terms of T and V as well.

$$\left(\frac{\partial p}{\partial V}\right)_T = -\frac{RT}{V^2} \tag{2.1.2}$$

and

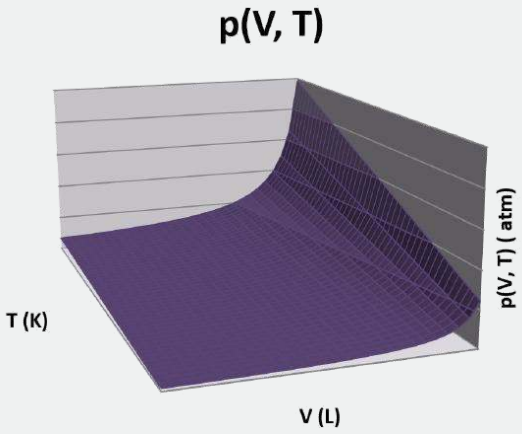
$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{R}{V} \tag{2.1.3}$$

So that the change in pressure can be expressed

$$dp = \left(\frac{\partial p}{\partial V}\right)_T dV + \left(\frac{\partial p}{\partial T}\right)_V dT \tag{2.1.4}$$

or by substituting Equations 2.1.2 and 2.1.3

$$dp = \left(-\frac{RT}{V^2}\right) dV + \left(\frac{R}{V}\right) dT$$



Macroscopic changes can be expressed by integrating the individual pieces of Equation 2.1.4 over appropriate intervals.

$$\Delta p = \int_{V_1}^{V_2} \left(\frac{\partial p}{\partial V}\right)_T dV + \int_{T_1}^{T_2} \left(\frac{\partial p}{\partial T}\right)_V dT$$

This can be thought of as two consecutive changes. The first is an **isothermal** (constant temperature) expansion from V_1 to V_2 at T_1 and the second is an **isochoric** (constant volume) temperature change from T_1 to T_2 at V_2. For example, suppose one needs to calculate the change in pressure for an ideal gas expanding from 1.0 L/mol at 200 K to 3.0 L/mol at 400 K. The set up might look as follows.

$$\Delta p = \underbrace{\int_{V_1}^{V_2} \left(-\frac{RT}{V^2}\right) dV}_{\text{isothermal expansion}} + \underbrace{\int_{T_1}^{T_2} \left(\frac{R}{V}\right) dT}_{\text{isochoric heating}}$$

or

$$\begin{aligned}
\Delta p &= \int_{1.0\ L/mol}^{3.0\ L/mol} \left(-\frac{R(400\ K)}{V^2}\right) dV + \int_{200\ K}^{400,\ K} \left(\frac{R}{1.0\ L/mol}\right) dT \\
&= \left[\frac{R(200\ K)}{V}\right]_{1.0\ L/mol}^{3.0\ L/mol} + \left[\frac{RT}{3.0\ L/mol}\right]_{200\ K}^{400\ K} \\
&= R\left[\left(\frac{200\ K}{3.0\ L/mol} - \frac{200\ K}{1.0\ L/mol}\right) + \left(\frac{400\ K}{3.0\ L/mol} - \frac{200\ K}{3.0\ L/mol}\right)\right] \\
&= -5.47\ atm
\end{aligned}$$

Alternatively, one could calculate the change as an isochoric temperature change from T_1 to T_2 at V_1 followed by an isothermal expansion from V_1 to V_2 at T_2:

$$\Delta p = \int_{T_1}^{T_2} \left(\frac{R}{V}\right) dT + \int_{V_1}^{V_2} \left(-\frac{RT}{V^2}\right) dV$$

or

$$\begin{aligned}\Delta p &= \int_{200\ K}^{400,\ K}\left(\frac{R}{1.0\ L/mol}\right)dT + \int_{1.0\ L/mol}^{3.0\ L/mol}\left(-\frac{R(400\ K)}{V^2}\right)dV \\ &= \left[\frac{RT}{1.0\ L/mol}\right]_{200\ K}^{400\ K} + \left[\frac{R(400\ K)}{V}\right]_{1.0\ L/mol}^{3.0\ L/mol} \\ &= R\left[\left(\frac{400\ K}{1.0\ L/mol} - \frac{200\ K}{1.0\ L/mol}\right) + \left(\frac{400\ K}{3.0\ L/mol} - \frac{400\ K}{1.0\ L/mol}\right)\right] \\ &= -5.47\ atm\end{aligned}$$

This results demonstrates an important property of pressure in that pressure is a state variable, and so the calculation of changes in pressure do not depend on the pathway!

Work

Work can take several forms, such as expansion against a resisting pressure, extending length against a resisting tension (like stretching a rubber band), stretching a surface against a surface tension (like stretching a balloon as it inflates) or pushing electrons through a circuit against a resistance. The key to defining the work that flows in a process is to start with an infinitesimal amount of work defined by what is changing in the system.

Table 3.1.1: Changes to the System

Type of work	Displacement	Resistance	dw
Expansion	dV (volume)	-p_{ext} (pressure)	-p_{ext}dV
Electrical	dQ (charge)	W (resistence)	-W dQ
Extension	dL (length)	-t (tension)	t dL
Stretching	dA	-s (surf. tens.)	sdA

The pattern followed is always an infinitesimal displacement multiplied by a resisting force. The total work can then be determined by integrating along the pathway the change follows.

✔ Example 2.1.2: Work from a Gas Expansion

What is the work done by 1.00 mol an ideal gas expanding from a volume of 22.4 L to a volume of 44.8 L against a constant external pressure of 0.500 atm?

Solution

$$dw = -p_{ext}dV$$

since the pressure is constant, we can integrate easily to get total work

$$\begin{aligned}w &= -p_{exp}\int_{V_1}^{V_2} dV \\ &= -p_{exp}(V_2 - V_1) \\ &= -(0.500\ am)(44.8\ L - 22.4\ L)\left(\frac{8.314\ J}{0.08206\ atm\ L}\right) \\ &= -1130\ J = -1.14\ kJ\end{aligned}$$

Note: The ratio of gas law constants can be used to convert between atm·L and J quite conveniently!

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2.2: Pressure-Volume Work

Work in general is defined as a product of a force $\mathbf{F}$ and a path element $\mathbf{ds}$. Both are vectors and work is computed by integrating over their inner product:

$$w = \int \mathbf{F} \cdot \mathbf{ds}$$

Moving an object against the force of friction as done in the above dissipation experiment is but one example of work:

$$w_{friction} = \int \mathbf{F}_{\text{friction}} \cdot \mathbf{ds}$$

We could also think of *electrical* work. In that case we would be moving a charge e (e.g. the negative charge of an electron) against an electrical (vector) field $\mathbf{E}$. The work would be:

$$w_{electical} = \int e\mathbf{E} \cdot \mathbf{ds}$$

Other examples are the stretching of a rubber band against the elastic force or moving a magnet in a magnetic field etc, etc.

Pressure-volume (PV) work

In the case of a cylinder with a piston, the pressure of gas molecules on the inside of the cylinder, P, and the gas molecules external to the piston, P_{ext} both exert a force against each other. Pressure, (\P\), is the force, F, being exerted by the particles per area, A:

$$P = \frac{F}{A}$$

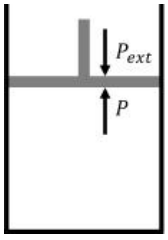


Figure 19.2.1 : A piston with internal pressure P and external pressure P_{ext}.

We can assume that all the forces generated by the pressure of the particles operate parallel to the direction of motion of the piston. That is, the force moves the piston up or down as the movement of the piston is constrained to one direction. The piston moves as the molecules of the gas rapidly equilibrate to the applied pressure such that the internal and external pressures are the same. The result of this motion is work:

$$w_{volume} = \int \left(\frac{F}{A}\right)(A\,ds) = \int P\,dV \tag{2.2.1}$$

This particular form of work is called **pressure-volume (PV) work** and will play an important role in the development of our theory. Notice however that volume work is only ***one form*** of work.

Sign Conventions

It is important to create a sign convention at this point: positive heat, positive work is always energy you put in into the system. If the system decides to remove energy by giving off heat or work, that gets a minus sign.

In other words: ***you pay the bill***.

To comply with this convention we need to rewrite volume work (Equation 2.2.1) as

$$w_{PV} = -\int \left(\frac{F}{A}\right)(A\,ds) = -\int P\,dV$$

> Hence, to decrease the volume of the gas (ΔV is negative), we must put in (positive) work.

Thermodynamics would not have come very far without cylinders to hold gases, in particular steam. The following figure shows when the external pressure, P_{ext}, is greater than and less than the internal pressure, P, of the piston.

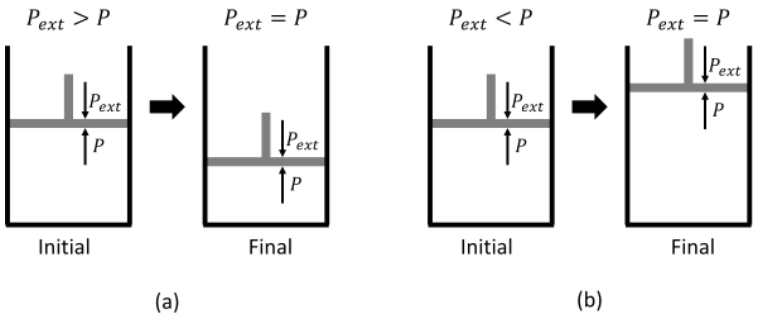


Figure 19.2.2 : Pistons showing a compression (left) and an expansion (right).

If the pressure, P_{ext}, being exerted on the system is constant, then the integral becomes:

$$w = -P_{ext} \int_{V_{initial}}^{V_{final}} dV = -P_{ext} \Delta V \tag{2.2.2}$$

Since the system pressure (inside the piston) is not the same as the pressure exerted on the system, the system is not in a state of equilibrium and cannot be shown directly on and PV diagram. This type of process is called an irreversible process. For a system that undergoes irreversible work at constant external pressure, we can show the amount of work being done on a PV diagram despite not being able to show the process itself.

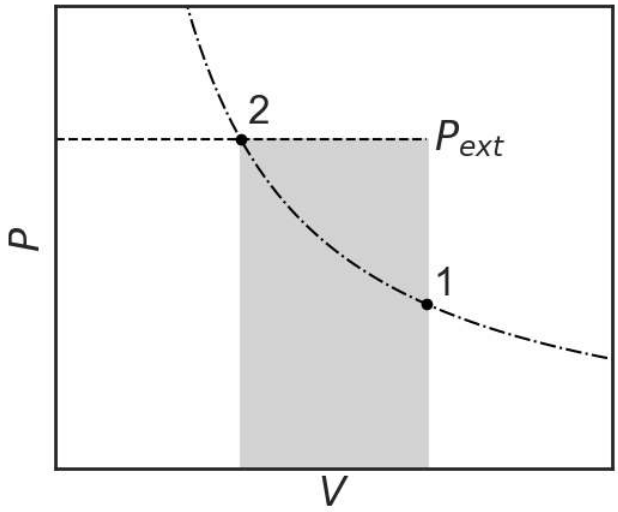


Figure 19.2.3 : A system is compressed under constant external pressure, P_{ext}, from state 1 to state 2. The shaded area shows the amount of work being done for the compression. The dash-dot line is an isotherm, a path of constant temperature, showing that the initial and final temperature of the irreversible compression are the same.

Note that the external pressure, P_{ext}, exerted on the system is constant. If the external pressure changes during the compression, we must *integrate* over the whole range:

$$w = -\int_{V_{initial}}^{V_{final}} P_{ext}(V)\, dV$$

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2.2.1: Work and Heat are not State Functions

2.2.1.1: Heat and work are path functions

Heat (q) and work (w) are path functions, not state functions:

1. They are path dependent.
2. They are energy transfer → they are not intrinsic to the system.

Path Functons

Functions that depend on the path taken, such as work (w) and heat (q), are referred to as **path functions**.

2.2.1.2: Reversible versus irreversible

Let's consider a piston that is being compressed at constant temperature (isothermal) to half of its initial volume:

1. Start with cylinder 1 liter, both external and internal pressure 1 bar.
2. ***Peg*** the piston in a fixed position.
3. Put cylinder in a pressure chamber with $P_{ext} = 2$ bar.
4. Suddenly pull the peg.

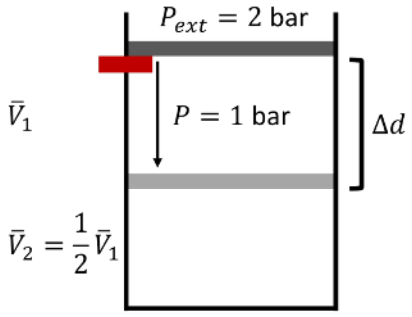


Figure 19.3.1 : A piston is being irreversibly and isothermally compressed under constant external pressure from state 1 to state 2.

The piston will shoot down till the internal and external pressures balance out again and the volume is 1/2 L. Notice that the external pressure was ***maintained*** constant at 2 bar during the peg-pulling and that the internal and external pressures were ***not*** balanced at all time. In a $P-V$ diagram of an ideal gas, P is a hyperbolic function of V under constant temperature (isothermal), but this refers to the *internal* pressure of the gas. It is the external one that counts when computing work and they are not necessarily the same. As long as $P_{external}$ is constant, work is represented by a rectangle.

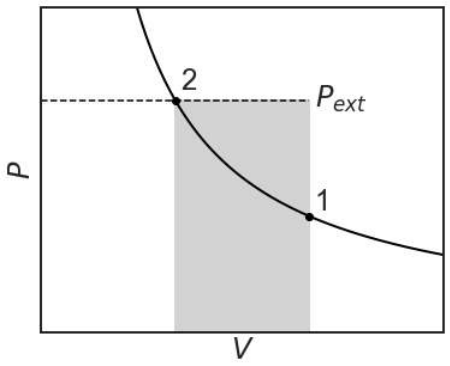


Figure 19.3.1 : The system is being irreversibly and isothermally compressed from state 1 to 2. The amount of work being done on the system is shown by the shaded area.

The amount of work being done is equal to the shaded region and in equation:

$$w = -\int_{V_1}^{V_2} PdV = -P_{ext}(V_2 - V_1) = -P\Delta V$$

This represents the maximum amount of work that can be done for an isothermal compression. Work is being done on the system, so the overall work being done is positive. Let's repeat the experiment, but this time the piston will compress reversibly over infinitesimally small steps where the $P_{ext} = P_{system}$:

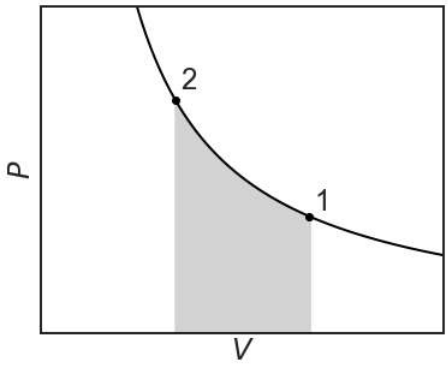


Figure 19.3.1 : The system is being reversibly and isothermally compressed from state 1 to 2. The amount of work being done on the system is shown by the shaded area. Note that for a compression, a reversible process does less work than an irreversible process.

For an ideal gas, the amount of work being done along the reversible compression is:

$$w = -\int_{V_1}^{V_2} PdV = -nRT\int_{V_1}^{V_2} \frac{1}{V} = -nRT\ln\left(\frac{V_2}{V_1}\right)$$

The amount of work being done to the two systems are not the same in the two diagrams (see the gray areas). Work is not a state, but a path function, as it depends on the path taken. You may say, what's the big difference. In both cases, the system is compressed from state 1 to state 2. The key is the word ***suddenly***. By pegging the position in place for the first compression, we have created a situation where the external pressure is higher than the internal pressure ($P_{ext} > P$). Because work is done suddenly by pulling the peg out, the internal pressure is struggling to catch up with the external one. During the second compression, we have $P_{ext} = P$ at all times. It's a bit like falling off a cliff versus gently sliding down a hill. Path one is called an irreversible path, the second a reversible path.

Reversible vs. Irreversible Processes

A reversible path is a path that follows a series of states at rest (i.e., the forces are allowed to balance at all times). In an irreversible one the forces only balance at the very end of the process.

Notice that less work is being done on the reversible isothermal compression than the one-step irreversible isothermal compression. In fact, the minimum amount of work that can be done during a compression always occurs along the reversible path.

2.2.1.2.1: Isothermal Expansion

Let's consider a piston that is being expanded at constant temperature (isothermal) to twice of its initial volume:

1. Start with cylinder 1 liter in a pressure chamber with both an external and internal pressure of 2 bar.
2. ***Peg*** the piston in a fixed position.
3. Take the cylinder out of the pressure chamber with P_{ext}= 1 bar.
4. Suddenly pull the peg.

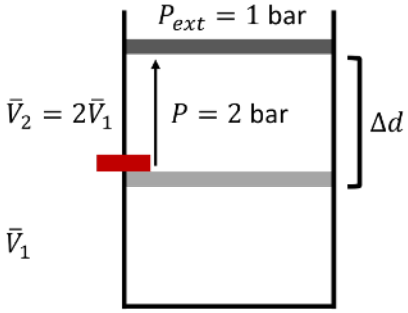


Figure 19.3.1 : A piston is being irreversibly and isothermally expanded under constant external pressure from state 1 to state 2.

The piston will shoot up till the internal and external pressures balance out again and the volume is 2 L. Notice that the external pressure was ***maintained*** constant at 1 bar during the peg-pulling and that the internal and external pressures were ***not*** balanced at all time.

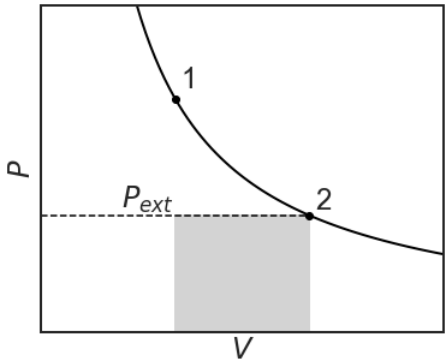


Figure 19.3.1 : The system is being irreversibly and isothermally expanded from state 1 to 2. The amount of work being done by the system is shown by the shaded area.

The amount of irreversible work being done is again equal to the shaded region and the equation:

$$w = -P\Delta V = -P_{ext}(V_2 - V_1) = -P\Delta V$$

This represents the minimum amount of work that can be done for an isothermal expansion. Work is being done on the system, so the overall work being done is negative. Let's repeat the experiment, but this time the piston will compress reversibly over infinitesimally small steps where the $P_{ext} = P_{system}$:

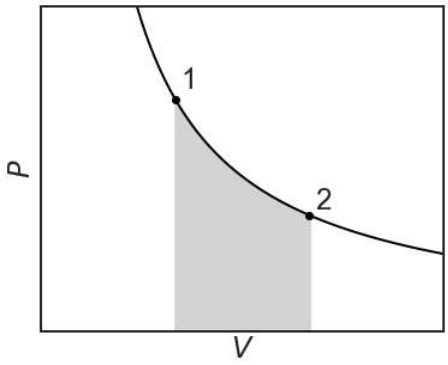


Figure 19.3.1 : The system is being reversibly and isothermally expanded from state 1 to 2. The amount of work being done by the system is shown by the shaded area. Note that for an expansion, a reversible process does more work than an irreversible process.

Notice that not only is more work is being done than the one-step irreversible isothermal expansion, but it is the same amount of work being done as the reversible isothermal compression. This is the maximum amount of work that can be done during an expansion.

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2.3: Internal Energy and Enthalpy

2.3.1: Work and heat are not state functions

A Better Definition of the First law of thermodynamics

The change in internal energy of a system is the sum of w and q, which is a state function.

The realization that work and heat are both forms of energy transfer undergoes quite an extension by saying that internal energy is a state function. It means that although heat and work can be produced and destroyed (and transformed into each other), energy is conserved. This allows us to do some serious bookkeeping! We can write the law as:

$$\Delta U = w + q$$

But the (important!) bit about the state function is better represented if we talk about small changes of the energy:

$$dU = \delta w + \delta q$$

We write a straight Latin d for U to indicate when the change in a state function, where as the changes in work and heat are path-dependent. This is indicated by the 'crooked' δ. We can represent changes as integrals, but only for U can we say that regardless of path we get $\Delta U = U_2 - U_1$ if we go from state one to state two. (I.e. it only depends on the end points, not the path).

Notice that when we write dU or δq, we always mean infinitesimally small changes, i.e. we are implicitly taking a limit for the change approaching zero. To arrive at a macroscopic difference like ΔU or a macroscopic (finite) amount of heat q or work w **we need to integrate**.

We will now invoke the **first law of thermodynamics**:

- $dU = \delta q + \delta w$
- $\oint dU = 0$
- Internal energy is conserved

These are all ways of saying that internal energy is a state function.

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2.3.1: Enthalpy

2.3.1.1: Enthalpy

An important point is that pressure-volume work $-PdV$ is only one kind of work. It is the important one for gases but for most other systems we are interested in other kinds of work (e.g. electrical work in a battery).

A good way to measure ΔU's is to make sure there are no work terms at all. If so:

$$\Delta U_{nowork} = q + w = q + 0 = q$$

However, this means that the $-PdV$ volume work term should also be zero and this implies we must keep volumes the same. That can actually be hard. Therefore we define at new state function ENTHALPY

$$H \equiv U + PV$$

(The $\equiv$ symbol is used to show that this equality is actually a definition.)

If we differentiate we get:

$$dH = dU + d(PV) = dU + PdV + VdP$$

We know that under reversible conditions we have

$$dU = \delta w + \delta q = -PdV + \delta q$$

(+ other work terms that we assume zero)

Thus,

$$dH = -PdV + \delta q + PdV + VdP$$

$$dH = \delta q + VdP$$

That means that as long as there is no other work and we keep the pressure constant:

$$\Delta H = q_P$$

instead of

$$\Delta U = q_V$$

Working at constant P is a lot easier to do than at constant V. This means that the enthalpy is a much easier state function to deal with than the energy U.

For example when we melt ice volumes change whether we like or not, but at long as the weather does not change too much pressure is constant. So if we measure how much heat we need to add to melt a mole of ice we get the molar heat of fusion:

Image:CH431 Image71.gif

Such enthalpies are measured and tabulated.

In this case the volume change is actually quite small, as it usually is for condensed matter. Only if we are dealing with gases is the difference between enthalpy and energy really important

So, U H for condensed matter, but U and H differ for gases.

A good example of this is the difference between the heat capacity at constant V and at constant P. For most materials there is not much of a difference, but for an ideal gas we have

$$C_p = C - V + nR$$

Needless to say that the heat capacity is a path function: it depends on what you keep constant.

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2.4: Ideal Gas Processes

The most common example of work in the systems discussed in this book is the work of expansion. It is also convenient to use the work of expansion to exemplify the difference between work that is done reversibly and that which is done irreversibly. The example of expansion against a constant external pressure is an example of an irreversible pathway. It does not mean that the gas cannot be re-compressed. It does, however, mean that there is a definite direction of spontaneous change at all points along the expansion.

Imagine instead a case where the expansion has no spontaneous direction of change as there is no net force push the gas to seek a larger or smaller volume. The only way this is possible is if the pressure of the expanding gas is the same as the external pressure resisting the expansion at all points along the expansion. With no net force pushing the change in one direction or the other, the change is said to be **reversible** or to occur **reversibly**. The work of a reversible expansion of an ideal gas is fairly easy to calculate.



If the gas expands reversibly, the external pressure (p_{ext}) can be replaced by a single value (p) which represents both the pressure of the gas and the external pressure.

$$dw = -pdV$$

or

$$w = -\int pdV$$

But now that the external pressure is not constant, p cannot be extracted from the integral. Fortunately, however, there is a simple relationship that tells us how p changes with changing V – **the equation of state**! If the gas is assumed to be an ideal gas

$$w = -\int pdV - \int \left(\frac{nRT}{V}\right) dV$$

And if the temperature is held constant (so that the expansion follows an **isothermal** pathway) the nRT term can be extracted from the integral.

$$w = -nRT\int_{V_1}^{V_2} \frac{dV}{V} = -nRT\ln\left(\frac{V_2}{V_1}\right) \tag{2.4.1}$$

Equation 2.4.1 is derived for ideal gases only; a van der Waal gas would result in a different version.

Example 2.4.1: Gas Expansion

What is the work done by 1.00 mol an ideal gas expanding reversibly from a volume of 22.4 L to a volume of 44.8 L at a constant temperature of 273 K?

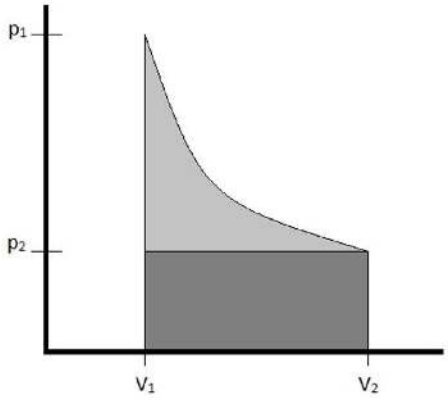
Solution

Using Equation 2.4.1 to calculate this

$$w = -(1.00\ \cancel{mol})\left(8.314\ \frac{J}{\cancel{mol}\ \cancel{K}}\right)(273\ \cancel{K})\ln\left(\frac{44.8\ \cancel{L}}{22.4\ \cancel{L}}\right)$$
$$= -1570\ J = 1.57\ kJ$$

Note: A reversible expansion will **always** require more work than an irreversible expansion (such as an expansion against a constant external pressure) when the final states of the two expansions are the same!

The work of expansion can be depicted graphically as the area under the p-V curve depicting the expansion. Comparing examples **2.4.1** and **3.1.2**, for which the initial and final volumes were the same, and the constant external pressure of the irreversible expansion was the same as the final pressure of the reversible expansion, such a graph looks as follows.



The work is depicted as the shaded portion of the graph. It is clear to see that the reversible expansion (the work for which is shaded in both light and dark gray) exceeds that of the irreversible expansion (shaded in dark gray only) due to the changing pressure of the reversible expansion. In general, it will always be the case that the work generated by a reversible pathway connecting initial and final states will be the maximum work possible for the expansion.

It should be noted (although it will be proven in a later chapter) that ΔU for an isothermal reversible process involving only p-V work is 0 for an ideal gas. This is true because the internal energy, U, is a measure of a system's capacity to convert energy into work. In order to do this, the system must somehow store that energy. The only mode in which an ideal gas can store this energy is in the translational kinetic energy of the molecules (otherwise, molecular collisions would not need to be elastic, which as you recall, was a postulate of the kinetic molecular theory!) And since the average kinetic energy is a function only of the temperature, it (and therefore U) can only change if there is a change in temperature. Hence, for any isothermal process for an ideal gas, $\Delta U = 0$. And, perhaps just as usefully, for an isothermal process involving an ideal gas, $q = -w$, as any energy that is expended by doing work must be replaced with heat, lest the system temperature drop.

Constant Volume Pathways

One common pathway which processes can follow is that of constant volume. This will happen if the volume of a sample is constrained by a great enough force that it simply cannot change. It is not uncommon to encounter such conditions with gases (since they are highly compressible anyhow) and also in geological formations, where the tremendous weight of a large mountain may force any processes occurring under it to happen at constant volume.

If reversible changes in which the only work that can be done is that of expansion (so-called p-V work) are considered, the following important result is obtained:

$$dU = dq + dw = dq - pdV$$

However, $dV = 0$ since the volume is constant! As such, dU can be expressed only in terms of the heat that flows into or out of the system at constant volume

$$dU = dq_v$$

Recall that dq can be found by

$$dq = \frac{dq}{\partial T} dT = C\,dt \tag{2.4.2}$$

This suggests an important definition for the **constant volume heat capacity** (C_V) which is

$$C_V \equiv \left(\frac{\partial U}{\partial T}\right)_V$$

When Equation **2.4.2** is integrated the

$$q = \int_{T_1}^{T_2} nC_V dt \tag{2.4.3}$$

Example 2.4.2: Isochoric Pathway

Consider 1.00 mol of an ideal gas with $C_V = 3/2R$ that undergoes a temperature change from 125 K to 255 K at a constant volume of 10.0 L. Calculate ΔU, q, and w for this change.

Solution

Since this is a constant volume process

$$w = 0$$

Equation 2.4.3 is applicable for an isochoric process,

$$q = \int_{T_1}^{T_2} nC_V dt$$

Assuming C_V is independent of temperature:

$$\begin{aligned} q &= nC_V \int_{T_1}^{T_2} dt \\ &= nC_V(T_2 - T_1) \\ &= (1.00\,mol)\left(\frac{3}{2}8.314\,\frac{J}{mol\,K}\right)(255\,K - 125\,K) \\ &= 1620\,J = 1.62\,kJ \end{aligned}$$

Since this a constant volume pathway,

$$\begin{aligned} \Delta U &= q + \cancel{w} \\ &= 1.62\,kJ \end{aligned}$$

Constant Pressure Pathways

Most laboratory-based chemistry occurs at constant pressure. Specifically, it is exposed to the constant air pressure of the laboratory, glove box, or other container in which reactions are taking place. For constant pressure changes, it is convenient to define a new thermodynamic quantity called **enthalpy**.

$$H \equiv U + pV$$

or

$$\begin{aligned} dH &\equiv dU + d(pV) \\ &= dU + pdV + Vdp \end{aligned}$$

For reversible changes at constant pressure ($dp = 0$) for which only p-V work is done

$$dH = dq + dw + pdV + Vdp \tag{2.4.4}$$

$$= dq - \cancel{pdV} + \cancel{pdV} + \cancel{Vdp}^{0} \tag{2.4.5}$$

$$= dq \tag{2.4.6}$$

And just as in the case of constant volume changes, this implies an important definition for the **constant pressure heat capacity**

$$C_p \equiv \left(\frac{\partial H}{\partial T}\right)_p$$

Example 2.4.3: Isobaric Gas Expansion

Consider 1.00 mol of an ideal gas with $C_p = 5/2R$ that changes temperature change from 125 K to 255 K at a constant pressure of 10.0 atm. Calculate ΔU, ΔH, q, and w for this change.

Solution

$$q = \int_{T_1}^{T_2} nC_p dT$$

assuming C_p is independent of temperature:

$$\begin{aligned} q &= nC_p \int_{T_1}^{T_2} dT \\ &= nC_p(T_2 - T_1) \\ &= (1.00\,mol)\left(\frac{5}{2}8.314\frac{J}{mol\,K}\right)(255\,K - 125\,K) = 2700\,J = 1.62\,kJ \end{aligned}$$

So via Equation 2.4.6 (specifically the integrated version of it using differences instead of differentials)

$$\Delta H = q = 1.62\,kJ$$

$$\begin{aligned} \Delta U &= \Delta H - \Delta(pV) \\ &= \Delta H - nR\Delta T \\ &= 2700\,J - (1.00\,mol)\left(8.314\,\frac{J}{mol\,K}\right)(255\,K - 125\,K) \\ &= 1620\,J = 1.62\,kJ \end{aligned}$$

Now that ΔU and q are determined, then work can be calculated

$$\begin{aligned} w &= \Delta U - q \\ &= 1.62\,kJ - 2.70\,kJ = -1.08\,kJ \end{aligned}$$

It makes sense that w is negative since this process is an gas expansion.

Example 2.4.4: Isothermal Gas Expansion

Calculate q, w, ΔU, and ΔH for 1.00 mol of an ideal gas expanding reversibly and isothermally at 273 K from a volume of 22.4 L and a pressure of 1.00 atm to a volume of 44.8 L and a pressure of 0.500 atm.

Solution

Since this is an isothermal expansion, Equation2.4.1 is applicable

$$\begin{aligned} w &= -nRT\ln\frac{V_2}{V_1} \\ &= (1.00\,mol)\left(8.314\,\frac{J}{mol\,K}\right)(255\,K)\ln\left(\frac{44.8\,L}{22.4\,L}\right) \\ &= 1572\,J = 1.57\,kJ \end{aligned}$$

$$\begin{aligned} \Delta U &= q + w \\ &= q + 1.57\,KJ \\ &= 0 \\ q &= -1.57\,kJ \end{aligned}$$

Since this is an isothermal expansion

$$\Delta H = \Delta U + \Delta(pV) = 0 + 0$$

where $\Delta(pV) = 0$ due to Boyle's Law!

Adiabatic Pathways

An **adiabatic** pathway is defined as one in which no heat is transferred ($q = 0$). Under these circumstances, if an ideal gas expands, it is doing work ($w < 0$) against the surroundings (provided the external pressure is not zero!) and as such the internal energy must drop ($\Delta U < 0$). And since ΔU is negative, there must also be a decrease in the temperature ($\Delta T < 0$). How big will the decrease in temperature be and on what will it depend? The key to answering these questions comes in the solution to how we calculate the work done.

If the adiabatic expansion is reversible and done on an ideal gas,

$$dw = -pdV$$

and

$$dw = nC_v dT \tag{2.4.7}$$

Equating these two terms yields

$$-pdV = nC_v dT$$

Using the ideal gas law for an expression for p ($p = nRT/V$)

$$-\frac{nRT}{V}dV = nC_v dT$$

And rearranging to gather the temperature terms on the right and volume terms on the left yields

$$\frac{dV}{V} = -\frac{C_V}{R}\frac{dT}{T}$$

This expression can be integrated on the left between V_1 and V_2 and on the right between T_1 and T_2. Assuming that C_v/nR is independent of temperature over the range of integration, it can be pulled from the integrand in the term on the right.

$$\int_{V_1}^{V_2} \frac{dV}{V} = -\frac{C_V}{R}\int_{T_1}^{T_2} \frac{dT}{T}$$

The result is

$$\ln\left(\frac{V_2}{V_1}\right) = -\frac{C_V}{R}\ln\left(\frac{T_2}{T_1}\right)$$

or

$$\left(\frac{V_2}{V_1}\right) = \left(\frac{T_2}{T_1}\right)^{-\frac{C_V}{R}}$$

or

$$V_1 T_1^{\frac{C_V}{R}} = V_2 T_2^{\frac{C_V}{R}}$$

or

$$T_1\left(\frac{V_1}{V_2}\right)^{-\frac{R}{C_V}} = T_2 \tag{2.4.8}$$

Once ΔT is known, it is easy to calculate w, ΔU and ΔH.

Example 2.4.5:

1.00 mol of an ideal gas (C_V = 3/2 R) initially occupies 22.4 L at 273 K. The gas expands adiabatically and reversibly to a final volume of 44.8 L. Calculate ΔT, q, w, ΔU, and ΔH for the expansion.

Solution

Since the pathway is adiabatic:

$$q = 0$$

Using Equation 2.4.8

$$\begin{aligned} T_2 &= T_1 \left(\frac{V_1}{V_2}\right)^{-\frac{R}{C_V}} \\ &= (273\,K)\left(\frac{22.4\,L}{44.8\,L}\right)^{2/3} \\ &= 172\,K \end{aligned}$$

So

$$\Delta T = 172\,K - 273\,K = -101\,K$$

For calculating work, we integrate Equation 2.4.7 to get

$$\begin{aligned} w &= \Delta U = nC_v\Delta T \\ &= (1.00\,mol)\left(\frac{3}{2}8.314\,\frac{J}{mol\,K}\right)(-101\,K) \\ &= 1.260\,kJ \end{aligned}$$

$$\begin{aligned} \Delta H &= \Delta U + nR\Delta T \\ &= -1260\,J + (1.00\,mol)\left(\frac{3}{2}8.314\,\frac{J}{mol\,K}\right)(-101\,K) \\ &= -2100\,J \end{aligned}$$

The following table shows recipes for calculating q, w, ΔU, and ΔH for an ideal gas undergoing a reversible change along the specified pathway.

Table 3.2.1: Thermodynamics Properties for a Reversible Expansion or Compression

Pathway	q	w	ΔU	ΔH
Isothermal	$nRT\ln(V_2/V_1)$	$-nRT\ln(V_2/V_1)$	0	0
Isochoric	$C_V\Delta T$	0	$C_V\Delta T$	$C_V\Delta T + V\Delta p$
Isobaric	$C_p\Delta T$	$-p\Delta V$	$C_p\Delta T - p\Delta V$	$C_p\Delta T$
adiabatic	0	$C_V\Delta T$	$C_V\Delta T$	$C_p\Delta T$

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- **3.3: Reversible and Irreversible Pathways** by Patrick Fleming is licensed CC BY-NC-SA 4.0.

2.5: Exact and Inexact Differentials

Many important thermochemical quantities can be expressed in terms of partial derivatives. Two important examples are the molar heat capacities C_p and C_V which can be expressed as

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p$$

and

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

These are properties that can be measured experimentally and tabulated for many substances. These quantities can be used to calculate changes in quantities since they represent the slope of a surface (H or U) in the direction of the specified path (constant p or V). This allows us to use the following kinds of relationships:

$$dH = \left(\frac{\partial H}{\partial T}\right)_p dT$$

and

$$\Delta H = \int \left(\frac{\partial H}{\partial T}\right)_p dT$$

Because thermodynamics is kind enough to deal in a number of **state variables**, the functions that define how those variable change must behave according to some very well determined mathematics. This is the true power of thermodynamics!

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- **4.1: Prelude to Putting the First Law to Work** by Patrick Fleming is licensed CC BY-NC-SA 4.0.

2.5.1: Total and Exact Differentials

The fact that we can define the *constant volume heat capacity* as

$$C_V \equiv \left(\frac{\partial U}{\partial T}\right)_V \tag{2.5.1.1}$$

suggests that the internal energy depends very intimately on two variables: volume and temperature. In fact, we will see that for a single component system, state variables are always determined when two state variables are defined. In the case of internal energy, we might write $U = f(V,T)$ or $U(V,T)$.

This suggests that the way to change U is to change either V or T (or both!) And if there is a mathematical function that relates the internal energy to these two variables, it should easy to see how it changes when either (or both!) are changed. This can be written as a total differential:

$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT \tag{2.5.1.2}$$

Even without knowing the actually mathematical function relating the variables to the property, we can imagine how to calculate changes in the property from this expression.

$$\Delta U = \int_{V_1}^{V_2} \left(\frac{\partial U}{\partial V}\right)_T dV + \int_{T_1}^{T_2} \left(\frac{\partial U}{\partial T}\right)_V dT$$

In words, this implies that we can think of a change in U occurring due to an *isothermal change* followed by an *isochoric change*. And all we need to know is the slope of the surface in each pathway direction. There are a couple of very important experiments people have done to explore the measurement of those kinds of slopes. Understanding them, it turns out, depends on two very important physical properties of substances.

Exact Differentials

We have seen that the total differential of $U(V,T)$ can be expressed as Equation 2.5.1.2. In general, if a differential can be expressed as

$$df(x,y) = P\,dx + Q\,dy$$

the differential will be an **exact differential** if it follows the **Euler relation**

$$\left(\frac{\partial P}{\partial y}\right)_x = \left(\frac{\partial Q}{\partial x}\right)_y \tag{2.5.1.3}$$

In order to illustrate this concept, consider $p(V,T)$ using the ideal gas law.

$$p = \frac{RT}{V}$$

The total differential of p can be written

$$dp = \left(-\frac{RT}{V^2}\right) dV + \left(\frac{R}{V}\right) dT \tag{2.5.1.4}$$

Example 2.5.1.1: Euler Relation

Does Equation 2.5.1.4 follow the Euler relation (Equation 2.5.1.3)?

Solution

Let's confirm!

$$\left[\frac{1}{\partial T}\left(-\frac{RT}{V^2}\right)\right]_V \stackrel{?}{=} \left[\frac{1}{\partial V}\left(\frac{R}{V}\right)\right]_T$$

$$\left(-\frac{R}{V^2}\right) \stackrel{\checkmark}{=} \left(-\frac{R}{V^2}\right)$$

> dp is, in fact, an exact differential.

The differentials of all of the **thermodynamic functions** that are **state functions** will be exact. Heat and work are not exact differential and dw and dq are called *inexact differentials* instead.

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2.5.2: Compressibility and Expansivity

Isothermal Compressibility (κ_T)

A very important property of a substance is how compressible it is. Gases are very compressible, so when subjected to high pressures, their volumes decrease significantly (think Boyle's Law!) Solids and liquids however are not as compressible. However, they are not entirely incompressible! High pressure will lead to a decrease in volume, even if it is only slight. And, of course, different substances are more compressible than others.

To quantify just how compressible substances are, it is necessary to define the property. The **isothermal compressibility** is defined by the fractional differential change in volume due to a change in pressure.

$$\kappa_T \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T \tag{2.5.2.1}$$

The negative sign is important in order to keep the value of κ_T positive, since an increase in pressure will lead to a decrease in volume. The $1/V$ term is needed to make the property intensive so that it can be tabulated in a useful manner.

Isobaric Thermal Expansivity (α)

Another very important property of a substance is how its volume will respond to changes in temperature. Again, gases respond profoundly to changes in temperature (think Charles' Law!) whereas solids and liquid will have more modest (but not negligible) responses to changes in temperature. (For example, If mercury or alcohol didn't expand with increasing temperature, we wouldn't be able to use those substances in thermometers.)

The definition of the **isobaric thermal expansivity** (or sometimes called the expansion coefficient) is

$$\alpha \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \tag{2.5.2.2}$$

As was the case with the compressibility factor, the $1/V$ term is needed to make the property intensive, and thus able to be tabulated in a useful fashion. In the case of expansion, volume tends to increase with increasing temperature, so the partial derivative is positive.

Deriving an Expression for a Partial Derivative (Type I): The reciprocal rule

Consider a system that is described by three variables, and for which one can write a mathematical constraint on the variables

$$F(x,y,z) = 0$$

Under these circumstances, one can specify the state of the system varying only two parameters independently because the third parameter will have a fixed value. As such one could define two functions: $z(x,y)$ and $y(x,z)$.

This allows one to write the total differentials for dz and dy as follows

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy \tag{2.5.2.3}$$

and

$$dy = \left(\frac{\partial y}{\partial x}\right)_z dx + \left(\frac{\partial y}{\partial z}\right)_x dz \tag{2.5.2.4}$$

Substituting the Equation 2.5.2.4 expression into Equation 2.5.2.3:

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x \left[\left(\frac{\partial y}{\partial x}\right)_z dx + \left(\frac{\partial y}{\partial z}\right)_x dz\right] \tag{2.5.2.5}$$

$$= \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z dx + \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial z}\right)_x dz \tag{2.5.2.6}$$

If the system undergoes a change following a pathway where x is held constant ($dx = 0$), this expression simplifies to

$$dz = \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial z}\right)_x dz$$

And so for changes for which $dz \neq 0$,

$$\left(\frac{\partial z}{\partial y}\right)_x = \frac{1}{\left(\frac{\partial y}{\partial z}\right)_x}$$

This *reciprocal rule* is very convenient in the manipulation of partial derivatives. But it can also be derived in a straightforward, albeit less rigorous, manner. Begin by writing the total differential for $z(x, y)$ (Equation 2.5.2.3):

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

Now, divide both sides by dz and constrain to constant x.

$$\left.\frac{dz}{dz}\right|_x = \left(\frac{\partial z}{\partial x}\right)_y \left.\frac{dx}{dz}\right|_x + \left(\frac{\partial z}{\partial y}\right)_x \left.\frac{dy}{dz}\right|_x \tag{2.5.2.7}$$

Noting that

$$\left.\frac{dz}{dz}\right|_x = 1$$

$$\left.\frac{dx}{dz}\right|_x = 0$$

and

$$\left.\frac{dy}{dz}\right|_x = \left(\frac{\partial y}{\partial z}\right)_x$$

Equation 2.5.2.7 becomes

$$1 = \left(\frac{\partial z}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x$$

or

$$\left(\frac{\partial z}{\partial y}\right)_z = \frac{1}{\left(\frac{\partial y}{\partial z}\right)_x}$$

This “formal” method of partial derivative manipulation is convenient and useful, although it is not mathematically rigorous. However, it does work for the kind of partial derivatives encountered in thermodynamics because the variables are **state variables** and the differentials are **exact**.

Deriving an Expression for a Partial Derivative (Type II): The Cyclic Permutation Rule

This alternative derivation follow the initial steps in the derivation above to Equation 2.5.2.6:

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z dx + \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial z}\right)_x dz$$

If the system undergoes a change following a pathway where z is held constant ($dz = 0$), this expression simplifies to

$$0 = \left(\frac{\partial z}{\partial x}\right)_y dy + \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z dx$$

And so for and changes in which $dx \neq 0$

$$\left(\frac{\partial z}{\partial x}\right)_y = -\left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z$$

This *cyclic permutation rule* is very convenient in the manipulation of partial derivatives. But it can also be derived in a straight-forward, albeit less rigorous, manner. As with the derivation above, we wegin by writing the total differential of $z(x,y)$

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

Now, divide both sides by dx and constrain to constant z.

$$\left.\frac{dz}{dx}\right|_z = \left(\frac{\partial z}{\partial x}\right)_y \left.\frac{dx}{dx}\right|_z + \left(\frac{\partial z}{\partial y}\right)_x \left.\frac{dy}{dx}\right|_z \tag{2.5.2.8}$$

Note that

$$\left.\frac{dz}{dx}\right|_z = 0$$

$$\left.\frac{dx}{dx}\right|_z = 1$$

and

$$\left.\frac{dy}{dx}\right|_z = \left(\frac{\partial y}{\partial x}\right)_z$$

Equation 2.5.2.8 becomes

$$0 = \left(\frac{\partial z}{\partial x}\right)_y + \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z$$

which is easily rearranged to

$$\left(\frac{\partial z}{\partial x}\right)_y = -\left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z$$

This type of transformation is very convenient, and will be used often in the manipulation of partial derivatives in thermodynamics.

Example 2.5.2.1: Expanding Thermodynamic Functions

Derive an expression for

$$\frac{\alpha}{\kappa_T}. \tag{2.5.2.9}$$

in terms of derivatives of thermodynamic functions using the definitions in Equations 2.5.2.1 and 2.5.2.2.

Solution

Substituting Equations 2.5.2.1 and 2.5.2.2 into the Equation 2.5.2.9

$$\frac{\alpha}{\kappa_T} = \frac{\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p}{-\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T}$$

Simplifying (canceling the $1/V$ terms and using transformation Type I to invert the partial derivative in the denominator) yields

$$\frac{\alpha}{\kappa_T} = -\left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial p}{\partial V}\right)_T$$

Applying Transformation Type II give the final result:

$$\frac{\alpha}{\kappa_T} = \left(\frac{\partial p}{\partial T}\right)_V$$

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2.6: The Joule Experiment

Going back to the expression for changes in internal energy that stems from assuming that U is a function of V and T (or $U(V,T)$ for short)

$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT$$

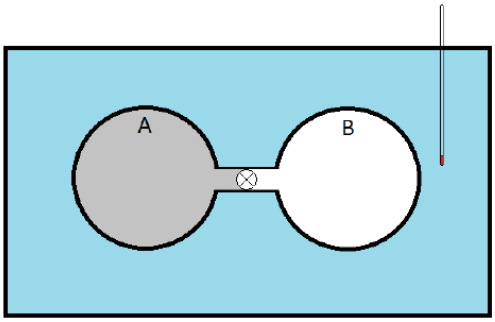
one quickly recognizes one of the terms as the constant volume heat capacity, C_V. And so the expression can be re-written

$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + C_V dT$$

But what about the first term? The partial derivative is a coefficient called the "internal pressure", and given the symbol π_T.

$$\pi_T = \left(\frac{\partial U}{\partial V}\right)_T$$

James Prescott Joule (1818-1889) recognized that π_T should have units of pressure (Energy/volume = pressure) and designed an experiment to measure it.



He immersed two copper spheres, A and B, connected by a stopcock. Sphere A is filled with a sample of gas while sphere B was evacuated. The idea was that when the stopcock was opened, the gas in sphere A would expand ($\Delta V > 0$) against the vacuum in sphere B (doing no work since $p_{ext} = 0$. The change in the internal energy could be expressed

$$dU = \pi_T dV + C_V dT$$

But also, from the first law of thermodynamics

$$dU = dq + dw$$

Equating the two

$$\pi_T dV + C_V dT = dq + dw$$

and since $dw = 0$

$$\pi_T dV + C_V dT = dq$$

Joule concluded that $dq = 0$ (and $dT = 0$ as well) since he did not observe a temperature change in the water bath which could only have been caused by the metal spheres either absorbing or emitting heat. And because $dV > 0$ for the gas that underwent the expansion into an open space, π_T must also be zero! In truth, the gas did undergo a temperature change, but it was too small to be detected within his experimental precision. Later, we (once we develop the *Maxwell Relations*) will show that

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p \tag{2.6.1}$$

Application to an Ideal Gas

For an ideal gas $p = RT/V$, so it is easy to show that

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{R}{V} \tag{2.6.2}$$

so combining Equations 2.6.1 and 2.6.2 together to get

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{RT}{V} - p \tag{2.6.3}$$

And since also becuase $p = RT/V$, then Equation 2.6.3 simplifies to

$$\left(\frac{\partial U}{\partial V}\right)_T = p - p = 0$$

So while Joule's observation was consistent with limiting ideal behavior, his result was really an artifact of his experimental uncertainty masking what actually happened.

Appliation to a van der Waals Gas

For a van der Waals gas,

$$p = \frac{RT}{V-b} - \frac{a}{V^2} \tag{2.6.4}$$

so

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{R}{V-b} \tag{2.6.5}$$

and

$$\left(\frac{\partial U}{\partial V}\right)_T = T\frac{R}{V-b} - p \tag{2.6.6}$$

Substitution of the expression for p (Equation 2.6.4) into this Equation 2.6.6

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{a}{V^2}$$

In general, it can be shown that

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{\alpha}{\kappa_T}$$

And so the internal pressure can be expressed entirely in terms of measurable properties

$$\left(\frac{\partial U}{\partial V}\right)_T = T\frac{\alpha}{\kappa_T} - p$$

and need not apply to only gases (real or ideal)!

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2.6.1: The Joule-Thomson Effect

In 1852, working with William Thomson (who would later become Lord Kelvin), Joule conducted an experiment in which they pumped gas at a steady rate through a lead pipe that was cinched to create a construction. On the upstream side of the constriction, the gas was at a higher pressure than on the downstream side of the constriction. Also, the temperature of the gas was carefully monitored on either side of the construction. The cooling that they observed as the gas expanded from a high pressure region to a lower pressure region was extremely important and lead to a common design of modern refrigerators.

Not all gases undergo a cooling effect upon expansion. Some gases, such as hydrogen and helium, will experience a warming effect upon expansion under conditions near room temperature and pressure. The direction of temperature change can be determined by measuring the Joule-Thomson coefficient, μ_{JT}. This coefficient has the definition

$$\mu_{JT} \equiv \left(\frac{\partial T}{\partial p}\right)_H$$

Schematically, the Joule-Thomson coefficient can be measured by measuring the temperature drop or increase a gas undergoes for a given pressure drop (Figure **2.6.1.1**). The apparatus is insulated so that no heat can be transferred in or out, making the expansion isenthalpic.

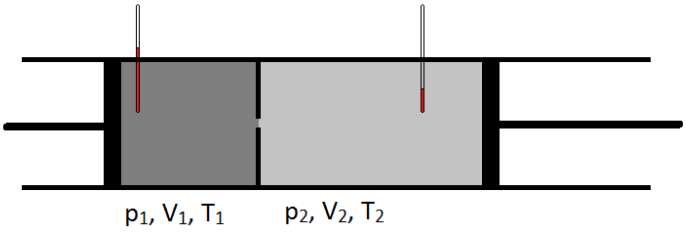


Figure **2.6.1.1**:

The typical behavior of the Joule-Thomson coefficient can be summarized in Figure **2.6.1.2**. At the combinations of T and p for which $\mu_{JT} > 0$ (inside the shaded region), the sample will cool upon expansion. At those p and T conditions outside of the shaded region, where $\mu_{JT} < 0$, the gas will undergo a temperature increase upon expansion. And along the boundary, a gas will undergo neither a temperature increase not decrease upon expansion. For a given pressure, there are typically two temperatures at which μ_{JT} changes sign. These are the upper and lower inversion temperatures.

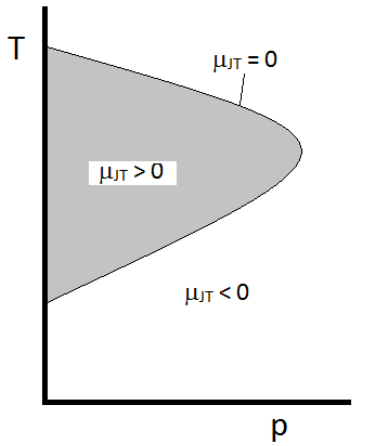


Figure **2.6.1.2**: The typical behavior of the Joule-Thomson coefficient at different temperatures and pressures.

Using the tools of mathematics, it is possible to express the Joule-Thomson coefficient in terms of measurable properties. Consider enthalpy as a function of pressure and temperature: $H(p,T)$. This suggests that the total differential dH can be expressed

$$dH = \left(\frac{\partial H}{\partial p}\right)_T dp + \left(\frac{\partial H}{\partial T}\right)_p dT \qquad (2.6.1.1)$$

It will be shown later (again, once we develop the *Maxwell Relations*) that

$$\left(\frac{\partial H}{\partial p}\right)_T dp = -T\left(\frac{\partial V}{\partial T}\right)_p + V$$

A simple substitution shows

$$\left(\frac{\partial H}{\partial p}\right)_T dp = -TV\alpha + V = V(1 - T\alpha)$$

So

$$dH = V(1 - T\alpha)dP + C_p dT$$

For an ideal gas, $\alpha = 1/T$, so

$$dH = \cancel{V\left(1 - T\frac{1}{T}\right)^{0} dP} + C_p dT$$

which causes the first term to vanish. So for constant enthalpy expansion ($dH = 0$), there can be no change in temperature ($dT = 0$). This will mean that gases will only show non-zero values for μ_{JT} only because they deviate from ideal behavior!

Example 2.6.1.1:

Derive an expression for μ_{JT} in terms of α, C_p, V, and T.

Solution

Using the total differential for $H(p,T)$ (Equation 2.6.1.1):

$$dH = \left(\frac{\partial H}{\partial p}\right)_T dp + \left(\frac{\partial H}{\partial T}\right)_p dT$$

Dividing by dp and constraining to constant H:

$$\left.\frac{dH}{dp}\right|_H = \left(\frac{\partial H}{\partial p}\right)_T \left.\frac{dp}{dp}\right|_H + \left(\frac{\partial H}{\partial T}\right)_p \left.\frac{dT}{dp}\right|_H$$

Noting that

$$\left.\frac{dH}{dp}\right|_H = 0$$

$$\left.\frac{dp}{dp}\right|_H = 1$$

and

$$\left.\frac{dT}{dp}\right|_H = \left(\frac{\partial T}{\partial p}\right)_H$$

so

$$0 = \left(\frac{\partial H}{\partial p}\right)_T + \left(\frac{\partial H}{\partial T}\right)_p \left(\frac{\partial T}{\partial p}\right)_H$$

We can then use the following substitutions:

$$\left(\frac{\partial H}{\partial p}\right)_T = V(1 - T\alpha)$$

$$\left(\frac{\partial H}{\partial T}\right)_p = C_p$$

$$\left(\frac{\partial T}{\partial p}\right)_H = \mu_{JT}$$

To get

$$0 = V(1 - T\alpha) + C_p\mu_{JT}$$

And solving for μ_{JT} gives

$$\mu_{JT} = \frac{V}{C_p}(T\alpha - 1)$$

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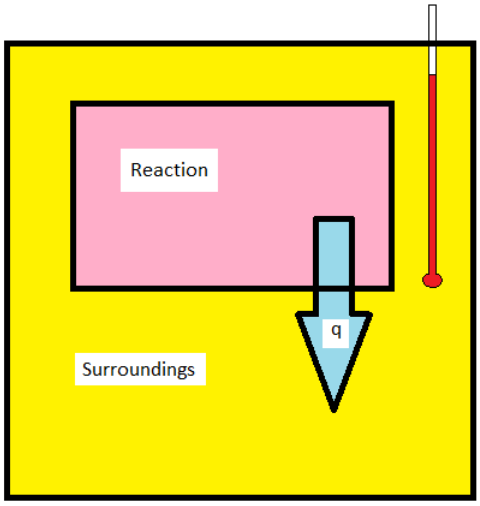
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2.7: Calorimetry

As chemists, we are concerned with chemical changes and reactions. The thermodynamics of chemical reactions can be very important in terms of controlling the production of desired products and preventing safety hazards such as explosions. As such, measuring and understanding the thermochemistry of chemical reactions is not only useful, but essential!

Calorimetry

The techniques of **calorimetry** can be used to measure q for a chemical reaction directly. The enthalpy change for a chemical reaction is of significant interest to chemists. An exothermic reaction will release heat ($q_{reaction} < 0$, $q_{surroundings} > 0$) causing the temperature of the surrounding to increase. Conversely, an endothermic reaction ($q_{reaction} > 0$, $q_{surroundings} < 0$) will draw heat from the surroundings, causing the temperature of the surrounding to drop. Measuring the temperature change in the surroundings allows for the determination of how much heat was released or absorbed in the reaction.



Bomb Calorimetry

Bomb calorimetry is used predominantly to measure the heat evolved in combustion reactions, but can be used for a wide variety of reactions. A typical bomb calorimetry set up is shown here. The reaction is contained in a heavy metallic container (the bomb) forcing the reaction to occur at constant volume. As such, the heat evolved (or absorbed) by the reaction is equal to the change in internal energy (DU_{rxn}). The bomb is then submerged in a reproducible quantity of water, the temperature of which is monitored with a high-precision thermometer.

For combustion reactions, the bomb will be loaded with a small sample of the compound to be combusted, and then the bomb is filled with a high pressure (typically about 10 atm) of O_2. The reaction is initiated by supplying heat using a short piece of resistive wire carrying an electrical current.

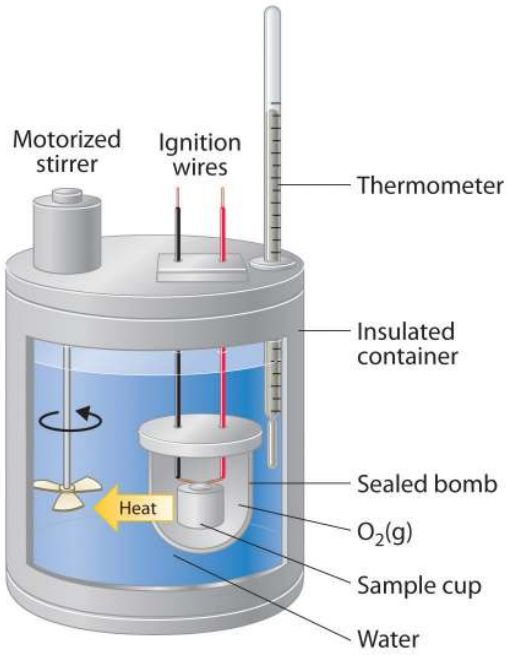


Figure **2.7.1**: A Bomb Calorimeter. After the temperature of the water in the insulated container has reached a constant value, the combustion reaction is initiated by passing an electric current through a wire embedded in the sample. Because this calorimeter operates at constant volume, the heat released is not precisely the same as the enthalpy change for the reaction. (CC BY-SA-NC; Anonymous by request).

The calorimeter must be calibrated by carrying out a reaction for which ΔU_{rxn} is well known, so that the resulting temperature change can be related to the amount of heat released or absorbed. A commonly used reaction is the combustion of benzoic acid. This makes a good choice since benzoic acid reacts reliably and reproducibly under normal bomb calorimetry conditions. The "water equivalent" of the calorimeter can then be calculated from the temperature change using the following relationship:

$$W = \frac{n\Delta U_c + e_{wrire} + e_{other}}{\Delta T}$$

where n is the number of moles of benzoic acid used, ΔU_c is the internal energy of combustion for benzoic acid (3225.7 kJ mol^{-1} at 25 °C), e_{wire} accounts for the energy released in the combustion of the fuse wire, e_{other} account for any other corrections (such as heat released due to the combustion of residual nitrogen in the bomb), and DT is the measured temperature change in the surrounding water bath.

Once the "water equivalent" is determined for a calorimeter, the temperature change can be used to find ΔU_c for an unknown compound from the temperature change created upon combustion of a known quantity of the substance.

$$\Delta U_c = \frac{W\Delta T - e_{wire} - e_{other}}{n_{sample}}$$

The experiment above is known as "isothermal bomb calorimetry" as the entire assembly sits in a constant temperature laboratory. Another approach is to employ "adiabatic bomb calorimetry" in which the assembly sits inside of a water jacket, the temperature of which is controlled to match the temperature of the water inside the insulated container. By matching this temperature, there is no thermal gradient, and thus no heat leaks into or out of the assembly during an experiment (and hence the experiment is effectively "adiabatic").

Finding ΔU_c

The **enthalpy of combustion** can be calculated from the internal energy change if the balanced chemical reaction is known. Recall from the definition of enthalpy

$$\Delta H = \Delta U + \Delta(pV)$$

and if the gas-phase reactants and products can be treated as ideal gases ($pV = nRT$)

$$\Delta H = \Delta U + RT\Delta n_{gas}$$

at constant temperature. For the combustion of benzoic acid at 25 °C

$$\mathrm{C_6H_5COOH\,(s) + \tfrac{15}{2}\,O_2\,(g) \longrightarrow 7\,CO_2\,(g) + 3\,H_2O\,(l)}$$

it can be seen that Δn_{gas} is -0.5 mol of gas for every mole of benzoic acid reacted.

Example 2.7.1: Combustion of Naphthalene

A student burned a 0.7842 g sample of benzoic acid ($\mathrm{C_7H_6O_2}$) in a bomb calorimeter initially at 25.0 °C and saw a temperature increase of 2.02 °C. She then burned a 0.5348 g sample of naphthalene ($\mathrm{C_{10}H_8}$) (again from an initial temperature of 25 °C) and saw a temperature increase of 2.24 °C. From this data, calculate ΔH_c for naphthalene (assuming e_{wire} and e_{other} are unimportant.)

Solution

First, the water equivalent:

$$W = \frac{\left[(0.7841\,g)\left(\frac{1\,mol}{122.124\,g}\right)\right](3225.7\,kJ/mol)}{2.02\,°C} = 10.254\,kJ/°C$$

Then ΔU_c for the sample:

$$\Delta U_c = \frac{(10.254\,kJ/°C)(2.24\,°C)}{(0.5308\,g)\left(\frac{1\,mol}{128.174\,g}\right)} = 5546.4\,kJ/°C$$

ΔH_c is then given by

$$\Delta H_c = \Delta U_c + RT\Delta n_{gas}$$

The reaction for the combustion of naphthalene at 25 °C is:

$$\mathrm{C_{10}H_8\,(s) + 12\,O_2\,(g) \longrightarrow 10\,CO_2\,(g) + 4\,H_2O\,(l)}$$

with $\Delta n_{gas} = -2$.

So

$$\Delta H_c = 5546.4\,kJ/mol + \left(\frac{8.314}{1000}kJ/(mol\,K)\right)(298\,L)(-2) = 5541\,kJ/mol$$

The literature value (Balcan, Arzik, & Altunata, 1996) is 5150.09 kJ/mol. So that's not too far off!

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2.7.1: Temperature Dependence of Enthalpy

It is often required to know thermodynamic functions (such as enthalpy) at temperatures other than those available from tabulated data. Fortunately, the conversion to other temperatures is not difficult.

At constant pressure

$$dH = C_p\,dT$$

And so for a temperature change from T_1 to T_2

$$\Delta H = \int_{T_2}^{T_2} C_p\,dT \tag{2.7.1.1}$$

Equation 2.7.1.1 is often referred to as *Kirchhoff's Law*. If C_p is independent of temperature, then

$$\Delta H = C_p\,\Delta T \tag{2.7.1.2}$$

If the temperature dependence of the heat capacity is known, it can be incorporated into the integral in Equation 2.7.1.1. A common *empirical* model used to fit heat capacities over broad temperature ranges is

$$C_p(T) = a + bT + \frac{c}{T^2} \tag{2.7.1.3}$$

After combining Equations 2.7.1.3 and 2.7.1.1, the enthalpy change for the temperature change can be found obtained by a simple integration

$$\Delta H = \int_{T_1}^{T_2} \left(a + bT + \frac{c}{T^2}\right) dT \tag{2.7.1.4}$$

Solving the definite integral yields

$$\Delta H = \left[aT + \frac{b}{2}T^2 - \frac{c}{T}\right]_{T_1}^{T_2} \tag{2.7.1.5}$$

$$= a(T_2 - T_1) + \frac{b}{2}(T_2^2 - T_1^2) - c\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{2.7.1.6}$$

This expression can then be used with experimentally determined values of a, b, and c, some of which are shown in the following table.

Table **2.7.1.1**: *Empirical Parameters for the temperature dependence of* C_p

Substance	a (J mol^{-1} K^{-1})	b (J mol^{-1} K^{-2})	c (J mol^{-1} K)
C(gr)	16.86	4.77 x 10^{-3}	-8.54 x 10^{5}
CO_2(g)	44.22	8.79 x 10^{-3}	-8.62 x 10^{5}
H_2O(l)	75.29	0	0
N_2(g)	28.58	3.77 x 10^{-3}	-5.0 x 10^{4}
Pb(s)	22.13	1.172 x 10^{-2}	9.6 x 10^{4}

Example 2.7.1.1: Heating Lead

What is the molar enthalpy change for a temperature increase from 273 K to 353 K for Pb(s)?

Solution

The enthalpy change is given by Equation 2.7.1.1 with a temperature dependence C_p given by Equation 2.7.1.1 using the parameters in Table **2.7.1.1**. This results in the integral form (Equation 2.7.1.6):

$$\Delta H = a(T_2 - T_1) + \frac{b}{2}(T_2^2 - T_1^2) - c\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

when substituted with the relevant parameters of Pb(s) from Table 2.7.1.1.

$$\begin{aligned}\Delta H =& (22.14\,\frac{J}{mol\,K}(353\,K - 273\,K) \\ &+ \frac{1.172 \times 10^{-2}\frac{J}{mol\,K^2}}{2}\left((353\,K)^2 - (273\,K)^2\right) \\ &- 9.6 \times 10^4 \frac{J\,K}{mol}\left(\frac{1}{(353\,K)} - \frac{1}{(273\,K)}\right) \\ \Delta H =& 1770.4\,\frac{J}{mol} + 295.5\,\frac{J}{mol} + 470.5\,\frac{J}{mol} \\ =& 2534.4\,\frac{J}{mol}\end{aligned}$$

For chemical reactions, the reaction enthalpy at differing temperatures can be calculated from

$$\Delta H_{rxn}(T_2) = \Delta H_{rxn}(T_1) + \int_{T_1}^{T_2} \Delta C_p \Delta T$$

Example 2.7.1.2: Enthalpy of Formation

The enthalpy of formation of NH_3(g) is -46.11 kJ/mol at 25 ^oC. Calculate the enthalpy of formation at 100 ^oC.

Solution

$$\mathrm{N_2\,(g) + 3\,H_2\,(g) \rightleftharpoons 2\,NH_3\,(g)}$$

with $\Delta H\,(298\,K) = -46.11\,kJ/mol$

Compound	Cp (J mol^{-1} K^{-1})
N_2(g)	29.12
H_2(g)	28.82
NH_3(g)	35.06

$$\begin{aligned}\Delta H(373\,K) &= \Delta H(298\,K) + \Delta C_p \Delta T \\ &= -46110 + \frac{J}{mol} \\ &\quad \left[2\left(35.06\frac{J}{mol\,K}\right) - \left(29.12\,\frac{J}{mol\,K}\right) - 3\left(28.82\,\frac{J}{mol\,K}\right)\right](373\,K - 298\,K) \\ &= -49.5\,\frac{kJ}{mol}\end{aligned}$$

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2.7.2: Reaction Enthalpies

Reaction enthalpies are important, but difficult to tabulate. However, because enthalpy is a state function, it is possible to use **Hess' Law** to simplify the tabulation of reaction enthalpies. Hess' Law is based on the addition of reactions. By knowing the reaction enthalpy for constituent reactions, the enthalpy of a reaction that can be expressed as the sum of the constituent reactions can be calculated. The key lies in the canceling of reactants and products that °Ccur in the "data" reactions but not in the "target reaction.

Example 2.7.2.1:

Find ΔH_{rxn} for the reaction

$$2CO(g) + O_2(g) \rightarrow 2CO_2(g)$$

Given

$$C(gr) + ½O_2(g) \rightarrow CO(g)$$

with $\Delta H_1 = -110.53\,kJ$

$$C(gr) + O_2(g) \rightarrow CO_2(g)$$

with $\Delta H_2 = -393.51\,kJ$

Solution

The target reaction can be generated from the data reactions.

$$2\times\ [CO(g) \rightarrow C(gr) + O_2(g)]$$

plus

$$2\times\ [C(gr) + 2O_2(g) \rightarrow 2CO_2(g)]$$

equals

$$2CO(g) + O_2(g) \rightarrow 2CO_2(g)$$

so

$$2\times\Delta H_1 = -787.02\,kJ$$

$$2\times\Delta H_2 = 221.06\,kJ$$

$$2\times\Delta H_1 + 2\times\Delta H_2 = -565.96\,kJ$$

Standard Enthalpy of Formation

One of the difficulties with many thermodynamic state variables (such as enthalpy) is that while it is possible to measure changes, it is impossible to measure an absolute value of the variable itself. In these cases, it is necessary to define a zero to the scale defining the variable. For enthalpy, the definition of a zero is that the standard enthalpy of formation of a pure element in its standard state is zero. All other enthalpy changes are defined relative to this standard. Thus it is essential to very carefully define a standard state.

Definition: the Standard State

The standard state of a substance is the most stable form of that substance at 1 atmosphere pressure and the specified temperature.

Using this definition, a convenient reaction for which enthalpies can be measured and tabulated is the **standard formation reaction**. This is a reaction which forms one mole of the substance of interest in its standard state from elements in their standard states. The enthalpy of a standard formation reaction is the **standard enthalpy of formation** (ΔH_{f°). Some examples are

- $NaCl(s)$:

- $NaCl(s)$:

$$Na(s) + ½Cl_2(g) \rightarrow NaCl(s)$$

with $\Delta H_f^o = -411.2\, kJ/mol$

- $C_3H_8(g)$:

$$3C(gr) + 4H_2(g) \rightarrow C_3H_8(g)$$

with $\Delta H_f^o = -103.8\, kJ/mol$

It is important to note that the standard state of a substance is **temperature dependent**. For example, the standard state of water at -10 °C is solid, whereas the standard state at room temperature is liquid. Once these values are tabulated, calculating reaction enthalpies becomes a snap. Consider the heat combustion (ΔH_c) of methane (at 25 °C) as an example.

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$

The reaction can expressed as a sum of a combination of the following standard formation reactions.

$$C(gr) + 2H_2(g) \rightarrow CH_4(g)$$

with $\Delta H_f^o = -74.6\, kJ/mol$

$$C(gr) + O_2(g) \rightarrow CO_2(g)$$

with $\Delta H_f^o = -393.5\, kJ/mol$

$$H_2(g) + ½O_2(g) \rightarrow H_2O(l)$$

with $\Delta H_f^o = -285.8\, kJ/mol$

The target reaction can be generated from the following combination of reactions

$$-1\times [C(gr) + 2H_2(g) \rightarrow CH_4(g)]$$

$$CH_4(g) \rightarrow C(gr) + 2H_2(g)$$

with $\Delta H_f^o = -1\times [-74.6\, kJ/mol] = 74.6\, kJ/mol$

$$C(gr) + O_2(g) \rightarrow CO_2(g)$$

with $\Delta H_f^o = -393.5\, kJ/mol$

$$2\times [H_2(g) + ½O_2(g) \rightarrow H_2O(l)]$$

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$$

with $\Delta H_f^o = 2\times [-285.8\, kJ/mol] = -571.6\, kJ/mol.$

$$CH_4(g) + 2O_2(g) \rightarrow CO2_(g) + 2H_2O(l)$$

with $\Delta H_c^o = -890.5\, kJ/mol$

Alternately, the reaction enthalpy could be calculated from the following relationship

$$\Delta H_{rxn} = \sum_{products} \nu \cdot \Delta H_f^o - \sum_{reactants} \nu \cdot \Delta H_f^o$$

where ν is the stoichiometric coefficient of a species in the balanced chemical reaction. For the combustion of methane, this calculation is

$$\Delta_{rxn} = (1\, mol)\left(\Delta H_f^o(CO_2)\right) + (2\, mol)\left(\Delta H_f^o(H_2O)\right) - (1\, mol)\left(\Delta H_f^o(CH_4)\right) \quad (2.7.2.1)$$

$$= (1\, mol)(-393.5\, kJ/mol) + (2\, mol)\,(-285.8\, kJ/mol) - (1\, mol)\,(-74.6\, kJ/mol) \quad (2.7.2.2)$$

$$= -890.5\, kJ/mol \quad (2.7.2.3)$$

A note about units is in order. Note that reaction enthalpies have units of kJ, whereas enthalpies of formation have units of kJ/mol. The reason for the difference is that enthalpies of formation (or for that matter enthalpies of combustion, sublimation, vaporization,

fusion, etc.) refer to specific substances and/or specific processes involving those substances. As such, the total enthalpy change is scaled by the amount of substance used. General reactions, on the other hand, have to be interpreted in a very specific way. When examining a reaction like the combustion of methane

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$

with $\Delta H_{rxn} = -890.5\ kJ$. The correct interpretation is that the reaction of one mole of CH_4(g) with two moles of O_2(g) to form one mole of CO_2(g) and two moles of H_2O(l) releases 890.5 kJ at 25 °C.

Ionization Reactions

Ionized species appear throughout chemistry. The energy changes involved in the formation of ions can be measured and tabulated for several substances. In the case of the formation of positive ions, the enthalpy change to remove a single electron at 0 K is defined as the **ionization potential**.

$$M(g) \rightarrow M^+(g) + e^-$$

with $\Delta H(0K) \equiv 1^{st}\ \text{ionization potential (IP)}$

The removal of subsequent electrons requires energies called the 2nd Ionization potential, 3rd ionization potential, and so on.

$$M^+(g) \rightarrow M^{2+}(g) + e^-$$

with $\Delta H(0K) \equiv 2^{nd} IP$

$$M^{2+}(g) \rightarrow M^{3+}(g) + e^-$$

with $\Delta H(0K) \equiv 3^{rd} IP$

An atom can have as many ionization potentials as it has electrons, although since very highly charged ions are rare, only the first few are important for most atoms.

Similarly, the **electron affinity** can be defined for the formation of negative ions. In this case, the first electron affinity is defined by

$$X(g) + e^- \rightarrow X^-(g)$$

with $-\Delta H(0K) \equiv 1^{st}\ \text{electron affinity (EA)}$

The minus sign is included in the definition in order to make electron affinities mostly positive. Some atoms (such as noble gases) will have negative electron affinities since the formation of a negative ion is very unfavorable for these species. Just as in the case of ionization potentials, an atom can have several electron affinities.

$$X^-(g) + e^- \rightarrow X^{2-}(g)$$

with $-\Delta H(0K) \equiv 2^{nd} EA$.

$$X^{2-}(g) + e^- \rightarrow X^{3-}(g)$$

with $-\Delta H(0K) \equiv 3^{rd} EA$.

Average Bond Enthalpies

In the absence of standard formation enthalpies, reaction enthalpies can be estimated using average bond enthalpies. This method is not perfect, but it can be used to get ball-park estimates when more detailed data is not available. A **bond dissociation energy** D is defined by

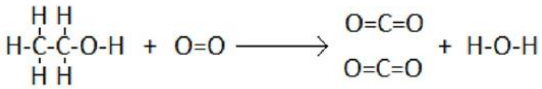
$$XY(g) \rightarrow X(g) + Y(g)$$

with $\Delta H \equiv D(X-Y)$

In this process, one adds energy to the reaction to break bonds, and extracts energy for the bonds that are formed.

$$\Delta H_{rxn} = \sum(\text{bonds broken}) - \sum(\text{bonds formed})$$

As an example, consider the combustion of ethanol:



In this reaction, five C-H bonds, one C-C bond, and one C-O bond, and one O=O bond must be broken. Also, four C=O bonds, and one O-H bond are formed.

Bond	Average Bond Energy (kJ/mol)
C-H	413
C-C	348
C-O	358
O=O	495
C=O	799
O-H	463

The reaction enthalpy is then given by

$$\begin{aligned}\Delta H_c &= 5(413\,kJ/mol) + 1(348\,kJ/mol) + 1(358\,kJ/mol) \\ &\quad + 1(495\,kJ/mol) - 4(799\,kJ/mol) - 2(463\,kJ/mol) \\ &= -856\,kJ/mol\end{aligned} \tag{2.7.2.4}$$

Because the bond energies are defined for gas-phase reactants and products, this method does not account for the enthalpy change of condensation to form liquids or solids, and so the result may be off systematically due to these differences. Also, since the bond enthalpies are averaged over a large number of molecules containing the particular type of bond, the results may deviate due to the variance in the actual bond enthalpy in the specific molecule under consideration. Typically, reaction enthalpies derived by this method are only reliable to within ± 5-10%.

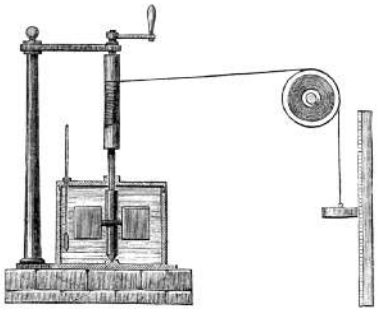
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2.E: First Law of Thermodynamics Exercises

Q2.1

In the attempt to measure the heat equivalent of mechanical work (as Joule did in his famous experiment) a student uses an apparatus similar to that shown below:



The 1.50 kg weight is lifted 30.0 cm against the force due to gravity (9.8 N). If the specific heat of water is 4.184 J/(g °C), what is the expected temperature increase of the 1.5 kg of water in the canister?

Q2.2

1.00 mol of an ideal gas, initially occupying 12.2 L at 298 K, expands isothermally against a constant external pressure of 1.00 atm until the pressure of the gas is equal to the external pressure. Calculate Δp, q, w, ΔU, and ΔH for the expansion.

Q2.3

Consider 1.00 mol of an ideal gas expanding isothermally at 298 K from an initial volume of 12.2 L to a final volume of 22.4 L. Calculate Δp, q, w, ΔU, and ΔH for the expansion.

Q2.4

Consider 1.00 mol of an ideal gas (C_V = 3/2 R) Occupying 22.4 L that undergoes an isochoric (constant volume) temperature increase from 298 K to 342 K. Calculate Δp, q, w, ΔU, and ΔH for the change.

Q2.5

Consider 1.00 mol of an ideal gas (C_p = 5/2 R) initially at 1.00 atm that undergoes an isobaric expansion from 12.2 L to 22.4 L. Calculate ΔT, q, w, ΔU, and ΔH for the change.

Q2.6

Consider 1.00 mol of an ideal gas (C_V = 3/2 R) initially at 12.2 L that undergoes an adiabatic expansion to 22.4 L. Calculate ΔT, q, w, ΔU, and ΔH for the change.

Q2.7

Derive an expression for the work of an isothermal, reversible expansion of a gas that follows the equation of state (in which a is a parameter of the gas)

$$pV = nRT - \frac{an^2}{V} \tag{2.E.1}$$

from V_1 to V_2.

Q2.8

Use the following data [Huff, Squitieri, and Snyder, J. Am. Chem. Soc., **70**, 3380 (1948)] to calculate the standard enthalpy of formation of tungsten carbide, $WC(s)$.

Reaction	ΔH^o (kJ)
$C(gr) + O_2(g) \rightarrow CO_2(g)$	-393.51
$WC(s) + 5/2O_2(g) \rightarrow WO_3(s) + CO_2(g)$	-1195.79
$W(s) + 3/2O_2(g) \rightarrow WO_3(s)$	-837.42

Q2.9

The standard molar enthalpy of combustion (ΔH_c) of propane gas is given by

$$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l) \tag{2.E.2}$$

with $\Delta H_c = -2220\,kJ/mol$

The standard molar enthalpy of vaporization (ΔH_{vap}) for liquid propane

$$C_3H_8(l) \rightarrow C_3H_8(g) \tag{2.E.3}$$

with $\Delta H_{vap} = 15\,kJ/mol$

a. Calculate the standard enthalpy of combustion of liquid propane.
b. Calculate the standard internal energy change of vaporization (ΔU_{vap}) for liquid propane.
c. Calculate the standard internal energy change of combustion (ΔH_c) for liquid propane.

Q2.10

The enthalpy of combustion (ΔH_c) of aluminum borohydride, $Al(BH_4)_3(l)$, was measured to be -4138.4 kJ/mol [Rulon and Mason, *J. Am. Chem. Soc.*, **73**, 5491 (1951)]. The combustion reaction for this compound is given by

$$Al(BH_4)_3(l) + 6O_2(g) \rightarrow ½Al_2O_3(s) + 3/2B_2O_3(s) + 6H_2O(l) \tag{2.E.4}$$

Given the following additional data, calculate the enthalpy of formation of $Al(BH_4)_3(g)$.

- $Al_2O_3(s)$: $\Delta H_f = -1669.8\,kJ/mol$
- $B_2O_3(s)$: $\Delta H_f = -1267.8\,kJ/mol$
- $H_2O(l)$: $\Delta H_f = -285.84\,kJ/mol$
- $Al(BH_4)_3(l)$: $\Delta H_{vap} = 30.125\,kJ/mol$

Q2.11

The standard enthalpy of formation (ΔH_f^o) for water vapor is -241.82 kJ/mol at 25 °C. Use the data in the following table to calculate the value at 100 °C.

Substance	C_p (J mol^{-1} K^{-1})
H_2(g)	28.84
O_2(g)	29.37
H_2O(g)	33.58

Q2.12

$\Delta C_p = (1.00 + 2.00 \times 10^{-3}T)\,J/K$ and $\Delta H_{298} = -5.00\,kJ$ for a dimerization reaction

$$2A \rightarrow A_2 \tag{2.E.5}$$

Find the temperature at which \(\Delta H = 0\).

Q2.13

From the following data, determine the lattice energy of $BaBr_2$.

$$Ca(s) \rightarrow Ca(g) \tag{2.E.6}$$

with $\Delta H_{sub} = 129\,kJ/mol$

$$Br_2(l) \rightarrow Br_2(g) \tag{2.E.7}$$

with $\Delta H_{vap} = 31\,kJ/mol$

$$Br_2(g) \rightarrow 2Br(g) \tag{2.E.8}$$

with $D(Br-Br) = 193\,kJ/mol$

$$Ca(g) \rightarrow Ca^+(g) + e^- \tag{2.E.9}$$

with $1^{st}\,IP(K) = 589.8\,kJ/mol$

$$Ca^+(g) \rightarrow Ca^{2+}(g) + e^- \tag{2.E.10}$$

with $2^{nd} IP(K) = 1145.4\,kJ/mol$

$$Br(g) + e^- \rightarrow Br-(g) \tag{2.E.11}$$

with $1^{st} EA(Br) = 194\,kJ/mol$

$$Ca(s) + Br_2^-(l) \rightarrow CaBr_2(s) \tag{2.E.12}$$

with $\Delta H_f = -675\,kJ/mol$

Q2.14

Using average bond energies (Table T3) estimate the reaction enthalpy for the reaction

$$C_2H_4 + HBr \rightarrow C_2H_5Br \tag{2.E.13}$$

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1.E: Putting the First Law to Work (Exercises)

Q2.15

Given the relationship

$$\left(-\frac{\partial U}{\partial V}\right)_T = T\left(-\frac{\partial p}{\partial T}\right)_V - p \tag{1.E.1}$$

show that

$$\left(-\frac{\partial U}{\partial V}\right)_T = 0 \tag{1.E.2}$$

for an ideal gas.

Q2.16

Determine if the following differential is exact, and if so, find the function $z(x, y)$ that satisfies the expression.

$$dz = 4xy\,dz + 2x^2 dy \tag{1.E.3}$$

Q2.17

For a van der Waals gas,

$$\left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{an^2}{V^2}\right) \tag{1.E.4}$$

Find an expression in terms of a, n, V, and R for

$$\left(\frac{\partial T}{\partial V}\right)_U \tag{1.E.5}$$

if $C_V = 3/2R$. Use the expression to calculate the temperature change for 1.00 mol of Xe (a = 4.19 atm L^2 mol^{-2}) expanding *adiabatically* against a vacuum from 10.0 L to 20.0 L.

Q2.18

Given the following data, calculate the change in volume for 50.0 cm^3 of

a. neon and
b. copper

due to an increase in pressure from 1.00 atm to 0.750 atm at 298 K.

Substance	T (at 1.00 atm and 298 K)
Ne	1.00 atm^{-1}
Cu	0.735 x 10^{-6} atm^{-1}

Q2.19

Consider a gas that follows the equation of state

$$p = \frac{nRT}{V - nb} \tag{1.E.6}$$

derive an expression for

a. the isobaric thermal expansivity, α
b. the Joule-Thomson coefficient, μ_{JT}

$$\mu_{JT} = \frac{V}{C_p}(T\alpha - 1) \tag{1.E.7}$$

Q2.20

Given

$$\left(\frac{\partial H}{\partial p}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_p + V \tag{1.E.8}$$

derive an expression for

$$\left(\frac{\partial U}{\partial p}\right)_T \tag{1.E.9}$$

in terms of measurable properties. Use your result to calculate the change in the internal energy of 18.0 g of water when the pressure is increased from 1.00 atm to 20.0 atm at 298 K.

Q2.21

Derive an expression for

$$\left(\frac{\partial U}{\partial T}\right)_p \tag{1.E.10}$$

Begin with the definition of enthalpy, in order to determine

$$dH = dU + pdV + Vdp \tag{1.E.11}$$

Finish by dividing by dT and constraining to constant pressure. Make substitutions for the measurable quantities, and solve for

$$\left(\frac{\partial U}{\partial T}\right)_p. \tag{1.E.12}$$

Q2.22

Derive an expression for the difference between C_p and C_V in terms of the internal pressure, α, p and V. Using the definition for H as a starting point, show that

$$\left(\frac{\partial H}{\partial T}\right)_p = \left(\frac{\partial U}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p \tag{1.E.13}$$

Now, find an expression for by starting with $U(V,T)$ and writing an expression for the total differential $dU(V,T)$.

Divide this expression by dp and constrain to constant T. Substitute this into the previous expressions and solve for

$$\left(\frac{\partial G}{\partial T}\right)_p - \left(\frac{\partial U}{\partial T}\right)_V. \tag{1.E.14}$$

Q4.9

Evaluate the expression you derived in problem 8 for an ideal, assuming that the internal pressure of an ideal gas is zero.

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CHAPTER OVERVIEW

3: The Second and Third Laws of Thermodynamics

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3.1: Introduction to the Second Law

Rudolph Clausius is kind enough in his 1879 work "The Mechanical Theory of Heat" (Clausius, 1879) to indicate where we have been in our discussion of thermodynamics, as well as where we are going.

> "The fundamental laws of the universe which correspond to the two fundamental theorems of the mechanical theory of heat:
> 1. The energy of the universe is constant.
> 2. The entropy of the universe tends to a maximum."
> — Rudolf Clausius, The Mechanical Theory Of Heat

The **second law of thermodynamics**, which introduces us to the topic of entropy, is amazing in how it constrains what we can experience and what we can do in the universe. As Sean M. Carroll, a CalTech Theoretical physicist, suggests in a 2010 interview with Wired Magazine (Biba, 2010),

> *I'm trying to understand how time works. And that's a huge question that has lots of different aspects to it. A lot of them go back to Einstein and spacetime and how we measure time using clocks. But the particular aspect of time that I'm interested in is the arrow of time: the fact that the past is different from the future. We remember the past but we don't remember the future. There are irreversible processes. There are things that happen, like you turn an egg into an omelet, but you can't turn an omelet into an egg.*

We, as observers of nature, are time travelers. And the constraints on what we can observe as we move through time step from the **second law of thermodynamics**. But more than just understanding what the second law says, we are interested in what sorts of processes are possible. And even more to the point, what sorts of processes are **spontaneous**.

A spontaneous process is one that will occur without external forces pushing it. A process can be spontaneous even if it happens very slowly. Unfortunately, Thermodynamics is silent on the topic of how fast processes will occur, but is provides us with a powerful toolbox for predicting which processes will be spontaneous. But in order to make these predictions, a new thermodynamic law and variable is needed since the first law (which defined ΔU and ΔH) is insufficient.

Consider the following processes:

$$NaOH(s) \rightarrow Na^{+}(aq) + OH^{-}(aq)$$

with $\Delta H < 0$

$$NaHCO_3(s) \rightarrow Na + (aq) + HCO_3^{-}(aq)$$

with $\Delta H > 0$

Both reactions will occur spontaneously, but one is exothermic and the other endothermic. So while it is intuitive to think that an exothermic process will be spontaneous, there is clearly more to the picture than simply the release of energy as heat when it comes to making a process spontaneous. The Carnot cycle because a useful thought experiment to explore to help to answer the question of why a process is spontaneous.

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3.2: Heat Engines and the Carnot Cycle

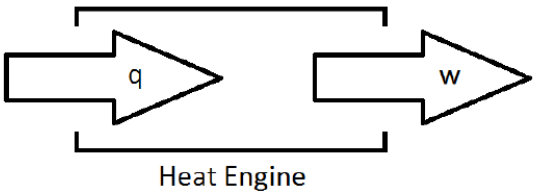
Heat Engines

Sadi Carnot (1796 – 1832) (Mendoza, 2016), a French physicist and engineer was very interested in the improvement of steam engines to perform the tasks needed by modern society.



Figure **3.2.1**: Sadi Carnot (1796 - 1832)

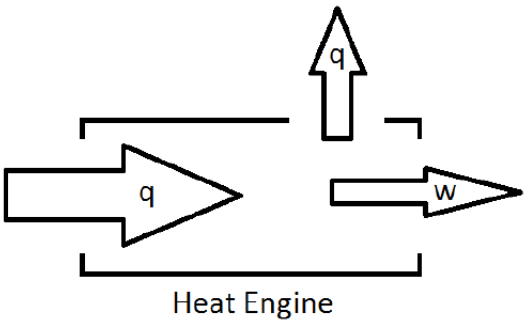
To simplify his analysis of the inner workings of an engine, Carnot devised a useful construct for examining what affect engine efficiency. His construct is the **heat engine**. The idea behind a heat engine is that it will take energy in the form of heat, and transform it into an equivalent amount of work.



Unfortunately, such a device is impractical. As it turns out, nature prevents the complete conversion of energy into work with perfect efficiency. This leads to an important statement of the **Second Law of Thermodynamics**.

> *It is impossible to convert heat into an equivalent amount of work without some other changes occurring in the universe.*

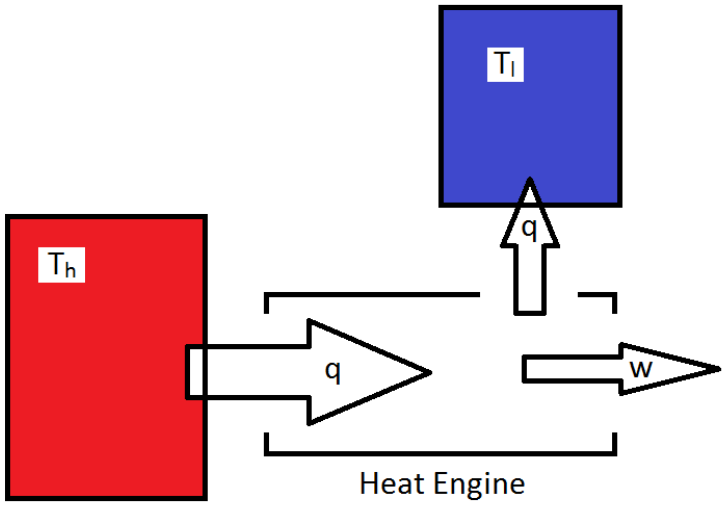
As such, a more reasonable picture of the heat engine is one which will allow for losses of energy to the surroundings.



The fraction of energy supplied to the engine that can be converted to work defines the efficiency of the engine.

The Carnot Cycle

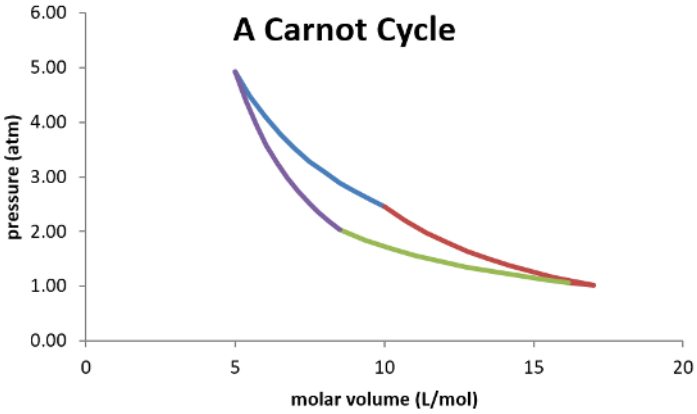
The Carnot cycle is a theoretical cyclic heat engine that can used to examine what is possible for an engine for which the job is convert heat into work. For simplicity, all energy provided to the engine occurs isothermally (and reversibly) at a temperature T_h and all of the energy lost to the surroundings also occurs isothermally and reversibly at temperature T_l. In order to insure this, the system must change between the two temperatures adiabatically.



Thus, the cycle consists of four reversible legs, two of which are isothermal, and two of which are adiabatic.

I. Isothermal expansion from p_1 and V_1 to p_2 and V_2 at T_h.
II. Adiabatic expansion from p_2, V_2, T_h to p_3, V_3, T_l.
III. Isothermal compression from p_3 and V_3 to p_4 and V_4 at T_l.
IV. Adiabatic compression from p_4, V_4, T_l to p_1, V_1, T_h.

Plotted on a pressure-volume diagram, the Carnot cycle looks as follows:



Because this is a closed cycle (the ending state is identical initial state) any state function must have a net change of zero as the system moves around the cycle. Furthermore, the efficiency of the engine can be expressed by the net amount of work the engine produces per unit of heat supplied to power the engine.

$$\epsilon = \frac{w_{net}}{q_h}$$

In order to examine this expression, it is useful to write down expressions fo the heat and work flow in each of the four legs of the engine cycle.

Leg	Heat	Work
I	$q_h = -nRT_h \ln(V_2/V_1)$	$nRT_h \ln(V_2/V_1)$
II	0	$C_V(T_l - T_h)$
III	$q_l = -nRT_l \ln(V_4/V_3)$	$nRT_l \ln(V_4/V_3)$
IV	0	$C_V(T_h - T_l)$

The total amount of work done is given by the sum of terms in the thirst column. Clearly the terms for the two adiabatic legs cancel (as they have the same magnitude, but opposite signs.) So the total work done is given by

$$w_{tot} = nRT_h \ln\left(\frac{V_2}{V_1}\right) + nRT_l \ln\left(\frac{V_4}{V_3}\right)$$

The efficiency of the engine can be defined as the total work produced per unit of energy provided by the high temperature reservoir.

$$\epsilon = \frac{w_{tot}}{q_h}$$

or

$$\epsilon = \frac{nRT_h \ln\left(\frac{V_2}{V_1}\right) + nRT_l \ln\left(\frac{V_4}{V_3}\right)}{nRT_h \ln\left(\frac{V_2}{V_1}\right)} \tag{3.2.1}$$

That expression has a lot of variables, but it turns out that it can be simplified dramatically. It turns out that by the choice of pathways connecting the states places a very important restriction on the relative values of V_1, V_2, V_3 and V_4. To understand this, we must consider how the work of adiabatic expansion is related to the initial and final temperatures and volumes. In Chapter 3, it was shown that the initial and final temperatures and volumes of an adiabatic expansion are related by

$$V_i T_i^{C_V/R} = V_f T_f^{C_V/R}$$

or

$$\frac{V_i}{V_f} = \left(\frac{T_f}{T_i}\right)^{C_V/R}$$

Using the adiabatic expansion and compression legs (II and IV), this requires that

$$\frac{V_2}{V_2} = \left(\frac{T_h}{T_l}\right)^{C_V/R}$$

and

$$\frac{V_4}{V_1} = \left(\frac{T_l}{T_h}\right)^{C_V/R}$$

Since the second terms are reciprocals of one another, the first terms must be as well!

$$\frac{V_2}{V_2} = \frac{V_1}{V_4}$$

A simple rearrangement shows that

$$\frac{V_2}{V_1} = \frac{V_3}{V_4}$$

This is very convenient! It is what allows for the simplification of the efficiency expression (Equation 3.2.1) becomes

$$\epsilon = \frac{\cancel{nRT_h \ln\left(\frac{V_2}{V_1}\right)} + \cancel{nRT_l \ln\left(\frac{V_2}{V_1}\right)}}{\cancel{nRT_h \ln\left(\frac{V_2}{V_1}\right)}}$$

Canceling terms in the numerator and denominator yields

$$\epsilon = \frac{T_g - T_l}{T_h} \tag{3.2.2}$$

This expression gives the maximum efficiency and depends only on the high and low temperatures!

Also, it should be noted that the heat engine can be run backwards. By providing work to the engine, it can be forces to draw heat from the low temperature reservoir and dissipate it into the high temperature reservoir. This is how a refrigerator or heat pump works. The limiting efficiency of such a device can also be calculated using the temperatures of the hot can cold reservoirs.

Example 3.2.1:

What is the maximum efficiency of a freezer set to keep ice cream at a cool -10 ^{o}C, which it is operating in a room that is 25^{o}C? What is the minimum amount of energy needed to remove 1.0 J from the freezer and dissipate it into the room?

Solution

The efficiency is given by Equation 3.2.2 and converting the temperatures to an absolute scale, the efficiency can be calculated as

$$\epsilon = \frac{298\,K - 263\,K}{298\,K}$$

This value can be used in the following manner

$$energy_{transferred} = \epsilon(work_{required})$$

So

$$1.0\,J = 0.1174(w)$$

or

$$w = 8.5\,J$$

It is interesting to note that any arbitrary closed cyclical process can be described as a sum of infinitesimally small Carnot cycles, and so all of the conclusions reached for the Carnot cycle apply to any cyclical process.

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3.3: Entropy

In addition to learning that the efficiency of a Carnot engine depends only on the high and low temperatures, more interesting things can be derived through the exploration of this system. For example, consider the total heat transferred in the cycle:

$$q_{tot} = nRT_h \ln\left(\frac{V_2}{V_1}\right) - nRT_l \ln\left(\frac{V_4}{V_3}\right)$$

Making the substitution

$$\frac{V_2}{V_1} = \frac{V_3}{V_4}$$

the total heat flow can be seen to be given by

$$q_{tot} = nRT_h \ln\left(\frac{V_4}{V_3}\right) - nRT_l \ln\left(\frac{V_4}{V_3}\right)$$

It is clear that the two terms do not have the same magnitude, unless $T_h = T_l$. This is sufficient to show that q is **not a state function**, since it's net change around a closed cycle is not zero (as any value of a state function must be.) However, consider what happens when the sum of q/T is considered:

$$\begin{aligned}\sum \frac{q}{T} &= \frac{nR\cancel{T_h}\ln\left(\frac{V_4}{V_3}\right)}{\cancel{T_h}} - \frac{nR\cancel{T_l}\ln\left(\frac{V_4}{V_3}\right)}{\cancel{T_l}} \\ &= nR\ln\left(\frac{V_4}{V_3}\right) - nR\ln\left(\frac{V_4}{V_3}\right) \\ &= 0\end{aligned}$$

This is the behavior expected for a state function! It leads to the definition of entropy in differential form,

$$dS \equiv \frac{dq_{rev}}{T}$$

In general, dq_{rev} will be larger than dq (since the reversible pathway defines the maximum heat flow.) So, it is easy to calculate entropy changes, as one needs only to define a reversible pathway that connects the initial and final states, and then integrate dq/T over that pathway. And since \(\Delta S\) is defined using q for a reversible pathway, ΔS is *independent* of the actual path a system follows to undergo a change.

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3.4: Calculating Entropy Changes

Entropy changes are fairly easy to calculate so long as one knows initial and final state. For example, if the initial and final volume are the same, the entropy can be calculated by assuming a reversible, isochoric pathway and determining an expression for $\frac{dq}{T}$. That term can then be integrated from the initial condition to the final conditions to determine the entropy change.

Isothermal Changes

If the initial and final temperatures are the same, the most convenient reversible path to use to calculate the entropy is an isothermal pathway. As an example, consider the isothermal expansion of an ideal gas from V_1 to V_2. As was derived in Chapter 3,

$$dq = nRT\frac{dV}{V}$$

So dq/T is given by

$$\frac{dq}{T} = nR\frac{dV}{V}$$

and so

$$\Delta S = \int \frac{dq}{T} = nR\int_{V_1}^{V_2} \frac{dV}{V} = nR\ln\left(\frac{V_2}{V_1}\right) \tag{3.4.1}$$

Example 3.4.1: Entropy Change for a Gas Expansion

Calculate the entropy change for 1.00 mol of an ideal gas expanding isothermally from a volume of 24.4 L to 48.8 L.

Solution

Recognizing that this is an isothermal process, we can use Equation 3.4.1

$$\begin{aligned}\Delta S &= nR\ln\left(\frac{V_2}{V_1}\right)\\ &= (1.00\,mol)(8.314 J/(mol\,K))\ln\left(\frac{44.8\,L}{22.4\,L}\right)\\ &= 5.76\,J/K\end{aligned}$$

Isobaric Changes

For changes in which the initial and final pressures are the same, the most convenient pathway to use to calculate the entropy change is an isobaric pathway. In this case, it is useful to remember that

$$dq = nC_p dT$$

So

$$\frac{dq}{T} = nC_p\frac{dT}{T}$$

Integration from the initial to final temperature is used to calculate the change in entropy. If the heat capacity is constant over the temperature range

$$\int_{T_1}^{T_2} \frac{dq}{T} = nC_p\int_{T_1}^{T_2} \frac{dT}{T} = nC_p\ln\left(\frac{T_2}{T_1}\right)$$

If the temperature dependence of the heat capacity is known, it can be incorporated into the integral. For example, if C_p can be expressed as

$$C_p = a + bT + \frac{c}{T^2}$$

ΔS takes the form

$$\int_{T_1}^{T_2} \frac{dq}{T} = n \int_{T_1}^{T_2} \frac{a + bT + \frac{c}{T^2}}{T} dT$$

which simplifies to

$$\Delta S = n \int_{T_1}^{T_2} \left(\frac{a}{T} + bT + \frac{c}{T^3} \right) dT$$

or

$$\Delta S = n \left[a \ln \left(\frac{T_2}{T_1} \right) + b(T_2 - T_1) - \frac{c}{2} \left(\frac{1}{T_2^2} - \frac{1}{T_1^2} \right) \right]$$

Isochoric Changes

Similarly to the cast of constant pressure, it is fairly simple to calculate ΔS. Since

$$dq = nC_V dt$$

$\frac{dq}{T}$ is given by

$$\frac{dq}{T} = nC_V \frac{dT}{T}$$

And so for changes over which C_V is independent of the temperature ΔS is given by

$$\Delta S = nC_v \ln \left(\frac{T_2}{T_1} \right)$$

Adiabatic Changes

The easiest pathway for which to calculate entropy changes is an adiabatic pathway. Since $dq = 0$ for an adiabatic change, then $dS = 0$ as well.

Phase Changes

The entropy change for a phase change at constant pressure is given by

$$\Delta S = \frac{q}{T} = \frac{\Delta H_{phase}}{T} \tag{3.4.2}$$

Example 3.4.2: Entropy Change for Melting Ice

The enthalpy of fusion for water is 6.01 kJ/mol. Calculate the entropy change for 1.0 mole of ice melting to form liquid at 273 K.

Solution

This is a phase transition at constant pressure (assumed) requiring Equation 3.4.2:

$$\Delta S = \frac{(1\,mol)(6010\,J/mol)}{273\,K} = 22\,J/K$$

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3.5: Comparing the System and the Surroundings

It is oftentimes important (for reasons that will be discussed in the next section) to calculate both the entropy change of the system as well as that of the surroundings. Depending on the size of the surroundings, they can provide or absorb as much heat as is needed for a process without changing temperature. As such, it is oftentimes a very good approximation to consider the changes to the surroundings as happening isothermally, even though it may not be the case for the system (which is generally smaller.)

Example 3.5.1

Consider 18.02 g (1.00 mol) of ice melting at 273 K in a room that is 298 K. Calculate DS for the ice, the surrounding room, and of the universe. (DH_{fus} = 6.01 kJ/mol)

Solution

For the process under constant pressure: $q_{ice} = -q_{room}$:

$$q = n\Delta H_{fus} = (1.00\,mol)(6010\,J/mol) = 6010\,J$$

For the ice:

$$\Delta S_{ice} = \frac{q_{ice}}{T_{ice}} = \frac{6010\,J}{273\,K} = 22.0\,J/K$$

For the room:

$$\Delta S_{room} = \frac{q_{room}}{T_{room}} = \frac{-6010\,J}{298\,K} = -20.2\,J/K$$

For the universe:

$$\begin{aligned}\Delta S_{univ} &= \Delta S_{ice} + \Delta S_{room} \\ &= 22.0 J/K - 20.2\,J/K = 1.8\,J/K\end{aligned}$$

Note: ΔS_{univ} is positive, which is characteristic of a spontaneous change!

Example 3.5.2

A 10.0 g piece of metal (C = 0.250 J/g °C) initially at 95 °C is placed in 25.0 g of water initially at 15 °C in an insulated container. Calculate the final temperature of the metal and water once the system has reached thermal equilibrium. Also, calculate the entropy change for the metal, the water, and the entire system.

Solution

Heat will be transferred from the hot metal to the cold water. Since it has nowhere else to go, the final temperature can be calculated from the expression

$$q_w = -q_m$$

where q_w is the heat absorbed by the water, and q_m is the heat lost by the metal. And since

$$q = mC\Delta T$$

it follows that

$$(25\,g)(4.184\,J/g°C))(T_f - 15\,°C) = -(10.0\,g)(0.250\,J/g°C))(T_f - 95\,J/g°C)$$

A bit of algebra determines the final temperature to be:

$$T_f = 16.9\,°C.$$

To get the entropy changes, use the expression:

$$\Delta S = mC_p \ln\left(\frac{T_f}{T_i}\right)$$

So, for the water:

$$\begin{aligned}\Delta S_{water} &= (25\,g)(4.184\,J/g\,°C))\ln\left(\frac{289.9\,K}{288\,K}\right)\\ &= 0.689\,J/K\end{aligned}$$

And for the metal:

$$\begin{aligned}\Delta S_{metal} &= (10.0\,g)(0.250\,J/g\,°C))\ln\left(\frac{289.9\,K}{368\,K}\right)\\ &= -0.596\,J/K\end{aligned}$$

For the system:

$$\begin{aligned}\Delta S_{sys} &= \Delta S_{water} + \Delta S_{metal}\\ &= 0.689\,J/K + -0.596\,J/K = 0.093\,J/K\end{aligned}$$

Note: The total entropy change is positive, suggesting that this will be a spontaneous process. This should make some sense since one expects heat to flow from the hot metal to the cool water rather than the other way around. Also, note that the sign of the entropy change is positive for the part of the system that is absorbing the heat, and negative for the part losing the heat.

In summary, ΔS can be calculated for a number of pathways fairly conveniently.

Table 3.5.1: Summary of different ways to calculate ΔS depending on the pathway. * for an ideal gas.

Pathway	$\Delta S_{sys} = \frac{dq_{rev}}{T_{sys}}$	$\Delta S_{surr} = \frac{q_{sys}}{T_{surr}}$
Adiabatic	0	$\Delta S_{surr} = \frac{q_{sys}}{T_{surr}}$
Isothermal	$\frac{q_{rev}}{T}$ and $nR\ln\left(\frac{V_2}{V_1}\right)$*	
Isobaric	$mC_p \ln\left(\frac{T_f}{T_i}\right)$	
Isochoric	$mC_V \ln\left(\frac{T_f}{T_i}\right)$	
Phase Change	$\frac{\Delta H_{phase}}{T}$	

And

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}.$$

This calculation is important as ΔS_{univ} provides the criterion for spontaneity for which we were searching from the outset. This also suggests a new way to state the second law:

> *The entropy of the universe increases in any spontaneous change.*

If we think of “the direction of spontaneous” to be the natural direction of chance, we can see that entropy and the second law are tied inexorably with the natural direction of the flow of time. Basically, we can expect the entropy of the universe to continue to increase as time flows into the future. We can overcome this natural tendency to greater entropy by doing work on a system. This is why it requires such great effort, for example, to straighten a messy desk, but little effort for the desk to get messy over time.

Clausius Inequality

The Second Law can be summed up in a very simple mathematical expression called the *Clausius Inequality*.

$$\Delta S_{universe} \geq 0$$

which must be true for any spontaneous process. It is not the most convenient criterion for spontaneity, but it will do for now. In the next chapter, we will derive a criterion which is more useful to us as chemists, who would rather focus on the system itself rather than both the system and its surroundings. Another statement of the Clausius theorem is

$$\oint \frac{dq}{T} \geq 0$$

with the only condition of the left hand side equaling zero is if the system transfers all heat reversibly.

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3.6: Entropy and Disorder

A common interpretation of entropy is that it is somehow a measure of chaos or randomness. There is some utility in that concept. Given that entropy is a measure of the dispersal of energy in a system, the more chaotic a system is, the greater the dispersal of energy will be, and thus the greater the entropy will be. Ludwig Boltzmann (1844 – 1906) (O'Connor & Robertson, 1998) understood this concept well, and used it to derive a statistical approach to calculating entropy. Boltzmann proposed a method for calculating the entropy of a system based on the number of energetically equivalent ways a system can be constructed.

Boltzmann proposed an expression, which in its modern form is:

$$S = k_b \ln(W) \tag{3.6.1}$$

This rather famous equation is etched on Boltzmann's grave marker in commemoration of his profound contributions to the science of thermodynamics (Figure **3.6.1**).



Figure **3.6.1**: Ludwig Boltzmann (1844 - 1906)

Example 3.6.1:

Calculate the entropy of a carbon monoxide crystal, containing 1.00 mol of CO, and assuming that the molecules are randomly oriented in one of two equivalent orientations.

Solution

Using the Boltzmann formula (Equation 3.6.1):

$$S = nK \ln(W)$$

And using $W = 2$, the calculation is straightforward.

$$\begin{aligned} S &= \left(1.00\,mol \cot \frac{6.022 \times 10^{23}}{1\,mol}\right)(1.38 \times 10^{-23} J/K) \ln 2 \\ &= 5.76\,J/K \end{aligned}$$

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3.7: The Third Law of Thermodynamics

One important consequence of Botlzmann's proposal is that a perfectly ordered crystal (i.e. one that has only one energetic arrangement in its lowest energy state) will have an entropy of 0. This makes entropy qualitatively different than other thermodynamic functions. For example, in the case of enthalpy, it is impossible have a zero to the scale without setting an arbitrary reference (which is that the enthalpy of formation of elements in their standard states is zero.) But entropy has a natural zero! It is the state at which a system has perfect order. This also has another important consequence, in that it suggests that there must also be a zero to the temperature scale. These consequences are summed up in the **Third Law of Thermodynamics**.

> *The entropy of a perfectly ordered crystal at 0 K is zero.*

This also suggests that absolute molar entropies can be calculated by

$$S = \int_0^T \frac{C}{T} dT$$

where C is the heat capacity. An entropy value determined in this manner is called a **Third Law Entropy**.

Naturally, the heat capacity will have some temperature dependence. It will also change abruptly if the substance undergoes a phase change. Unfortunately, it is exceedingly difficult to measure heat capacities very near zero K. Fortunately, many substances follow the **Debye Extrapolation** in that at very low temperatures, their heat capacities are proportional to T^3. Using this assumption, we have a temperature dependence model that allows us to extrapolate absolute zero based on the heat capacity measured at as low a temperature as can be found.

Example 3.7.1

SiO_2 is found to have a molar heat capacity of 0.777 J mol^{-1} K^{-1} at 15 K (Yamashita, et al., 2001). Calculate the molar entropy of SiO_2 at 15 K.

Solution

Using the Debye model, the heat capacity is given by



The value of a can be determined by





The entropy is then calculated by

Calculating a third Law Entropy

Start at 0 K, and go from there!

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3.8: Adiabatic Compressibility

In Chapter 4, we learned about the isothermal compressibility, κ_T, which is defined as

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$$

κ_T is a very useful quantity, as it can be measured for many different substances and tabulated. Also, as we will see in the next chapter, it can be used to evaluate several different partial derivatives involving thermodynamic variables.

In his seminal work, *Philosophiae Naturalis Principia Mathematica* (Newton, 1723), Isaac Newton (1643 - 1727) (Doc) calculated the speed of sound through air, assuming that sound was carried by isothermal compression waves. His calculated value of 949 m/s was about 15% smaller than experimental determinations. He accounted for the difference by pointing to “non-ideal effects”. But it turns out that his error, albeit an understandable one (since sound waves do not appear to change bulk air temperatures) was that the compression waves are adiabatic, rather than isothermal. As such, there are small temperature oscillations that occur due to the adiabatic compression followed by expansion of the gas carrying the sound waves. The oversight was correct by Pierre-Simon Laplace (1749 – 1827) (O'Connor & Robertson, Pierre-Simon Laplace, 1999).

LaPlace modeled the compression waves using the **adiabatic compressibility**, κ_S defined by

$$\kappa_S = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_S$$

Since the entropy is defined by

$$dS = \frac{dq_{rev}}{T}$$

it follows that any adiabatic pathway ($dq = 0$) is also **isentropic** ($dS = 0$), or proceeds at constant entropy.

> *Adiabatic pathways are also isentropic.*

A couple of interesting conclusions can be reached by following the derivation of an expression for the speed of sound where the sound waves are modeled as adiabatic compression waves. We can begin by expanding the description of κ_S by using Partial Derivative Transformation Type II. Applying this, the adiabatic compressibility can be expressed

$$\kappa_S = \frac{1}{V}\left(\frac{\partial V}{\partial S}\right)_p\left(\frac{\partial S}{\partial p}\right)_V$$

or by using transformation type I

$$\kappa_S = \frac{1}{V}\frac{\left(\frac{\partial S}{\partial p}\right)_V}{\left(\frac{\partial S}{\partial V}\right)_p}$$

Using a simple chain rule, the partial derivatives can be expanded to get something a little easier to evaluate:

$$\kappa_S = \frac{1}{V}\frac{\left(\frac{\partial S}{\partial T}\right)_V\left(\frac{\partial T}{\partial p}\right)_V}{\left(\frac{\partial S}{\partial T}\right)_p\left(\frac{\partial T}{\partial V}\right)_p} \tag{3.8.1}$$

The utility here is that

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T} \tag{3.8.2}$$

$$\left(\frac{\partial S}{\partial T}\right)_p = \frac{C_p}{T} \tag{3.8.3}$$

This means that Equation 3.8.1 simplifies to

$$\kappa_S = \frac{C_V}{C_p}\left(\frac{1}{V}\frac{\left(\frac{\partial T}{\partial p}\right)_V}{\left(\frac{\partial T}{\partial V}\right)_p}\right)$$

Simplifying what is in the parenthesis yields

$$\kappa_S = \frac{C_V}{C_p}\left(\frac{1}{V}\left(\frac{\partial T}{\partial p}\right)_V\left(\frac{\partial V}{\partial T}\right)_p\right)$$

$$\kappa_S = \frac{C_V}{C_p}\left(-\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T\right)$$

$$\kappa_S = \frac{C_V}{C_p}\kappa_T$$

As will be shown in the next chapter, C_p is always bigger than C_V, so κ_S is always smaller than κ_T.

But there is more! We can use this methodology to revisit how pressure affects volume along an adiabat. In order to do this, we would like to evaluate the partial derivative

$$\left(\frac{\partial V}{\partial p}\right)_S$$

This can be expanded in the same way as above

$$\left(\frac{\partial V}{\partial p}\right)_S = -\frac{\left(\frac{\partial V}{\partial S}\right)_p}{\left(\frac{\partial p}{\partial S}\right)_V}$$

And further expand

$$\left(\frac{\partial V}{\partial p}\right)_S = -\frac{\left(\frac{\partial V}{\partial T}\right)_p\left(\frac{\partial T}{\partial S}\right)_p}{\left(\frac{\partial p}{\partial T}\right)_V\left(\frac{\partial T}{\partial S}\right)_V} \tag{3.8.4}$$

And as before, noting that the relationships in Equations 3.8.2 and 3.8.3, Equation 3.8.4 can be simplified to

$$\left(\frac{\partial V}{\partial p}\right)_S = -\frac{C_V}{C_p}\left(\frac{\partial V}{\partial T}\right)_p\left(\frac{\partial T}{\partial p}\right)_V$$

$$= \frac{C_V}{C_p}\left(\frac{\partial V}{\partial p}\right)_T \tag{3.8.5}$$

Or defining $\gamma = C_p/C_V$, Equation 3.8.5 can be easily rearranged to

$$\gamma\left(\frac{\partial V}{\partial p}\right)_S = \left(\frac{\partial V}{\partial p}\right)_T$$

The right-hand derivative is easy to evaluate if we assume a specific equation of state. For an ideal gas,

$$\left(\frac{\partial V}{\partial p}\right)_T = -\frac{nRT}{p^2} = -\frac{V}{p}$$

Substitution yields

$$\gamma\left(\frac{\partial V}{\partial p}\right)_S = -\frac{V}{p}$$

which is now looking like a form that can be integrated. Separation of variables yields

$$\gamma\frac{dV}{V} = \frac{dP}{p}$$

And integration (assuming that g is independent of volume) yields

$$\gamma \int_{V_1}^{V_2} \frac{dV}{V} = \int_{p_1}^{p_2} \frac{dP}{p}$$

or

$$\gamma \ln\left(\frac{V_2}{V_1}\right) = \ln\left(\frac{p_2}{p_1}\right)$$

which is easily manipulated to show that

$$p_1 V_1^{\gamma} = p_2 V_2^{\gamma}$$

or

$$pV^{\gamma} = \text{constant}$$

which is what we previously determined for the behavior of an ideal gas along an adiabat.

Finally, it should be noted that the correct expression for the speed of sound is given by

$$v_{sound} = \sqrt{\frac{1}{\rho \kappa_S}}$$

where ρ is the density of the medium. For an ideal gas, this expression becomes

$$v_{sound} = \sqrt{\frac{\gamma RT}{M}}$$

where M is the molar mass of the gas. Isaac Newton's derivation, based on the idea that sound waves involved isothermal compressions, would produce a result which is missing the factor of γ, accounting for the systematic deviation from experiment which he observed.

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SECTION OVERVIEW

3.9: Putting the Second Law to Work

Physical Chemistry: Thermodynamics
Patrick Fleming

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3.9.1: Free Energy Functions

In the previous chapter, we saw that for a spontaneous process, $\Delta S_{universe} > 0$. While this is a useful criterion for determining whether or not a process is spontaneous, it is rather cumbersome, as it requires one to calculate not only the entropy change for the system, but also that of the surroundings. It would be much more convenient if there was a single criterion that would do the job and focus only on the system. As it turns out, there is.

Since we know that

$$\Delta S_{univ} \geq 0$$

for any natural process, and

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$$

all we need to do is to find an expression for ΔS_{sys} that can be determined by the changes in the system itself. Fortunately, we have already done that! Recalling that at constant temperature

$$\Delta S = -\frac{q_{rev}}{T}$$

and at constant pressure

$$\Delta H = q_p$$

it follows that at constant temperature and pressure

$$\Delta S_{surr} = -\frac{\Delta H_{sys}}{T}$$

Substitution into the above equations yields an expression for the criterion of spontaneity that depends only on variables describing the changes in the system!

$$\Delta S_{univ} \geq \Delta S_{sys} - \frac{\Delta H_{sys}}{T}$$

so

$$\Delta S_{sys} - \frac{\Delta H_{sys}}{T} \geq 0$$

Multiplying both sides by $-T$ yields

$$\Delta H - T\Delta S \leq 0 \tag{3.9.1.1}$$

A similar derivation for constant volume processes results in the expression (at constant volume and temperature)

$$\Delta U - T\Delta S \leq 0 \tag{3.9.1.2}$$

> Equation 3.9.1.1 is of great use to chemists, as most of chemistry occurs at constant pressure. For geologists, however, who are interested in processes that occur at very high pressures (say, under the weight of an entire mountain) and expansion is not a possibility, the constant volume expression of Equation 3.9.1.1 may be of greater interest.

All of the above arguments can be made for systems in which the temperature is not constant by considering infinitesimal changes. The resulting expressions are

$$dH - TdS \leq 0 \tag{3.9.1.3}$$

and

$$dU - TdS \leq 0 \tag{3.9.1.4}$$

The Gibbs and Helmholtz Functions

Equation 3.9.1.3 suggests a very convenient thermodynamic function to help keep track of both the effects of entropy and enthalpy changes. This function, the **Gibbs function** (or **Gibbs Free Energy**) is defined by

$$G \equiv H - TS$$

A change in the Gibbs function can be expressed

$$\Delta G = \Delta H - \Delta(TS)$$

Or at constant temperature

$$\Delta G = \Delta H - T\Delta S$$

And the criterion for a process to be spontaneous is the DG < 0. As such, it should be clear spontaneity is not merely a function the enthalpy change (although exothermic processes tend to be spontaneous) but also a function of the entropy change, weighted by the temperature. Going back to an earlier example,

$$NaOH(s) \rightarrow Na^{+}(aq) + OH^{-}(aq)$$

with $\Delta H < 0$.

and

$$NaHCO_3(s) \rightarrow Na^{+}(aq) + HCO_3^{-}(aq)$$

with $\Delta H > 0$.

It is easy to see why both processes are spontaneous. In the first case, the process is exothermic (favorable) and proceeds with an increase in entropy (also favorable) due to the formation of fragments in the liquid phase (more chaotic) from a very ordered solid (more ordered). The second reaction is endothermic (unfavorable) but proceeds with an increase in entropy (favorable). So, so long as the temperature is high enough, the entropy term will overwhelm the enthalpy term and cause the process to be spontaneous. The conditions for spontaneous processes at constant temperature and pressure can be summarized in Table 6.1.1.

Table 6.1.1: Spontaneity Conditions for a Process under Constant Temperature and Pressure

ΔH	ΔS	Spontaneous
> 0	> 0	At high T
> 0	< 0	At no T
< 0	> 0	At all T
< 0	< 0	At low T

Similarly to the Gibbs function, the **Helmholtz function** is defined by

$$A \equiv U - TS$$

and provides another important criterion for spontaneous processes at constant value and temperature. *At constant temperature*, the Helmholtz function can be expressed by

$$\Delta A \equiv \Delta U - T\Delta S$$

Based on similar arguments used for the Gibbs function, the Helmholtz function also can be used to predict which processes will be spontaneous at constant volume and temperature according to Table 6.1.2.

Table 6.1.2: Spontaneity Conditions for a Process under Constant Temperature and Volume

ΔU	ΔS	Spontaneous?
> 0	> 0	At high T
> 0	< 0	At no T
< 0	> 0	At all T
< 0	< 0	At low T

Calculating ΔG for Reactions

Much like in the case of enthalpy (and unlike entropy), free energy functions do not have an unambiguous zero to the energy scale. So, just like in the case of enthalpies of formation, by convention, the standard free energy of formation (ΔG_f^o) for elements in their standard states is defined as zero. This allows for two important things to happen. First, ΔG_f^o can be measured and tabulated for any substance (in principle, at least.) ΔG_f^o is determined to be ΔG_{rxn}^o for the reaction that forms one mole of a compound from elements in their standard states (similarly to how ΔH_f^o is defined.) Secondly, tabulated (ΔG_f^o) can be used to calculate standard reaction free energies (ΔG_{rxn}^o) in much the same way as ΔH_f^o is used for reaction enthalpies.

Example 3.9.1.1:

Given the following data at 298 K, calculate ΔG^o at 298 K for the following reaction:

$$C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$$

Substance	ΔG_f^o (kJ/mol)
$C_2H_4(g)$	68.4
$C_2H_6(g)$	-32.0

Solution

The ΔG_f^o values can be used to calculate ΔG^o for the reaction in exactly the same method as ΔH_f^o can be used to calculate a reaction enthalpy.

$$\Delta G^o = (1\,mol)(-32.0\,kJ/mol) - (1\,mol)(68.4\,kJ/mol)$$

$$\Delta G^o = 100.4\,kJ$$

Note: $H_2(g)$ is not included in the calculation since ΔG_f^o for $H_2(g)$ is 0 since it is an element in its standard state.

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3.9.2: Combining the First and Second Laws - Maxwell's Relations

Modeling the dependence of the Gibbs and Helmholtz functions behave with varying temperature, pressure, and volume is fundamentally useful. But in order to do that, a little bit more development is necessary. To see the power and utility of these functions, it is useful to combine the First and Second Laws into a single mathematical statement. In order to do that, one notes that since

$$dS = \frac{dq}{T}$$

for a reversible change, it follows that

$$dq = TdS$$

And since

$$dw = TdS - pdV$$

for a reversible expansion in which only p-V works is done, it also follows that (since $dU = dq + dw$):

$$dU = TdS - pdV \tag{3.9.2.1}$$

This is an extraordinarily powerful result. This differential for dU can be used to simplify the differentials for H, A, and G. But even more useful are the constraints it places on the variables T, S, p, and V due to the mathematics of exact differentials!

Maxwell Relations

The above result suggests that the natural variables of internal energy are S and V (or the function can be considered as $U(S,V)$). So the total differential (dU) in Equation 3.9.2.1 can be expressed:

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV \tag{3.9.2.2}$$

Also, by inspection (comparing the two expressions for dU in Equations 3.9.2.1 and 3.9.2.2) it is apparent that:

$$\left(\frac{\partial U}{\partial S}\right)_V = T \tag{3.9.2.3}$$

and

$$\left(\frac{\partial U}{\partial V}\right)_S = -p \tag{3.9.2.4}$$

But the value does not stop there! Since dU is an exact differential, the Euler relation must hold that

$$\left[\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial S}\right)_V\right]_S = \left[\frac{\partial}{\partial S}\left(\frac{\partial U}{\partial V}\right)_S\right]_V$$

By substituting Equations 3.9.2.3 and 3.9.2.4, we see that

$$\left[\frac{\partial}{\partial V}(T)_V\right]_S = \left[\frac{\partial}{\partial S}(-p)_S\right]_V$$

or

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$$

This is an example of a **Maxwell Relation**. These are very powerful relationship that allows one to substitute partial derivatives when one is more convenient (perhaps it can be expressed entirely in terms of α and/or κ_T for example.)

A similar result can be derived based on the definition of H.

$$H \equiv U + pV$$

Differentiating (and using the chain rule on $d(pV)$) yields

$$dH = dU + pdV + Vdp$$

Making the substitution using the combined first and second laws ($dU = TdS–pdV$) for a reversible change involving on expansion (p-V) work

$$dH = TdS–\cancel{pdV} + \cancel{pdV} + Vdp$$

This expression can be simplified by canceling the pdV terms.

$$dH = TdS + Vdp \tag{3.9.2.5}$$

And much as in the case of internal energy, this suggests that the natural variables of H are S and p. Or

$$dH = \left(\frac{\partial H}{\partial S}\right)_p dS + \left(\frac{\partial H}{\partial p}\right)_S dV \tag{3.9.2.6}$$

Comparing Equations 3.9.2.5 and 3.9.2.6 show that

$$\left(\frac{\partial H}{\partial S}\right)_p = T \tag{3.9.2.7}$$

and

$$\left(\frac{\partial H}{\partial p}\right)_S = V \tag{3.9.2.8}$$

It is worth noting at this point that both Equation 3.9.2.3

$$\left(\frac{\partial U}{\partial S}\right)_V$$

and Equation 3.9.2.7

$$\left(\frac{\partial H}{\partial S}\right)_p$$

are equal to T. So they are equation to each other

$$\left(\frac{\partial U}{\partial S}\right)_V = \left(\frac{\partial H}{\partial S}\right)_p$$

Moreover, the Euler Relation must also hold

$$\left[\frac{\partial}{\partial p}\left(\frac{\partial H}{\partial S}\right)_p\right]_S = \left[\frac{\partial}{\partial S}\left(\frac{\partial H}{\partial p}\right)_S\right]_p$$

so

$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$$

This is the Maxwell relation on H. Maxwell relations can also be developed based on A and G. The results of those derivations are summarized in Table 3.9.2.1.

Table 3.9.2.1: Maxwell Relations

Function	Differential	Natural Variables	Maxwell Relation
U	$dU = TdS - pdV$	S, V	$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$
H	$dH = TdS + Vdp$	S, p	$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$
A	$dA = -pdV - SdT$	V, T	$\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$
G	$dG = Vdp - SdT$	p, T	$\left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial S}{\partial p}\right)_T$

The Maxwell relations are extraordinarily useful in deriving the dependence of thermodynamic variables on the state variables of p, T, and V.

Example 3.9.2.1

Show that

$$\left(\frac{\partial V}{\partial T}\right)_p = T\frac{\alpha}{\kappa_T} - p$$

Solution

Start with the combined first and second laws:

$$dU = TdS - pdV$$

Divide both sides by dV and constraint to constant T:

$$\left.\frac{dU}{dV}\right|_T = \left.\frac{TdS}{dV}\right|_T - p\left.\frac{dV}{dV}\right|_T$$

Noting that

$$\left.\frac{dU}{dV}\right|_T = \left(\frac{\partial U}{\partial V}\right)_T$$

$$\left.\frac{TdS}{dV}\right|_T = \left(\frac{\partial S}{\partial V}\right)_T$$

$$\left.\frac{dV}{dV}\right|_T = 1$$

The result is

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - p$$

Now, employ the Maxwell relation on A (Table 6.2.1)

$$\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$$

to get

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p$$

and since

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{\alpha}{\kappa_T}$$

It is apparent that

$$\left(\frac{\partial V}{\partial T}\right)_p = T\frac{\alpha}{\kappa_T} - p$$

Note: How cool is that? This result was given without proof in Chapter 4, but can now be proven analytically using the Maxwell Relations!

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3.9.3: ΔA, ΔG, and Maximum Work

The functions A and G are oftentimes referred to as **free energy** functions. The reason for this is that they are a measure of the maximum work (in the case of ΔA) or non p-V work (in the case of ΔG) that is available from a process. To show this, consider the total differentials.

First, consider the differential of A.

$$dA = dU - TdS - SdT$$

Substituting the combined first and second laws for dU, but expressing the work term as dw, yields

$$dA = TdS - dw - TdS - SdT$$

And cancelling the TdS terms gives

$$dA = dw - SdT$$

or at constant temperature ($dT = 0$)

$$dA = dw$$

Since the only assumption made here was that the change is reversible (allowing for the substitution of TdS for dq), and dw for a reversible change is the maximum amount of work, it follows that dA gives the maximum work that can be produced from a process at constant temperature.

Similarly, a simple expression can be derived for dG. Starting from the total differential of G.

$$dG = dU + pdV - pdV + Vdp - TdS - SdT$$

Using an expression for $dU = dq + dw$, where $dq = TdS$ and dw is split into two terms, one (dw_{pV}) describing the work of expansion and the other (dw_e) describing any other type of work (electrical, stretching, etc.)

$$dU - TdS + dW_{pV} + dW_e$$

dG can be expressed as

$$dG = \cancel{TdS} - \cancel{pdV} + dw_e + \cancel{pdV} + Vdp - \cancel{TdS} - SdT$$

Cancelling the TdS and pdV terms leaves

$$dG = +dw_e + Vdp - SdT$$

So at constant temperature ($dT = 0$) and pressure ($dp = 0$),

$$dG = dw_e$$

This implies that dG gives the maximum amount of non p-V work that can be extracted from a process.

This concept of dA and dG giving the maximum work (under the specified conditions) is where the term “free energy” comes from, as it is the energy that is *free* to do work in the surroundings. If a system is to be optimized to do work in the soundings (for example a steam engine that may do work by moving a locomotive) the functions A and G will be important to understand. It will, therefore, be useful to understand how these functions change with changing conditions, such as volume, temperature, and pressure.

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3.9.4: Volume Dependence of Helmholtz Energy

If one needs to know how the Helmholtz function changes with changing volume at constant temperature, the following expression can be used:

$$\Delta A = \int_{V_1}^{V_2} \left(\frac{\partial A}{\partial V}\right)_T dV \tag{3.9.4.1}$$

But how does one derive an expression for the partial derivative in Equation 3.9.4.1? This is a fairly straight forward process that begins with the definition of A:

$$A = U - TS$$

Differentiating (and using the chain rule to evaluate $d(TS)$) yields

$$dA = dU - TdS - SdT \tag{3.9.4.2}$$

Now, it is convenient to use the combined first and second laws

$$dU = TdS - pdV \tag{3.9.4.3}$$

which assumes:

1. a reversible change and
2. only pV work is being done.

Substituting Equation 3.9.4.3 into Equation 3.9.4.2 yields

$$dA = \cancel{TdS} - pdV - \cancel{TdS} - SdT \tag{3.9.4.4}$$

Canceling the TdS terms gives the important result

$$dA = -pdV - SdT \tag{3.9.4.5}$$

The natural variables of A are therefore V and T! So the total differential of A is conveniently expressed as

$$dA = \left(\frac{\partial A}{\partial V}\right)_T dV + \left(\frac{\partial A}{\partial T}\right)_V dT \tag{3.9.4.6}$$

and by simple comparison of Equations 3.9.4.5 and 3.9.4.6, it is clear that

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

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

And so, one can evaluate Equation 3.9.4.1 as

$$\Delta A = -\int_{V_1}^{V_2} p\, dV$$

If the pressure is independent of the temperature, it can be pulled out of the integral.

$$\Delta A = -p\int_{V_1}^{V_2} dV = -p(V_2 - V_1)$$

Otherwise, the temperature dependence of the pressure must be included.

$$\Delta A = -\int_{V_1}^{V_2} p(V)\, dV$$

Fortunately, this is easy if the substance is an ideal gas (or if some other equation of state can be used, such as the van der Waals equation.)

Example 3.9.4.1: Ideal Gas Expansion

Calculate ΔA for the isothermal expansion of 1.00 mol of an ideal gas from 10.0 L to 25.0 L at 298 K.

Solution

For an ideal gas,

$$p = \frac{nRT}{V}$$

So

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

becomes

$$\left(\frac{\partial A}{\partial V}\right)_T = -\frac{nRT}{V}$$

And so (Equation 3.9.4.1)

$$\Delta A = \int_{V_1}^{V_2} \left(\frac{\partial A}{\partial V}\right)_T dV$$

becomes

$$\Delta A = -nRT \int_{V_1}^{V_2} \frac{dV}{V} dT$$

or

$$\Delta A = -nRT \ln\left(\frac{V_2}{V_1}\right)$$

Substituting the values from the problem

$$\Delta A = -(1.00\,mol)(8.314\,J/(mol\,K))(298\,K) \ln\left(\frac{25.0\,L}{10.0\,L}\right)$$

But further, it is easy to show that the Maxwell relation that arises from the simplified expression for the total differential of A is

$$\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$$

This particular Maxwell relation is exceedingly useful since one of the terms depends only on p, V, and T. As such it can be expressed in terms of our old friends, α and κ_T!

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{\alpha}{\kappa_T}$$

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3.9.5: Pressure Dependence of Gibbs Energy

The pressure and temperature dependence of G is also easy to describe. The best starting place is the definition of G.

$$G = U + pV - TS \tag{3.9.5.1}$$

Taking the total differential of G yields

$$dG = dU + pdV + Vdp - TdS - SdT$$

The differential can be simplified by substituting the combined first and second law statement for dU (consider a reversible process and pV work only).

$$dG = \cancel{TdS} - \cancel{pdV} + \cancel{pdV} + Vdp - \cancel{TdS} - SdT$$

Canceling the TdS and pdV terms leaves

$$dG = V\,dp - S\,dT \tag{3.9.5.2}$$

This suggests that the natural variables of G are p and T. So the total differential dG can also be expressed

$$dG = \left(\frac{\partial G}{\partial p}\right)_T dp + \left(\frac{\partial G}{\partial T}\right)_p dT \tag{3.9.5.3}$$

And by inspection of Equations 3.9.5.2 and 3.9.5.3, it is clear that

$$\left(\frac{\partial G}{\partial p}\right)_T = V$$

and

$$\left(\frac{\partial G}{\partial T}\right)_p = -S$$

It is also clear that the Maxwell relation on G is given by

$$\left(\frac{\partial V}{\partial T}\right)_p = \left(\frac{\partial S}{\partial p}\right)_T$$

which is an extraordinarily useful relationship, since one of the terms is expressible entirely in terms of measurable quantities!

$$\left(\frac{\partial V}{\partial T}\right)_p = V\alpha$$

The pressure dependence of G is given by the pressure derivative at constant temperature

$$\left(\frac{\partial G}{\partial p}\right)_T = V \tag{3.9.5.4}$$

which is simply the molar volume. For a fairly incompressible substance (such as a liquid or a solid) the molar volume will be essentially constant over a modest pressure range.

✔ Example 3.9.5.1: Gold under Pressure

The density of gold is 19.32 g/cm^3. Calculate ΔG for a 1.00 g sample of gold when the pressure on it is increased from 1.00 atm to 2.00 atm.

Solution

The change in the Gibbs function due to an isothermal change in pressure can be expressed as

$$\Delta G = \int_{p_1}^{p_2} \left(\frac{\partial G}{\partial p}\right)_T dp$$

And since substituting Equation 3.9.5.4, results in

$$\Delta G = \int_{p_1}^{p_2} V dp$$

Assuming that the molar volume is independent or pressure over the stated pressure range, ΔG becomes

$$\Delta G = V(p_2 - p_1)$$

So, the molar change in the Gibbs function can be calculated by substituting the relevant values.

$$\Delta G = \left(\frac{197.0\,g}{mol} \times \frac{1}{19.32\,g} \times \frac{1\,L}{1000\,cm^3}\right) (2.00\,atm - 1.00\,atm) \underbrace{\left(\frac{8.315\,J}{0.08206\,atm\,L}\right)}_{\text{conversion unit}} \tag{3.9.5.5}$$

$$= 1.033\,J \tag{3.9.5.6}$$

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3.9.6: Temperature Dependence of A and G

In differential form, the free energy functions can be expressed as

$$dA = -pdV - SdT$$

and

$$dG = -Vdp - SdT$$

So by inspection, it is easy to see that

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

and

$$\left(\frac{\partial G}{\partial T}\right)_p = -S$$

And so, it should be fairly straightforward to determine how each changes with changing temperature:

$$\Delta A = -\int_{T_1}^{T_2} \left(\frac{\partial A}{\partial T}\right)_V dT = -\int_{T_1}^{T_2} S\, dT$$

and

$$\Delta G = -\int_{T_1}^{T_2} \left(\frac{\partial G}{\partial T}\right)_p dT = -\int_{T_1}^{T_2} S\, dT$$

But the temperature dependence of the entropy needed to be known in order to evaluate the integral. A convenient work-around can be obtained starting from the definitions of the free energy functions.

$$A = U - TS$$

and

$$G = H - TS$$

Dividing by T yields

$$\frac{A}{T} = \frac{U}{T} - S$$

and

$$\frac{G}{T} = \frac{H}{T} - S$$

Now differentiating each expression with respect to T at constant V or p respectively yields

$$\left(\frac{\partial\left(\frac{A}{T}\right)}{\partial T}\right)_V = -\frac{U}{T^2}$$

and

$$\left(\frac{\partial\left(\frac{G}{T}\right)}{\partial T}\right)_p = -\frac{H}{T^2}$$

Or differentiating with respect to $1/T$ provides a simpler form that is mathematically equivalent:

$$\left(\frac{\partial\left(\frac{A}{T}\right)}{\partial\left(\frac{1}{T}\right)}\right)_V = U$$

and

$$\left(\frac{\partial\left(\frac{G}{T}\right)}{\partial\left(\frac{1}{T}\right)}\right)_p = H$$

Focusing on the second expression (since all of the arguments apply to the first as well), we see a system that can be integrated. Multiplying both sides by $d(1/T)$ yields:

$$d\left(\frac{G}{T}\right) = Hd\left(\frac{1}{T}\right)$$

Or for finite changes ΔG and ΔH:

$$d\left(\frac{\Delta G}{T}\right) = \Delta Hd\left(\frac{1}{T}\right)$$

and integration, assuming the *enthalpy change is constant over the temperature* interval yields

$$\int_{T_1}^{T_2} d\left(\frac{\Delta G}{T}\right) = \Delta H \int_{T_1}^{T_2} d\left(\frac{1}{T}\right)$$

$$\frac{\Delta G_{T_2}}{T_2} - \frac{\Delta G_{T_1}}{T_1} = \Delta H\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{3.9.6.1}$$

Equation ??? is the **Gibbs-Helmholtz equation** and can be used to determine how ΔG changes with changing temperature. The equivalent equation for the Helmholtz function is

$$\frac{\Delta A_{T_2}}{T_2} - \frac{\Delta A_{T_1}}{T_1} = \Delta U\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{3.9.6.2}$$

Example 3.9.6.1:

Given the following data at 298 K, calculate ΔG at 500 K for the following reaction:

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + H_2O(g)$$

Compound	ΔG_f^o (kJ/mol)	ΔH_f^o (kJ.mol)
CH_4(g)	-50.5	-74.6
CO_2(g)	-394.4	-393.5
H_2O(g)	-228.6	-241.8

Solution

ΔH and $\Delta G_{298\ K}$ and can be calculated fairly easily. It will be assumed that ΔH is constant over the temperature range of 298 K – 500 K.

$$\Delta H = (1\,mol)(-393.5\,kJ/mol) + (2\,mol)(-241.8\,kJ/mol) - (1\,mol)(-74.5\,kJ/mol) = -820.6\,kJ$$

$$\Delta G_{298} = (1\,mol)(-394.4\,kJ/mol) + (2\,mol)(-228,6\,kJ/mol) - (1\,mol)(-50.5\,kJ/mol) = -801.1\,kJ$$

So using Equation 3.9.6.1 with the data just calculated gives

$$\frac{\Delta G_{500\ K}}{500\,K} - \frac{-801.1\,kJ}{298\,K} = (-820.6\,kJ)\left(\frac{1}{500\,K} - \frac{1}{298\,K}\right)$$

$$\Delta G_{500\ K} = -787.9\,kJ$$

Note: ΔG became a little bit less negative at the higher temperature, which is to be expected for a reaction which is exothermic. An increase in temperature should tend to make the reaction less favorable to the formation of products, which is exactly what is seen in this case!

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3.9.7: When Two Variables Change at Once

So far, we have derived a number of expressions and developed methods for evaluating how thermodynamic variables change as one variable changes while holding the rest constant. But real systems are seldom this accommodating. For example, a piece of metal (such as a railroad rail) left in the sun will undergo both an increase in temperature and an expansion due to the absorption of energy from sunlight. So both T and V are changing at the same time! If the change in a thermodynamic variable (such as G) is needed, contributions from both changes are required to be taken into account. We've already seen how to express this in terms of a total differential.

$$dG = \left(\frac{\partial G}{\partial p}\right)_T dp + \left(\frac{\partial G}{\partial T}\right)_p dT \tag{3.9.7.1}$$

Fortunately, G (like the other thermodynamic functions U, H, S, and A) is kind enough to be a state variable. This means that we can consider the changes independently and then simply add the results. Another way to think of this is that the system may follow either of two pathways to get from the initial conditions to the final conditions:

- *Pathway I:*
    1. An isothermal expansion from V_1 to V_2 at T_1 followed by
    2. An isochoric temperature increase from T_1 to T_2 at V_2
- *Pathway 2:*
    1. An isochoric temperature increase from T_1 to T_2 at V_1 followed by
    2. And isothermal expansion from V_1 to V_2 at T_2

And since G has the good sense to be a state variable, the pathway connecting the initial and final states is unimportant. We are free to choose any path that is convenient to calculate the change.

Example 3.9.7.1: Non-Isothermal Gas Expansion

Calculate the entropy change for 1.00 mol of a monatomic ideal gas (C_V = 3/2 R) expanding from 10.0 L at 273 K to 22.0 L at 297 K.

Solution

If one considers entropy to be a function of temperature and volume, one can write the total differential of entropy as

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

and thus

$$\Delta S = \int_{T_1}^{T_2} \left(\frac{\partial S}{\partial T}\right)_V dT + \int_{V_1}^{V_2} \left(\frac{\partial S}{\partial V}\right)_T dV$$

The first term is the contribution due to an *isochoric temperature* change:

$$\Delta S_{T_1 \to T_2} = \int_{T_1}^{T_2} \left(\frac{\partial S}{\partial T}\right)_V dT \tag{3.9.7.2}$$

$$= \int_{T_1}^{T_2} \frac{nC_V}{T} dT \tag{3.9.7.3}$$

$$= nC_V \ln\left(\frac{T_2}{T_1}\right) \tag{3.9.7.4}$$

$$= (1.00\,mol)\left(\frac{3}{2} \cdot 8.314 \frac{J}{mol\,K}\right) \ln\left(\frac{297\,K}{273\,K}\right) \tag{3.9.7.5}$$

$$= 13.57\,J/K \tag{3.9.7.6}$$

The second term is the contribution due to an isothermal expansion:

$$\Delta S_{V_1 \to V_2} = \int_{V_1}^{V_2} \left(\frac{\partial S}{\partial V}\right)_T dV \tag{3.9.7.7}$$

From the Maxwell relation on A

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$$

So Equation 3.9.7.7 becomes

$$\Delta S_{V_1 \to V_2} = \int_{V_1}^{V_2} \left(\frac{\partial p}{\partial T}\right)_V dV \tag{3.9.7.8}$$

$$= \int_{V_1}^{V_2} \left(\frac{nR}{V}\right) dV \tag{3.9.7.9}$$

$$= nR \ln\left(\frac{V_2}{V_1}\right) \tag{3.9.7.10}$$

$$= (1.00\, mol)\left(8.314 \frac{J}{mol\, K}\right) \ln\left(\frac{22.0\, L}{10.0\, L}\right) \tag{3.9.7.11}$$

$$= 6.56\, J/K \tag{3.9.7.12}$$

And the total entropy change is

$$\Delta S_{tot} = \Delta S_{V_1 \to V_2} + \Delta S_{V_1 \to V_2} \tag{3.9.7.13}$$

$$= 13.57\, J/K + 6.56\, J/K \tag{3.9.7.14}$$

$$= 20.13\, J/K \tag{3.9.7.15}$$

Deriving an expression for a partial derivative (Type III)

Thermodynamics involves many variables. But for a single component sample of matter, only two state variables are needed to describe the system and fix all of the thermodynamic properties of the system. As such, it is conceivable that two functions can be specified as functions of the same two variables. In general terms: $z(x, y)$ and $w(x, y)$.

So an important question that can be answered is, "What happens to z if w is held constant, but x is changed?" To explore this, consider the total differential of z:

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy \tag{3.9.7.16}$$

but z can also be considered a function of x and $w(x, y)$. This implies that the total differential can also be written as

$$dz = \left(\frac{\partial z}{\partial x}\right)_w dx + \left(\frac{\partial z}{\partial w}\right)_x dy \tag{3.9.7.17}$$

and these two total differentials must be equal to one another!

$$= \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy = \left(\frac{\partial z}{\partial x}\right)_w dx + \left(\frac{\partial z}{\partial w}\right)_x dw$$

If we constrain the system to a change in which w remains constant, the last term will vanish since $dw = 0$.

$$\left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy = \left(\frac{\partial z}{\partial x}\right)_w dx \tag{3.9.7.18}$$

but also, since w is a function x and y, the total differential for w can be written

$$dw = \left(\frac{\partial w}{\partial x}\right)_y dx + \left(\frac{\partial w}{\partial y}\right)_x dy$$

And it too must be zero for a process in which w is held constant.

$$0 = \left(\frac{\partial w}{\partial x}\right)_y dx + \left(\frac{\partial w}{\partial y}\right)_x dy$$

From this expression, it can be seen that

$$dy = -\left(\frac{\partial w}{\partial x}\right)_y \left(\frac{\partial y}{\partial w}\right)_x dx$$

Substituting this into the Equation 3.9.7.18, yields

$$\left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x \left[-\left(\frac{\partial w}{\partial x}\right)_y \left(\frac{\partial y}{\partial w}\right)_x dx\right] = \left(\frac{\partial z}{\partial x}\right)_w dx \tag{3.9.7.19}$$

which simplifies to

$$\left(\frac{\partial z}{\partial x}\right)_y dx - \left(\frac{\partial z}{\partial w}\right)_x \left(\frac{\partial w}{\partial x}\right)_y dx = \left(\frac{\partial z}{\partial x}\right)_w dx$$

So for $dx \neq 0$, implies that

$$\left(\frac{\partial z}{\partial x}\right)_y - \left(\frac{\partial z}{\partial w}\right)_x \left(\frac{\partial w}{\partial x}\right)_y = \left(\frac{\partial z}{\partial x}\right)_w$$

or

$$\left(\frac{\partial z}{\partial x}\right)_y = \left(\frac{\partial z}{\partial x}\right)_w + \left(\frac{\partial z}{\partial w}\right)_x \left(\frac{\partial w}{\partial x}\right)_y \tag{3.9.7.20}$$

As with partial derivative transformation types I and II, this result can be achieved in a formal, albeit less mathematically rigorous method.

Consider $z(x, w)$. This allows us to write the total differential for z:

$$dz = \left(\frac{\partial z}{\partial x}\right)_w dx + \left(\frac{\partial z}{\partial w}\right)_x dw$$

Now, divide by dx and constrain to constant y.

$$\left.\frac{dz}{dx}\right|_y = \left(\frac{\partial z}{\partial x}\right)_w \left.\frac{dx}{dx}\right|_y + \left(\frac{\partial z}{\partial w}\right)_x \left.\frac{dw}{dx}\right|_y$$

noting that $dx/dx = 1$ and converting the other ratios to partial derivatives yields

$$\left(\frac{\partial z}{\partial x}\right)_y = \left(\frac{\partial z}{\partial x}\right)_w + \left(\frac{\partial z}{\partial w}\right)_x \left(\frac{\partial w}{\partial x}\right)_y \tag{3.9.7.21}$$

which agrees with the previous result (Equation 3.9.7.20)! Again, the method is not mathematically rigorous, but it works so long as w, x, y, and z are **state functions** and the total differentials dw, dx, dy, and dz are **exact**.

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3.9.8: The Difference between Cp and Cv

Constant volume and constant pressure heat capacities are very important in the calculation of many changes. The ratio $C_p/C_V = \gamma$ appears in many expressions as well (such as the relationship between pressure and volume along an adiabatic expansion.) It would be useful to derive an expression for the difference C_p–C_V as well. As it turns out, this difference is expressible in terms of measureable physical properties of a substance, such as α, κ_T, p, V, and T.

In order to derive an expression, let's start from the definitions.

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p$$

and

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

The difference is thus

$$C_p - C_v = \left(\frac{\partial H}{\partial T}\right)_p - \left(\frac{\partial U}{\partial T}\right)_V$$

In order to evaluate this difference, consider the definition of enthalpy:

$$H = U + pV$$

Differentiating this yields

$$dH = dU + pdV + Vdp$$

Dividing this expression by dT and constraining to constant p gives

$$\left.\frac{dH}{dT}\right|_p = \left.\frac{dU}{dT}\right|_p + p\left.\frac{dV}{dT}\right|_p + V\left.\frac{dp}{dT}\right|_p$$

The last term is kind enough to vanish (since $dp = 0$ at constant pressure). After converting the remaining terms to partial derivatives:

$$\left(\frac{\partial H}{\partial T}\right)_p = \left(\frac{\partial U}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p \tag{3.9.8.1}$$

This expression is starting to show some of the players. For example,

$$\left(\frac{\partial H}{\partial T}\right)_p = C_p$$

and

$$\left(\frac{\partial V}{\partial T}\right)_p = V\alpha$$

So Equation 3.9.8.1 becomes

$$C_p = \left(\frac{\partial U}{\partial T}\right)_p + pV\alpha \tag{3.9.8.2}$$

In order to evaluate the partial derivative above, first consider $U(V,T)$. Then the total differential du can be expressed

$$du = \left(\frac{\partial U}{\partial V}\right)_T dV - \left(\frac{\partial U}{\partial T}\right)_V dT$$

Dividing by dT and constraining to constant p will generate the partial derivative we wish to evaluate:

$$\left.\frac{dU}{dT}\right|_p = \left(\frac{\partial U}{\partial V}\right)_T \left.\frac{dV}{dT}\right|_p + \left(\frac{\partial U}{\partial T}\right)_V \left.\frac{dT}{dT}\right|_p$$

The last term will become unity, so after converting to partial derivatives, we see that

$$\left(\frac{\partial U}{\partial T}\right)_p = \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p + \left(\frac{\partial U}{\partial T}\right)_V \tag{3.9.8.3}$$

(This, incidentally, is an example of partial derivative transformation type III.) Now we are getting somewhere!

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

and

$$\left(\frac{\partial V}{\partial T}\right)_p = V\alpha$$

So the Equation 3.9.8.3 can be rewritten

$$\left(\frac{\partial U}{\partial T}\right)_p = \left(\frac{\partial U}{\partial V}\right)_T V\alpha + C_V$$

If we can find an expression for

$$\left(\frac{\partial U}{\partial V}\right)_T$$

we are almost home free! Fortunately, that is an easy expression to derive. Begin with the combined expression of the first and second laws:

$$d = TdS - pdV$$

Now, divide both sides by dV and constrain to constant T.

$$\left.\frac{dU}{dV}\right|_T = T\left.\frac{dS}{dV}\right|_T - p\left.\frac{dV}{dV}\right|_T$$

The last term is unity, so after conversion to partial derivatives, we see

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - p \tag{3.9.8.4}$$

A Maxwell relation (specifically the Maxwell relation on A) can be used

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$$

Substituting this into Equation 3.9.8.4 yields

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p$$

and since

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{\alpha}{\kappa_T}$$

then

$$\left(\frac{\partial U}{\partial V}\right)_T = T\frac{\alpha}{\kappa_T} - p$$

Now, substituting this into the expression into Equation 3.9.8.3 to get

$$\begin{aligned}\left(\frac{\partial U}{\partial T}\right)_p &= \left[T\frac{\alpha}{\kappa_T} - p\right] V\alpha + C_V \\ &= \frac{TV\alpha^2}{\kappa_T} - pV\alpha + C_V\end{aligned}$$

This can now be substituted into the Equation 3.9.8.2 yields

$$C_p = \left[\frac{TV\alpha^2}{\kappa_T} - \cancel{pV\alpha} + C_V\right] + \cancel{pV\alpha}$$

The $pV\alpha$ terms will cancel. And subtracting C_V from both sides gives the desired result:

$$C_p - C_V = \frac{TV\alpha^2}{\kappa_T} \tag{3.9.8.5}$$

And this is a completely general result since the only assumptions made were those that allowed us to use the combined first and second laws in the form

$$dU = TdS–pdV.$$

That means that this expression can be applied to any substance whether gas, liquid, animal, vegetable, or mineral. But what is the result for an ideal gas?

Since we know that for an ideal gas

$$\alpha = \frac{1}{T}$$

and

$$\kappa_T = \frac{1}{p}$$

Substitution back into Equation 3.9.8.5 yields

$$\begin{aligned} C_p - C_V &= \frac{TV\left(\frac{1}{T}\right)^2}{\left(\frac{1}{p}\right)} \\ &= \frac{pV}{T} \\ &= R \end{aligned}$$

So for an ideal gas, $C_p–C_V = R$. That is good to know, no?

Example 3.9.8.1

Derive the expression for the difference between C_p and C_V by beginning with the definition of H, differentiating, dividing by dV (to generate the partial derivative definition of C_V). In this approach, you will need to find expressions for

$$\left(\frac{\partial H}{\partial T}\right)_V$$

and

$$\left(\frac{\partial U}{\partial p}\right)_T$$

and also utilize the Maxwell-Relation on G.

Solution

Begin with the definition of enthalpy.

$$H = U + pV$$

Differentiate the expression.

$$dH = dU + pdV + Vdp$$

Now, divide by dV and constrain to constant T (as described in the instructions) to generate the partial derivative definition of C_V

$$\left.\frac{dH}{dT}\right|_V = \left.\frac{dU}{dT}\right|_V + p\left.\frac{dV}{dT}\right|_V + V\left.\frac{dp}{dT}\right|_V$$

$$\left(\frac{dH}{dT}\right)_V = \left(\frac{dU}{dT}\right)_V + V\left(\frac{dp}{dT}\right)_V \tag{3.9.8.6}$$

Now what is needed is an expression for

$$\left(\frac{dH}{dT}\right)_V.$$

This can be derived from the total differential for $H(p,T)$ by dividing by dT and constraining to constant V.

$$dH = \left(\frac{dH}{dp}\right)_T dp + \left(\frac{dH}{dT}\right)_p dT$$

$$\left(\frac{dH}{dT}\right)_V = \left(\frac{dH}{dp}\right)_T \left(\frac{dp}{dT}\right)_V + \left(\frac{dH}{dT}\right)_p \tag{3.9.8.7}$$

This again is an example of partial derivative transformation type III. To continue, we need an expression for

$$\left(\frac{dH}{dp}\right)_T.$$

This can be quickly generated by considering the total differential of $H(p,S)$, its natural variables:

$$dH = TdS + Vdp$$

Dividing by dp and constraining to constant T yields

$$\left.\frac{dH}{dp}\right|_T = T\left.\frac{dS}{dp}\right|_T + V\left.\frac{dp}{dp}\right|_T$$

$$\left(\frac{dH}{dp}\right)_T = T\left(\frac{dS}{dp}\right)_T + V \tag{3.9.8.8}$$

Using the Maxwell Relation on G, we can substitute

$$-\left(\frac{dV}{dT}\right)_p = \left(\frac{dS}{dp}\right)_T$$

So Equation 3.9.8.8 becomes

$$\left(\frac{dH}{dp}\right)_T = -T\left(\frac{dV}{dT}\right)_p + V$$

Now, substitute this back into the expression for (Equation 3.9.8.7):

$$\left(\frac{dH}{dT}\right)_V = \left[-T\left(\frac{dV}{dT}\right)_p + V\right]\left(\frac{dp}{dT}\right)_V + \left(\frac{dH}{dT}\right)_p$$

$$\left(\frac{dH}{dT}\right)_V = -T\left(\frac{dV}{dT}\right)_p\left(\frac{dp}{dT}\right)_V + V\left(\frac{dp}{dT}\right)_V + \left(\frac{dH}{dT}\right)_p$$

This can now substituted for the right-hand side of the initial expression for $\left(\frac{dH}{dT}\right)_V$ back into Equation 3.9.8.6:

$$-T\left(\frac{dV}{dT}\right)_p\left(\frac{dp}{dT}\right)_V + \cancel{V\left(\frac{dp}{dT}\right)_V} + \left(\frac{dH}{dT}\right)_p = \left(\frac{dU}{dT}\right)_V + \cancel{V\left(\frac{dp}{dT}\right)_V} \tag{3.9.8.9}$$

Several terms cancel one another. Equation 3.9.8.9 can then be rearranged to yield

$$\left(\frac{dH}{dT}\right)_p - \left(\frac{dU}{dT}\right)_V = T\left(\frac{dV}{dT}\right)_p\left(\frac{dp}{dT}\right)_V$$

or

$$C_p - C_V = \frac{TV\alpha^2}{\kappa_T}$$

which might look familiar (Equation 3.9.8.5)!

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3.E: The Second Law (Exercises)

Q5.1

What is the minimum amount of work needed to remove 10.0 J of energy from a freezer at -10.0 °C, depositing the energy into a room that is 22.4 °C?

Q5.2

Consider the isothermal, reversible expansion of 1.00 mol of a monatomic ideal gas (C_V = 3/2 R) from 10.0 L to 25.0 L at 298 K. Calculate q, w, ΔU, ΔH, and ΔS for the expansion.

Q5.3

Consider the isobaric, reversible expansion of 1.00 mol of a monatomic ideal gas (C_p = 5/2 R) from 10.0 L to 25.0 L at 1.00 atm. Calculate q, w, ΔU, ΔH, and ΔS for the expansion.

Q5.4

Consider the isochoric, reversible temperature increase of 1.00 mol of a monatomic ideal gas (C_V = 3/2 R) °Ccupying 25.0 L from 298 K to 345 K. Calculate q, w, ΔU, ΔH, and ΔS for this process.

Q5.5

Consider the adiabatic expansion of 1.00 mol of a monatomic ideal gas (C_V = 3/2 R) from 10.0 L at 273 K to a final volume of 45.0 L. Calculate ΔT, q, w, ΔU, ΔH, and ΔS for the expansion.

Q5.6

15.0 g of ice ($\Delta H_{fus} = 6.009\ kJ/mol$) at 0 °C sits in a room that is at 21 °C. The ice melts to form liquid at 0 °C. Calculate the entropy change for the ice, the room, and the universe. Which has the largest magnitude?

Q5.7

15.0 g of liquid water (C_p = 75.38 J mol^{-1} $°C^{-1}$) at 0 °C sits in a room that is at 21 °C. The liquid warms from 0 °C to 21 °C. Calculate the entropy change for the liquid, the room, and the universe. Which has the largest magnitude?

Q5.8

Calculate the entropy change for taking 12.0 g of H_2O from the solid phase (C_p = 36.9 J mol^{-1} K^{-1}) at -12.0 °C to liquid (C_p = 75.2 J mol^{-1} K^{-1}) at 13.0 °C. The enthalpy of fusion for water is $\Delta H_{fus} = 6.009\ kJ/mol$.

Q5.9

Using Table T1, calculate the standard reaction entropies ($\Delta S°$) for the following reactions at 298 K.

a. $CH_3CH_2OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$
b. $C_{12}H_{22}O_{11}(s) + 12O_2 \rightarrow 12CO_2(g) + 11H_2O(l)$
c. $2POCl_3(l) \rightarrow 2PCl_3(l) + O_2(g)$
d. $2KBr(s) + Cl2(g) \rightarrow 2KCl(s) + Br_2(l)$
e. $SiH_4(g) + 2Cl(g) \rightarrow SiCl_4(l) + 2H_2(g)$

Q5.10

1.00 mole of an ideal gas is taken through a cyclic process involving three steps:

I. Isothermal expansion from V_1 to V_2 at T_1
II. Isochoric heating from, T_1 to T_2 at V_2
III. Adiabatic compression from V_2 to V_1

a. Graph the process on a V-T diagram.

b. Find q, w, ΔU, and ΔS for each leg. (If you want, you can find ΔH too!)
c. Use the fact that ΔS for the entire cycle must be zero (entropy being a state function and all …), determine the relationship between V_1 and V_2 in terms of C_v, T_1 and T_2.

Q5.11

2.00 moles of a monatomic ideal gas (C_V = 3/2 R) initially exert a pressure of 1.00 atm at 300.0 K. The gas undergoes the following three steps, all of which are reversible:

I. isothermal compression to a final pressure of 2.00 atm,
II. Isobaric temperature increase to a final temperature of 400.0 K, and
III. A return to the initial state along a pathway in which

$$p = a + bT \tag{3.E.1}$$

where a and b are constants. Sketch the cycle on a pressure-temperature plot, and calculate \(\Delta U\) and \(\Delta S\) for each of the legs. Are ΔU and ΔS zero for the sum of the three legs?

Q5.12

A 10.0 g piece of iron (C = 0.443 J/g °C) initially at 97.6 °C is placed in 50.0 g of water (C = 4.184 J/g °C) initially at 22.3 °C in an insulated container. The system is then allowed to come to thermal equilibrium. Assuming no heat flow to or from the surroundings, calculate

a. the final temperature of the metal and water
b. the change in entropy for the metal
c. the change in entropy for the water
d. the change in entropy for the universe

Q5.13

Considers a crystal of $CHFClBr$ as having four energetically equivalent orientations for each molecule. What is the expected residual entropy at 0 K for 2.50 mol of the substance?

Q5.14

A sample of a certain solid is measured to have a constant pressure heat capacity of 0.436 J mol^{-1} K^{-1} at 10.0 K. Assuming the Debeye extrapolation model

$$C_p(T) = aT^3 \tag{3.E.2}$$

holds at low temperatures, calculate the molar entropy of the substance at 12.0 K.

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1.1: Putting the Second Law to Work (Exercises)

Q6.1

Using Table T1, calculate the standard reaction Gibbs functions (\(\Delta G^o\)) for the following reactions at 298 K.

a. $CH_3CH_2OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$
b. $C_6H_{12}O_6(s) + 6O_2 \rightarrow 6CO_2(g) + 6H_2O(l)$
c. $2POCl_3(l) \rightarrow 2PCl_3(l) + O_2(g)$
d. $2KBr(s) + Cl_2(g) \rightarrow 2KCl(s) + Br_2(l)$
e. $SiH_4(g) + 2Cl(g) \rightarrow SiCl_4(l) + 2H_2(g)$

Q6.2

Estimate \(\Delta G\) at 1000 K from its value at 298 K for the reaction

$$C(s) + 2H_2(g) \rightarrow CH_4(g) \tag{1.1.1}$$

with $\Delta G = -50.75\ kJ\ at\ 298\ K$/

Q6.3

The standard Gibbs function for formation (ΔG_f^o) of $PbO_2(s)$ is -217.4 kJ/mol at 298 K. Assuming O_2 is an ideal gas, find the standard Helmholtz function for formation (ΔA_f^o for PbO_2 at 298K.

Q6.4

Calculate the entropy change for 1.00 mol of an ideal monatomic gas (C_V = 3/2 R) undergoing an expansion and simultaneous temperature increase from 10.0 L at 298 K to 205.0 L at 455 K.

Q6.5

Consider a gas that obeys the equation of state

$$p = \frac{nRT}{V - nb} \tag{1.1.2}$$

a. Find expressions for α and κ_T for this gas.
b. Evaluate the difference between C_p and C_V for the gas.

Q6.6

Show that

$$\left(\frac{\partial C_p}{\partial p}\right)_T = 0 \tag{1.1.3}$$

for an ideal gas.

Q6.7

Derive the thermodynamic equation of state

$$\left(\frac{\partial H}{\partial p}\right)_T = V(1 - T\alpha) \tag{1.1.4}$$

Q6.8

Derive the thermodynamic equation of state

$$\left(\frac{\partial U}{\partial V}\right)_T = T\frac{\alpha}{\kappa_T} - p \tag{1.1.5}$$

Q6.9

The “Joule Coefficient” is defined by

$$\mu_J = \left(\frac{\partial T}{\partial V}\right)_U \tag{1.1.6}$$

Show that

$$\mu_J = \frac{1}{C_V}\left(p - \frac{T\alpha}{\kappa_T}\right) \tag{1.1.7}$$

and evaluate the expression for an ideal gas.

Q6.10

Derive expressions for the pressure derivatives

$$\left(\frac{\partial X}{\partial p}\right)_T \tag{1.1.8}$$

where X is U, H, A, G, and S at constant temperature in terms of measurable properties. (The derivation of $\left(\frac{\partial H}{\partial p}\right)_T$ was done in problem Q6.7).

Evaluate the expressions for

- $\left(\frac{\partial S}{\partial p}\right)_T$
- $\left(\frac{\partial H}{\partial p}\right)_T$
- $\left(\frac{\partial U}{\partial p}\right)_T$

for a van der Waals gas.

Q6.11

Derive expressions for the volume derivatives

$$\left(\frac{\partial X}{\partial V}\right)_T \tag{1.1.9}$$

where X is U, H, A, G, and S at constant temperature in terms of measurable properties. (The derivation of $\left(\frac{\partial U}{\partial V}\right)_T$ was done in problem Q8.8.)

Evaluate the expressions for

- $\left(\frac{\partial X}{\partial V}\right)_T$
- $\left(\frac{\partial X}{\partial V}\right)_T$

for a van der Waals gas.

Q6.12

Evaluate the difference between C_p and C_V for a gas that obeys the equation of state

$$p = \frac{nRT}{V - nb} \tag{1.1.10}$$

Q6.13

The adiabatic compressibility (k_S) is defined by

$$\kappa_S = \frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_S \tag{1.1.11}$$

Show that for an ideal gas,

$$\kappa_S = \frac{1}{p\gamma} \tag{1.1.12}$$

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CHAPTER OVERVIEW

4: Chemical Potential and Equilibrium

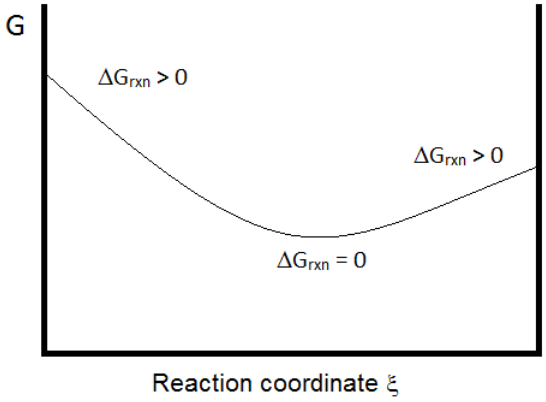
4.1: Prelude to Chemical Equilibria
4.2: Chemical Potential
4.3: Activities and Fugacities
4.4: Pressure Dependence of Kp - Le Châtelier's Principle
4.5: Degree of Dissociation
4.6: Temperature Dependence of Equilibrium Constants - the van ’t Hoff Equation
4.E: Chemical Equilibria (Exercises)

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4.1: Prelude to Chemical Equilibria

> *The small is great, the great is small; all is in equilibrium in necessity... - Victor Hugo in "Les Miserables"*

As was discussed in Chapter 6, the natural tendency of chemical systems is to seek a state of minimum Gibbs function. Once the minimum is achieved, movement in any chemical direction will not be spontaneous. It is at this point that the system achieves a state of equilibrium.



From the diagram above, it should be clear that the direction of spontaneous change is determined by minimizing

$$\left(\frac{\partial G}{\partial \xi}\right)_{p,T}.$$

If the slope of the curve is negative, the reaction will favor a shift toward products. And if it is positive, the reaction will favor a shift toward reactants. This is a non-trivial point, as it underscores the importance of the composition of the reaction mixture in the determination of the direction of the reaction.

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4.2: Chemical Potential

Equilibrium can be understood as accruing at the composition of a reaction mixture at which the aggregate chemical potential of the products is equal to that of the reactants. Consider the simple reaction

$$A(g) \rightleftharpoons B(g)$$

The criterion for equilibrium will be

$$\mu_A = \mu_B$$

If the gases behave ideally, the chemical potentials can be described in terms of the mole fractions of A and B

$$\mu_A^o + RT \ln\left(\frac{p_A}{p_{tot}}\right) = \mu_B^o + RT \ln\left(\frac{p_B}{p_{tot}}\right) \tag{4.2.1}$$

where Dalton's Law has been used to express the mole fractions.

$$\chi_i = \frac{p_i}{p_{tot}}$$

Equation 4.2.1 can be simplified by collecting all chemical potentials terms on the left

$$\mu_A^o - \mu_B^o = RT \ln\left(\frac{p_B}{p_{tot}}\right) - RT \ln\left(\frac{p_A}{p_{tot}}\right) \tag{4.2.2}$$

Combining the logarithms terms and recognizing that

$$\mu_A^o - \mu_B^o \text{–} \Delta G^o$$

for the reaction, one obtains

$$-\Delta G^o = RT \ln\left(\frac{p_B}{p_A}\right)$$

And since $p_A/p_B = K_p$ for this reaction (assuming perfectly ideal behavior), one can write

$$\Delta G^o = RT \ln K_p$$

Another way to achieve this result is to consider the Gibbs function change for a reaction mixture in terms of the **reaction quotient**. The reaction quotient can be expressed as

$$Q_p = \frac{\prod_i p_i^{\nu_i}}{\prod_j p_j^{\nu_j}}$$

where ν_i are the stoichiometric coefficients for the products, and ν_j are those for the reactants. Or if the stoichiometric coefficients are defined by expressing the reaction as a sum

$$0 = \sum_i \nu_i X_i$$

where X_i refers to one of the species in the reaction, and ν_i is then the stoichiometric coefficient for that species, it is clear that ν_i will be negative for a reactant (since its concentration or partial pressure will reduce as the reaction moves forward) and positive for a product (since the concentration or partial pressure will be increasing.) If the stoichiometric coefficients are expressed in this way, the expression for the reaction quotient becomes

$$Q_p = \prod_i p_i^{\nu_i}$$

Using this expression, the Gibbs function change for the system can be calculated from

$$\Delta G = \Delta G^o + RT \ln Q_p$$

And since at equilibrium

$$\Delta G = 0$$

and

$$Q_p = K_p$$

It is evident that

$$\Delta G^o_{rxn} = -RT \ln K_p \tag{4.2.3}$$

It is in this simple way that K_p and ΔG^o are related.

It is also of value to note that the criterion for a spontaneous chemical process is that $\Delta G_{rxn} < 0$, rather than ΔG^o_{rxn}, as is stated in many texts! Recall that ΔG^o_{rxn} is a function of all of the reactants and products being in their standard states of unit fugacity or activity. However, the direction of spontaneous change for a chemical reaction is dependent on the composition of the reaction mixture. Similarly, the magnitude of the equilibrium constant is insufficient to determine whether a reaction will spontaneously form reactants or products, as the direction the reaction will shift is also a function of not just the equilibrium constant, but also the composition of the reaction mixture!

Example 4.2.1:

Based on the data below at 298 K, calculate the value of the equilibrium constant (K_p) for the reaction

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$$

	$NO(g)$	$NO_2(g)$
G^o_f (kJ/mol)	86.55	51.53

Solution

First calculate the value of ΔG^o_{rxn} from the ΔG^o_f data.

$$\Delta G^o_{rxn} = 2 \times (51.53\, kJ/mol) - 2 \times (86.55\, kJ/mol) = -70.04\, kJ/mol$$

And now use the value to calculate K_p using Equation 4.2.3.

$$-70040\, J/mol = -(8.314 J/(mol\, K)(298\, K) \ln K_p$$

$$K_p = 1.89 \times 10^{12}$$

Note: as expected for a reaction with a very large negative ΔG^o_{rxn}, the equilibrium constant is **very** large, favoring the formation of the products.

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4.3: Activities and Fugacities

To this point, we have mostly ignored deviations from ideal behavior. But it should be noted that thermodynamic equilibrium constants are not expressed in terms of concentrations or pressures, but rather in terms of activities and fugacities (both being discussed in Chapter 7). Based on these quantities,

$$K_p = \prod_i f_i^{\nu_i} \tag{4.3.1}$$

and

$$K_c = \prod_i a_i^{\nu_i}$$

And since activities and fugacities are unitless, thermodynamic equilibrium constants are unitless as well. Further, it can be noted that the activities of solids and pure liquids are unity (assuming ideal behavior) since they are in their standard states at the given temperature. As such, these species never change the magnitude of the equilibrium constant and are generally omitted from the equilibrium constant expression.

> *Thermodynamic equilibrium constants are unitless.*

K_p and K_c

Oftentimes it is desirable to express the equilibrium constant in terms of concentrations (or activities for systems that deviate from ideal behavior.) To make this conversion, the relationship between pressure and concentration from the ideal gas law can be used.

$$p = RT\left(\frac{n}{V}\right)$$

And noting that the concentration is given by (n/V), the expression for the equilibrium constant (Equation 4.3.1) becomes

$$K_p = \prod_i (RT[X_i])^{\nu_i} \tag{4.3.2}$$

And since for a given temperature, RT is a constant and can be factored out of the expression, leaving

$$K_p = \left(\prod_i (RT)^{\nu_i}\right)\left(\prod_i [X_i]^{\nu_i}\right) \tag{4.3.3}$$

$$= (RT)^{\sum \nu_i} \prod [X_i]^{\nu_i} \tag{4.3.4}$$

$$= (RT)^{\sum \nu_i} K_c \tag{4.3.5}$$

This conversion works for reactions in which all reactants and products are in the gas phase. Care must be used when applying this relationship to heterogeneous equilibria.

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4.4: Pressure Dependence of Kp - Le Châtelier's Principle

Since the equilibrium constant K_p is a function of ΔG^o_{rxn} which is defined for a specific composition (all reactants in their standard states and at unit pressure (or fugacity), changes in pressure have no effect on equilibrium constants for a fixed temperature. However, changes in pressure can have profound effects on the compositions of equilibrium mixtures.

To demonstrate the relationship, one must recall Dalton's law of partial pressures. According to this relationship, the partial pressure of a component of a gas-phase mixture can be expressed

$$p_i = \chi_i p_{tot}$$

It is the combination of mole fractions that describes the composition of the equilibrium mixture.

Substituting the above expression into the expression for K_p yields

$$K_p = \prod_i (\chi_i p_{tot})^{\nu_i}$$

This expression can be factored into two pieces – one containing the mole fractions and thus describing the composition, and one containing the total pressure.

$$K_p = \left(\prod_i \chi_i^{\nu_i}\right)\left(\prod_i p_{tot}^{\nu_i}\right)$$

The second factor is a constant for a given total pressure. If the first term is given the symbol K_x, the expression becomes

$$K_p = K_x (p_{tot})^{\sum_i \nu_i}$$

In this expression, K_x has the same form as an equilibrium constant

$$K_x = \prod \chi_i^{\sum_i \nu_i}$$

but is not itself a constant. The value ofK_x will vary with varying composition, and will *need* to vary with varying total pressure (in most cases) in order to maintain a constant value of K_p.

Example 4.4.1:

Consider the following reaction at equilibrium.

$$A(g) + 2B(g) \rightleftharpoons C(g) + D(g)$$

In which direction will the equilibrium shift if the volume of the reaction vessel is decreased?

Solution

A decrease in the volume will lead to an increase in total pressure. Since the equilibrium constant can be expressed as

$$K_p = \frac{p_C p_D}{p_A p_B^2} = \frac{\chi_p \chi_D}{\chi_A \chi_B^2}(p_{tot})^{-1}$$

An increase in pressure will lead to an increase in K_x to maintain a constant value of K_p. So the reaction will shift to form more of the products C and D.

Note: This should make some sense, since a shift to the side of the reaction with fewer moles of gas will lower the total pressure of the reaction mixture, and thus relieving the stress introduced by increasing the pressure. This is exactly what is expected according to Le Chatelier's principle.

It should be noted that there are several ways one can affect the total pressure of a gas-phase equilibrium. These include the introduction or removal of reactants or products (perhaps through condensation or some other physical process), a change in volume of the reaction vessel, or the introduction of an inert gas that does not participate in the reaction itself. (Changes in the

temperature will be discussed in a later section.) The principle of Le Chatelier's can be used as a guide to predict how the equilibrium composition will respond to a change in pressure.

> *Le Chatelier's principle: When a stress is introduced to a system at equilibrium, the system will adjust so as to reduce the stress.*

Le Chatlier's principle is fairly clear on how to think about the addition or removal of reactants or products. For example, the addition of a reactant will cause the system to shift to reduce the partial pressure of the reactant. It can do this by forming more products.

An important exception to the rule that increasing the total pressure will cause a shift in the reaction favoring the side with fewer moles of gas occurs when the total pressure is increased by introducing an inert gas to the mixture. The reason is that the introduction of an inert gas will affect the total pressures *and* the partial pressures of each individual species.

Example 4.4.2:

A 1.0 L vessel is charged with 1.00 atm of A, and the following reaction is allowed to come to equilibrium at 298 K.

$$A(g) \rightleftharpoons 2B(g)$$

with $K_p = 3.10$.

a. What are the equilibrium partial pressures and mole fractions of A and B?
b. If the volume of the container is doubled, what are the equilibrium partial pressures and mole fractions of A and B?
c. If 1.000 atm of Ar (an inert gas) is introduced into the system described in b), what are the equilibrium partial pressures and mole fractions of A and B once equilibrium is reestablished?

Solution

Part a:

First, we can use an ICE[1] table to solve part a).

	A	2 B
Initial	1.00 atm	0
Change	-x	+2x
Equilibrium	1.00 atm - x	2x

So (for convenience, consider K_p to have units of atm)

$$3.10\,atm = \frac{(2x)^2}{1.00\,atm - x}$$

Solving for x yields values of

$$x_1 = -1.349\,atm$$

$$x_1 = 0.574\,atm$$

Clearly, x_1, while a solution to the mathematical problem, is not physically meaningful since the equilibrium pressure of B cannot be negative. So the equilibrium partial pressures are given by

$$p_A = 1.00\,atm - 0.574\,atm = 0.426\,atm$$

$$p_B = 2(0.574\,atm) = 1.148\,atm$$

So the mole fractions are given by

$$chi_A = \frac{0.426\,atm}{0.426\,atm + 1.148\,atm} = 0.271$$

$$\chi_B = 1 - \chi_A = 1 - 0.271 = 0.729$$

Part b:

The volume is doubled. Again, an ICE table is useful. The initial pressures will be half of the equilibrium pressures found in part a).

	A	2 B
Initial	0.213 atm	0.574 atm
Change	-x	+2x
Equilibrium	0.213 atm - x	0.574 atm + 2x

So the new equilibrium pressures can be found from

$$3.10\,atm = \frac{(0.574\,atm + 2x)^2}{0.213\,atm - x}$$

And the values of x that solve the problem are

$$x_1 = -1.4077\,atm$$

$$x_1 = 0.05875\,atm$$

We reject the negative root (since it would cause both of the partial pressures to become negative. So the new equilibrium partial pressures are

$$p_A = 0.154\,atm$$

$$p_B = 0.0692\,atm$$

And the mole fractions are

$$\chi_A = 0.182$$

$$\chi_B = 0.818$$

We can see that the mole fraction of A decreased and the mole fraction B increased. This is the result expected by Le Chatlier's principle since the lower total pressure favors the side of the reaction with more moles of gas.

Part c:

We introduce 1.000 atm of an inert gas. The new partial pressures are

$$p_A = 0.154\,atm$$

$$p_B = 0.692\,atm$$

$$p_{Ar} = 1.000\,atm$$

And because the partial pressures of A and B are unaffected, the equilibrium does not shift! What *is* affected is the composition, and so the mole fractions will change.

$$\chi_A = \frac{0.154\,atm}{0.154atm + 0.692\,atm + 1.000\,atm} = 0.08341$$

$$\chi_B = \frac{0.692\,atm}{0.154atm + 0.692\,atm + 1.000\,atm} = 0.08341$$

$$\chi_{Ar} = \frac{1.000\,atm}{0.154atm + 0.692\,atm + 1.000\,atm} = 0.08341$$

And since

$$K_p = K_x(p_{tot})$$

$$\frac{(0.3749)^2}{0.08342}(1.846\,atm) = 3.1$$

Within round-off error, the value obtained is the equilibrium constant. So the conclusion is that the introduction of an inert gas, even though it increases the total pressure, does not induce a change in the partial pressures of the reactants and products, so it does not cause the equilibrium to shift.

---

[1] ICE is an acronym for “Initial, Change, Equilibrium”. An ICE table is a tool that is used to solve equilibrium problems in terms of an unknown number of moles (or something proportional to moles, such as pressure or concentration) will shift for a system to establish equilibrium. See (Tro, 2014) or a similar General Chemistry text for more background and information.

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4.5: Degree of Dissociation

Reactions such as the one in the previous example involve the dissociation of a molecule. Such reactions can be easily described in terms of the fraction of reactant molecules that actually dissociate to achieve equilibrium in a sample. This fraction is called the **degree of dissociation**. For the reaction in the previous example

$$A(g) \rightleftharpoons 2B(g)$$

the degree of dissociation can be used to fill out an ICE table. If the reaction is started with n moles of A, and a is the fraction of A molecules that dissociate, the ICE table will look as follows.

	A	$2B$
Initial	n	0
Change	$-\alpha n$	$+2n\alpha$
Equilibrium	$n(1-\alpha)$	$2n\alpha$

The mole fractions of A and B can then be expressed by

$$\chi_A = \frac{n(1-\alpha)}{n(1-\alpha)+2n\alpha}$$
$$= \frac{1-\alpha}{1+\alpha}$$
$$\chi_B = \frac{2\alpha}{1+\alpha}$$

Based on these mole fractions

$$K_x = \frac{\left(\frac{2\alpha}{1+\alpha}\right)^2}{\frac{1-\alpha}{1+\alpha}} \tag{4.5.1}$$
$$= \frac{4\alpha^2}{1-\alpha^2} \tag{4.5.2}$$

And so K_p, which can be expressed as

$$K_p = K_x(p_{tot})^{\Sigma \nu_i} \tag{4.5.3}$$

is given by

$$K_p = \frac{4\alpha^2}{(1-\alpha^2)}(p_{tot})$$

Example 4.5.1

Based on the values given below, find the equilibrium constant at 25 °C and degree of dissociation for a system that is at a total pressure of 1.00 atm for the reaction

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

	$N_2O_4(g)$	$NO_2(g)$
ΔG_f^o (kJ/mol)	99.8	51.3

Solution

First, the value of K_p can be determined from ΔG_{rxn}^o via an application of Hess' Law.

$$\Delta G^o_{rxn} = 2\,(51.3\,kJ/mol) - 99.8\,kJ/mol \qquad = 2.8\,kJ/mol$$

So, using the relationship between thermodynamics and equilibria

$$\Delta G^o_f = -RT \ln K_p$$
$$2800\,kJ/mol = -(8.314 J/(mol\,K)(298\,K) \ln K_p$$
$$K_p = 0.323\,atm$$

The degree of dissociation can then be calculated from the ICE tables at the top of the page for the dissociation of $N_2O_4(g)$:

$$K_p = \frac{4\alpha^2}{1-\alpha^2}(p_{tot})$$
$$0.323\,atm = \frac{4\alpha^2}{1-\alpha^2}(1.00\,atm)$$

Solving for α,

$$\alpha = 0.273$$

Note: since a represents the fraction of N_2O_4 molecules dissociated, it **must** be a positive number between 0 and 1.

Example 4.5.2

Consider the gas-phase reaction

$$A + 2B \rightleftharpoons 2C$$

A reaction vessel is initially filled with 1.00 mol of A and 2.00 mol of B. At equilibrium, the vessel contains 0.60 mol C and a total pressure of 0.890 atm at 1350 K.

1. How many mol of A and B are present at equilibrium?
2. What is the mole fraction of A, B, and C at equilibrium?
3. Find values for K_x, K_p, and ΔG^o_{rxn}.

Solution

Let's build an ICE table!

	A	2 B	2 C
Initial	1.00 mol	2.00 mol	0
Change	-x	-2x	+2x
Equilibrium	1.00 mol - x	2.00 mol – 2x	2x = 0.60 mol

From the equilibrium measurement of the number of moles of C, x = 0.30 mol. So at equilibrium,

	A	2 B	2 C
Equilibrium	0.70 mol	1.40 mol	0.60 mol

The total number of moles at equilibrium is 2.70 mol. From these data, the mole fractions can be determined.

$$\chi_A = \frac{0.70\,mol}{2.70\,mol} = 0.259$$
$$\chi_B = \frac{1.40\,mol}{2.70\,mol} = 0.519$$
$$\chi_C = \frac{0.60\,mol}{2.70\,mol} = 0.222$$

So K_x is given by

$$K_x = \frac{(0.222)^2}{(0.259)(0.519)^2} = 0.7064$$

And K_p is given by Equation 4.5.3, so

$$K_p = 0.7604(0.890\,atm)^{-1} = 0.792\,atm^{-1}$$

The thermodynamic equilibrium constant is unitless, of course, since the pressures are all divided by 1 atm. So the actual value of K_p is 0.794. This value can be used to calculate ΔG^o_{rxn} using

$$\Delta G^o_{rxn} = -RT \ln K_p$$

so

$$\begin{aligned} \Delta G^o_{rxn} &= -(8.314\,J/(mol\,K))(1350\,K)\ln(0.792) \\ &= 2590\,J/mol \end{aligned}$$

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4.6: Temperature Dependence of Equilibrium Constants - the van 't Hoff Equation

The value of K_p is independent of pressure, although the composition of a system at equilibrium may be very much dependent on pressure. Temperature dependence is another matter. Because the value of ΔG^o_{rxn} is dependent on temperature, the value of K_p is as well. The form of the temperature dependence can be taken from the definition of the Gibbs function. At constant temperature and pressure

$$\frac{\Delta G^o_{T_2}}{T_2} - \frac{\Delta G^o_{T_1}}{T_1} = \Delta H^o \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Substituting

$$\Delta G^o = -RT \ln K$$

For the two values of ΔG^o and using the appropriate temperatures, yields

$$\frac{-RT_2 \ln K_2}{T_2} - \frac{-RT_1 \ln K_1}{T_1} = \Delta H^o \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

And simplifying the expression so that only terms involving K are on the left and all other terms are on the right results in the **van 't Hoff equation**, which describes the temperature dependence of the equilibrium constant.

$$\ln\left(\frac{K_2}{K_1}\right) = -\frac{\Delta H^o}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{4.6.1}$$

Because of the assumptions made in the derivation of the Gibbs-Helmholtz equation, this relationship only holds if ΔH^o is independent of temperature over the range being considered. This expression also suggests that a plot of $\ln(K)$ as a function of $1/T$ should produce a straight line with a slope equal to $-\Delta H^o/R$. Such a plot is known as a **van 't Hoff plot**, and can be used to determine the reaction enthalpy.

Example 4.6.1

A certain reaction has a value of $K_p = 0.0260$ at 25 °C and $\Delta H^o_{rxn} = 32.4\,kJ/mol$. Calculate the value of K_p at 37 °C.

Solution

This is a job for the van 't Hoff equation!

- T_1 = 298 K
- T_2 = 310 K
- $\Delta H^o_{rxn} = 32.4\,kJ/mol$
- K_1 = 0.0260
- K_2 = ?

So Equation 4.6.1 becomes

$$\ln\left(\frac{K_2}{0.0260}\right) = -\frac{32400\,J/mol}{8.314\,K/(mol\,K)}\left(\frac{1}{310\,K} - \frac{1}{298\,K}\right)$$

$$K_2 = 0.0431$$

Note: the value of K_2 **increased** with **increasing** temperature, which is what is expected for an **endothermic** reaction. An increase in temperature should result in an increase of product formation in the equilibrium mixture. But unlike a change in pressure, a change in temperature actually leads to a change in the value of the equilibrium constant!

Example 4.6.2

Given the following average bond enthalpies for P–Cl and Cl–Cl bonds, predict whether or not an increase in temperature will lead to a larger or smaller degree of dissociation for the reaction

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

X-Y	D(X-Y) (kJ/mol)
P-Cl	326
Cl-Cl	240

Solution

The estimated reaction enthalpy is given by the total energy expended breaking bonds minus the energy recovered by the formation of bonds. Since this reaction involves breaking two P-Cl bonds (costing 652 kJ/mol) and the formation of one Cl-Cl bond (recovering 240 kJ/mol), it is clear that the reaction is endothermic (by approximately 412 kJ/mol). As such, an increase in temperature should increase the value of the equilibrium constant, causing the degree of dissociation to be increased at the higher temperature.

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4.E: Chemical Equilibria (Exercises)

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CHAPTER OVERVIEW

5: Phase Equilibria

5.1: A Phase Diagram Summarizes the Solid-Liquid-Gas Behavior of a Substance

5.2: Gibbs Energies and Phase Diagrams

5.3: The Chemical Potentials of a Pure Substance in Two Phases in Equilibrium

5.4: The Clausius-Clapeyron Equation

5.E: Phase Equilibria (Exercises)

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5.1: A Phase Diagram Summarizes the Solid-Liquid-Gas Behavior of a Substance

A good map will take you to your destination with ease, provided you know how to read it. A map is an example of a *diagram*, a pictorial representation of a body of knowledge. In science they play a considerable role. Next to plots and tables *diagrams* are an important means of making information and/or theoretical knowledge accessible.

Constructing them takes quite a bit of thought. You want to represent as much of what you know and give as accurate a picture of it without conveying anything incorrect. If the drawing can be made to scale that makes it quite a bit more powerful, but this is not strictly necessary. A remark like *not to scale* or *schematically* does need to be given if applicable. A good caption or description is essential.

5.1.1: Thermodynamic Stability and Fluctuations

There are different kinds of equilibrium, besides the ***stable*** equilibrium that represents an absolute minimum in the G function. Of course G is potentially a function of a great number of variables, but let us look at a *diagram* in which G is shown as a function of only one unspecified variable. You could think of the density, the mole fraction of one of the components of a mixture or an applied electrical field or whatever, but the argument is general.

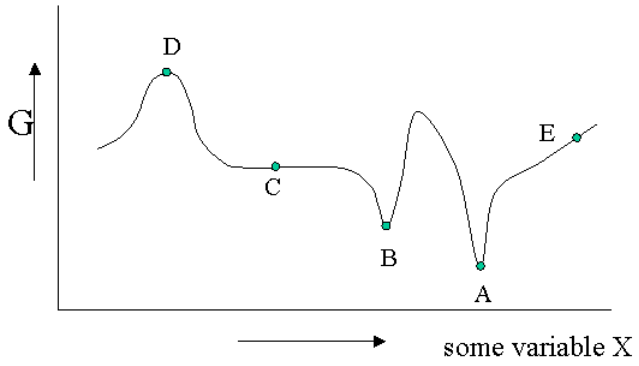


Figure 23.1.1 : A schematic G curve showing various Points of stability. Due to statistical fluctuations the value of G is not quite constant over time, because less likely realizations of the ensemble (having a slightly less favorable value of G) do occur from time to time. After all, the Boltzmann distribution is simply the most likely one, not the only one possible. The fluctuations have drastically different consequences depending on whether the system is in an unstable (E), labile (D) , indifferent (C), metastable (B) or stable (A) state. Notice that A and B just wobble around a bit. C fluctuates wildly in the value of X, while both E and D eventually vanish because the system transits to a more favorable state. For E this starts immediately, for D it starts once fluctuation has caused it to move from its peak sufficiently.

Figure 23.1.1 is helpful to point out that besides a stable equilibrium (A) there can also be an ***metastable*** equilibrium (B) or an ***indifferent*** equilibrium (C). The local derivatives of G (versus *all* variables of which we only show one) are zero in all three cases, which means that changes in the variables are *not spontaneous*. For a ***labile*** equilibrium (D) the opposite is true. Any small deviation will make the system role down hill. (Note that the second derivative has the opposite sign compared to cas A) and B)) A labile equilibrium is seldom or never observed except in a circus where artists delight in balancing objects on their heads (because you pay for it).. This usually requires continuous small corrections to maintain the precarious balance. All other points in our diagram represent state of ***instability*** because locally dG is not zero and a spontaneous process can take place.

The fact that $dG = 0$ in the equilibrium points does not mean small deviations from the minimum cannot happen at times. We have seen e.g. that the Boltzmann distribution was simply *the most likely* distribution. The most likely one is the one that has the highest number of realizations W. Another way of saying that is that it is the one with the highest entropy S. A slightly less likely distribution may occur from time to time by chance. It will have a little less entropy, but the same $\langle E \rangle$. That means it will have a slightly higher G ($G = H - TS$). From time to time therefore G will fluctuate a bit. Such fluctuations are very small for large systems, but they are of greater relative importance for small systems (like a nanoparticle). (Statistical averaging works best on large ensembles.)

The fluctuations in G mean that small fluctuations in its variables like density etc. can also occur. They are usually kept in check, because dG is no longer zero when moving away from the equilibrium state. This drives the system back to the minimum

spontaneously. You could picture the system wobbling a bit around in its G-well. This holds for stable and metastable equilibria alike.

In the indifferent case (*C*) however the derivative is zero (or very close to zero) for a *range* of neighboring values of some variable. In contrast to *A* and *B* also the *second derivative* is zero. This means that there is little penalty to much larger deviations in the variable. If this variable is the density the system becomes milky and shows *opalescence* a strong scattering of light because the refractive index depends on the strongly fluctuating density. This is observed near critical points and is called *critical opalescence*.

5.1.2: Unary Phase Diagrams

A unary phase diagram summarizes the equilibrium states of a single pure substance. We will see that we can also look at mixtures of two components (binary diagrams) or more (ternary, quaternary, quinary, senary etc.). Usually a phase diagram only maps out stable equilibria, but occasionally metastable ones may be given too (e.g., with a dashed line).

5.1.2.0.1: Liquid-Vapor Equilibrium Curve

We have seen that the Gibbs function *G* depends strongly (logarithmically) on pressure for a gas, but only slightly (and linearly) for a liquid. The two curves intersect in a point representing the *equilibrium vapor pressure* of the liquid. At lower pressures the vapor is more stable, at higher ones the liquid. (For a solid the same holds as for the liquid). This means that except at the intersection point we only will observe one phase.

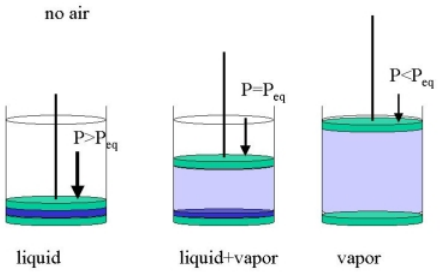


Figure 23.1.2 *: A cylinder with one substance*

It is important to stress that this holds *in the absence of other matter*, e.g., when we put only water into an evacuated cylinder (Figure 23.1.2). We may get three cases:

- we compress the cylinder until it only contains the liquid under hydrostatic pressure ($P > P_{eq}$)
- we expand the cylinder until all water has vaporized ($P < p_{eq}$)>
- we let part of the water evaporate, just enough so that the space above the liquid is filled with an equilibrium vapor pressure ($P = P_{eq}$)

At room temperature P_{eq} for water is only about 15 Torr. If we apply 1 bar -or let the atmosphere do the job- we will only have liquid water. If other gases are present, e.g., air, we must distinguish between the total pressure (e.g., 1 bar) and the equilibrium vapor pressure which will now be the *partial* pressure. In a cylinder with water and one bar of air just enough water will evaporate to establish equilibrium. The evaporation will be limited to the gas-liquid interface unless the partial pressure equals the total pressure. Then the liquid will *boil*.

> *(Do allow the volume to expand, though., why? If the volume is constant the pressure builds up and boiling will stop.*

If we consider the set of equilibrium pressures as a function of temperature and plot that in a P vs. T diagram we have one component of our phase diagram.

5.1.2.0.1: Gas-solid Equilibrium Curve

For solids the situation is similar as the $G(P)$ curve is once again an almost flat straight line. The intersection with the logarithmic curve for the gas will define an equilibrium pressure for gas-solid co-existence. Generally vapor pressures above solids are quite

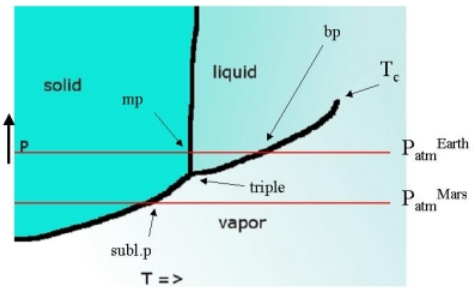
small, but not negligible. As for liquids we can construct a line representing the equilibrium pressures for sublimation as function of temperature and add it to the phase diagram.

5.1.2.0.1: Liquid-solid Equilibrium Curve

The $\mathbf{solid} \rightleftharpoons \mathbf{liquid}$ equilibrium is known as **melting** or **freezing** is not very dependent on pressure. Usually melting points increase a little bit with pressure, although water is a peculiar exception. It expands upon freezing and the melting point goes down (a bit) with pressure. In our diagram this will represent an almost vertical line leaning a little forwards for most substances, but backwards for water and a few others.

5.1.2.1: Putting the Curve Together

The three lines come together in the *triple point*, the only point where all three phases are at equilibrium with each other. For water, its temperature is only 0.01 K different from the normal melting point (273.16 K) and its pressure is only 4.58 Torr. The intersection points with a line representing atmospheric pressure give the melting and boiling points at that pressure.



A typical unary diagram

If the triple point lies above the line that represents atmospheric pressure this implies that a liquid is never observed. On earth CO_2 is such a substance. The intersection of the solid-vapor equilibrium line with the 1 bar line represents a state where the solid will *'boil'* (evaporate from inside out). This is known as the *sublimation point*. The melting points at P=1 bar are known as the *standard melting point*, the only slightly different one at 760 Torr = 1 atm is called *normal melting point*. The same goes for boiling and sublimation points.

There is *nothing magical* about $P = 1\ bar$. It just happens to be the pressure of our home planet. On a planet with higher atmospheric pressures CO_2 may well be a liquid and on such a planet, all boiling points will be quite different (higher than on earth). The melting points will also differ, but only slightly so. On Mars where atmospheric pressure is much lower water can not occur in liquid form, much like carbon dioxide on earth - it sublimes.

We should also realize that in a *closed container* (glass ampoule, hermetically sealed DSC pan), we can observe melting points at only very slightly different temperature values, but we will ***not*** see a boiling effect. Why?

To see a boiling point the container must be open to the (*constant!*) 1 bar pressure of the earths atmosphere that ***defines*** it and causes the boiling phenomenon. If the ampoule is sealed it will generate its *own* (autogenous) pressure, depending on what you put in, how much of it in relation to the volume, how volatile it is and the temperature. The autogenous pressure does not interfere with the melting point much (the melting line is almost vertical), but as P changes with temperature you may never reach boiling conditions.

In DSC experiments it is possible to observe boiling points only if the pan has been carefully *perforated* with a hole of known size. It must be big enough that the pressure inside the pan does not build up above atmospheric, but small enough that it does not cause premature loss of mass during the run. The latter spoils the calculation of the intensive value (per mole, per gram) of the heat of vaporization.

The liquid evaporation line ends in a point that we have encountered before: the critical point T_C. As temperature increases the liquid and vapor phases in equilibrium with each other start to resemble each other more and more and at T_c they coalesce. At

this point the liquid-gas equilibrium becomes indifferent with respect to density and large fluctuations occur leading to critical opalescence.

Notice that there is a relationship of dimensionality between the objects in the diagram and the number of phases present:

- 2 D planes: one phase
- 1 D curves: two phases
- 0 D point: three phases

As you see the sum is always three.

5.1.3: Number of moles

So far we have typically considered one substance at the time, but for chemists it is imperative to deal with more than one because we are typically changing one into the other in our reactions. This means that the number of moles n, that we often simply set equal to one now becomes an important variable in its own right. Besides we will actually have two (or more) of them: the number of moles of component one and the one for the other component. This makes n a much less trivial variable.

This is already the case at a simple melting point, say when ice melts, because we are dealing with changing quantities of ice and water:

$$n_{ice} + n_{water} = n_{total}$$

If all we do is turn water into ice or vice versa, we have $dn_{total} = 0$, so that:

$$dn_{ice} = -dn_{water}$$

To deal with changing n's, we need to expand our mathematical notation a bit.

5.1.3.1: Partial variables

So far we have simply divided our thermodynamic functions if they were extensive by the number of moles and arrived at intensive molar values:

$$G_{molar} = \frac{G}{n}$$

$$V_{molar} = \frac{V}{n}$$

We have written such intensive molar values by writing a bar over the symbol G or V. We should note that scaling the function this way departs from the assumption that the function G depends on the variable n as a straight line that passes through the origin.

If we have the same pure compound in two phases, like ice and water we can still apply this principle and write:

$$G^{ice}_{molar} = \frac{G^{ice}}{n^{ice}}$$

$$V^{ice}_{molar} = \frac{V^{ice}}{n^{ice}}$$

$$G^{water}_{molar} = \frac{G^{water}}{n^{water}}$$

$$V^{water}_{molar} = \frac{V^{water}}{n^{water}}$$

If we have a ***mixture*** of two substances present as n_1 and n_2 moles the dependency need not be linear on either if the two substances interact with each other. This is also true for function like the volume of a liquid mixture. In the presence of interactions volumes do *not* have to be linearly additive. We can define a partial molar value of e.g. for the volume:

$$V_{partialmolar,1} = \frac{\partial V}{\partial n_1}$$

at n_2 = constant

$$V_{partialmolar,2} = \frac{\partial V}{\partial n_2}$$

at n_1 = constant

The notation of putting a bar over the V symbol is used for these partial quantities as well. Partial molar volumes have been measured for many binary systems. They are functions of the composition (mole fraction) as well as the temperature and to a lesser extent the pressure.

The partial molar Gibbs free energy

The partial molar Gibbs free energy ($\left(\frac{\partial G}{\partial n_i}\right)_{P,T}$, all other n's) is denoted with μ and is called the thermodynamic potential.

When numbers of moles can change we can write the corresponding change in G as:

$$dG = -SdT + VdP + \sum_i^N \left(\frac{\partial G}{\partial n_1}\right)_{P,T,n_{j \neq i}} dn_i$$

$$dG = -SdT + VdP + \sum_i^N \mu_i dn_i$$

over N phases in the system. As you can see we are adding a set of conjugate variables $\mu_i n_i$ for each phase i. If we are considering a *pure* component (but in different modifications, like ice and steam), we can still write:

$$\mu_i = \left(\frac{\partial G}{\partial n_1}\right)_{P,T,n_{j \neq i}} = \frac{G_i}{n_i}$$

As soon as we are dealing with mixtures we really do have derivatives.

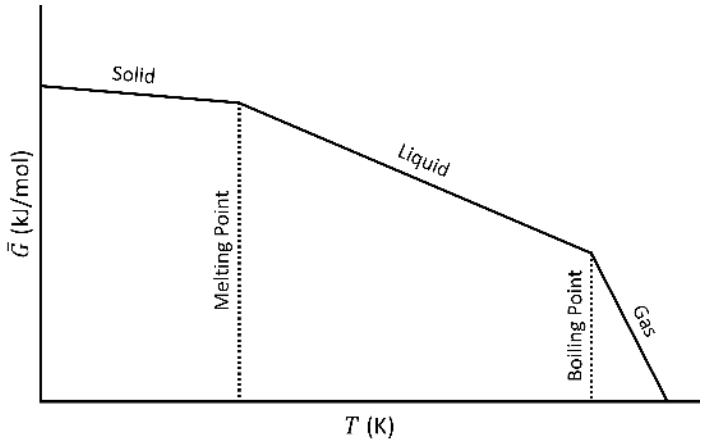
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5.2: Gibbs Energies and Phase Diagrams

5.2.1: First Order Transitions

The following plot shows the Gibbs energy as a function of temperature, including phase changes from solid to liquid (melting) and liquid to gas (boiling).



Gibbs energy ($\bar{G}$) as a function of temperature (T).

Although the G curve is continuous, its first order derivatives ($-S$) is discontinuous at the phase changes. This is why this transition it called a *first order transition*. We could say that:

- G is continuous but has a kink
- The first order derivatives (H,S,..) are discontinuous (have a jump)
- The second order derivatives (C_P, ..) have a singularity (go to ∞)

5.2.2: Second Order Transitions

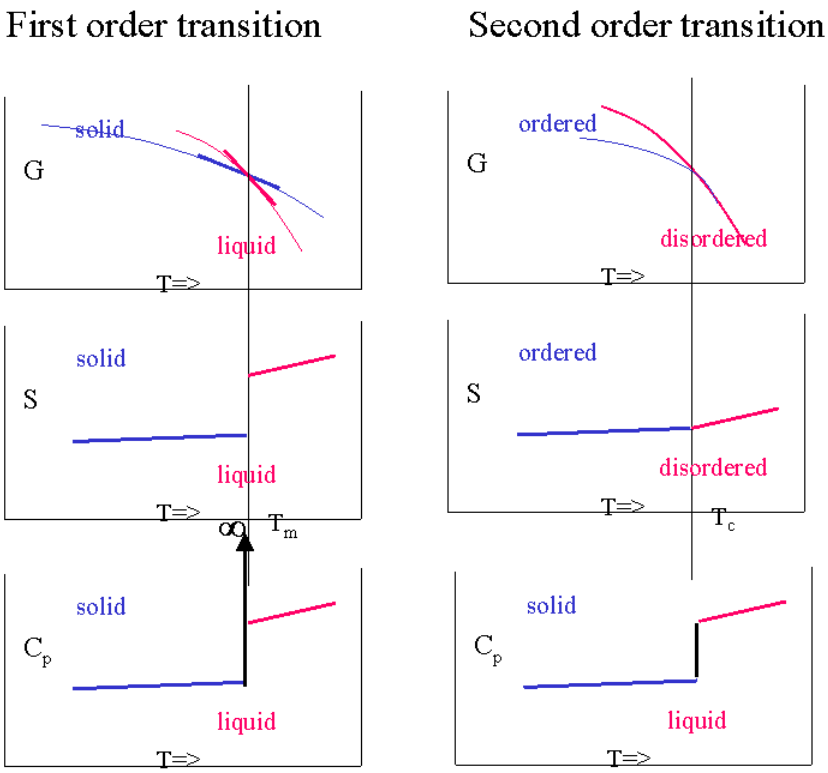
More subtle transitions where G is continuous, H and S are also continuous but have a kink and the discontinuity is only found in the second order derivatives (such as C_P) also exist. They are called *second order transitions*. In such a case:

- G is continuous and has no kink
- The first order derivatives (H,S,..) are continuous (but have a kink)
- The second order derivatives (C_P, ..) are discontinuous (have a jump)

Table 23.2.1: Properties of Phase Transitions

Transition Order	Function	1st Order	2nd Order
0	G,A	kink	smooth
1	H,S,V,..	jump	kink
2	CP,CV,α,κ	sing. ∞	jump

This classification goes back to Ehrenfest. Obviously it based on the question: what order derivative is the first to go discontinuous? Of course we could extend this principle and define *third order transitions* but there are reasons to be doubtful that such things exist. Another problem is that it is assumed that the order must be integer: 1,2, etc. Is it possible to have a transition of intermediate non-integer order, say 1.3? Although derivatives of fractional order are beyond the scope of the chemistry curriculum the mathematics does exist (Liouville).



Schematic comparison of G, S and C_P for 1st and 2nd order transitions

The Gibbs free energy is a particularly important function in the study of phases and phase transitions. The behavior of $G(N,P,T)$, particularly as a function of P and T, can signify a phase transition and can tell us some of the thermodynamic properties of different phases.

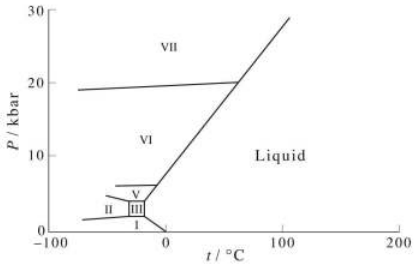


Figure 13.4: Some of the ice polymorphs.

Consider, first, the behavior of G vs. T between the solid and liquid phases of benzene: We immediately notice several things. First, although the free energy is continuous across the phase transition, its first derivative, $\partial G/\partial T$ is not: The slope of $G(T)$ in the solid region is different from the slope in the liquid region. When the first derivative of the free energy with respect to one of its dependent thermodynamic variables is discontinuous across a phase transition, this is an example of what is called a *first order phase transition*. The solid-liquid-gas phase transition of most substances is first order. When the free energy exhibits continuous first derivatives but discontinuous second derivatives, the phase transition is called *second order*. Examples of this type of phase transition are the order-disorder transition in paramagnetic materials.

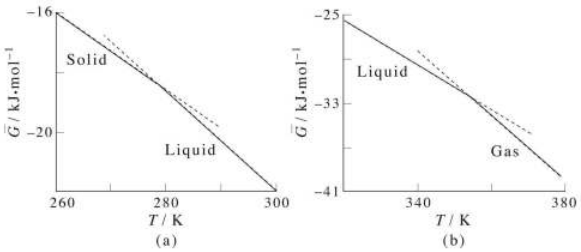


Figure 13.5: Behavior of the Gibbs free energy across the solid-liquid phase (left) and liquid-gas (right) transitions for benzene.

Now, recall that

$$S = -\frac{\partial G}{\partial T} \tag{5.2.1}$$

Consider the slopes in the solid and liquid parts of the graph:

$$\frac{\partial G^{(\text{solid})}}{\partial T} = -S^{(\text{solid})}, \qquad \frac{\partial G^{(\text{liquid})}}{\partial T} = -S^{(\text{liquid})} \tag{5.2.2}$$

However, since

$$\frac{\partial G^{(\text{liquid})}}{\partial T} < \frac{\partial G^{(\text{solid})}}{\partial T} \tag{5.2.3}$$

(*note that the slopes are all negative, and the slope of the liquid line is more negative than that of the solid line*), it follows that $-S^{(\text{liquid})} < -S^{(\text{solid})}$ or $S^{(\text{liquid})} > S^{(\text{solid})}$. This is what we might expect considering that the liquid phase is higher in entropy than the solid phase. The same argument can be made with regards to the gaseous phase.

Similarly, if we consider the dependence of G on pressure, we obtain a curve like that shown in the figure below:

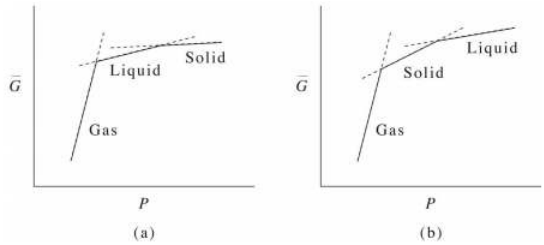


Figure 13.6: Dependence of the Gibbs free energy as a function of pressure for benzene (left) and water (right). For benzene, the temperature is above the triple point, whereas for water, it is set below triple point.

As noted previously, here again, we see that the first derivative of $\bar{G}(P)$ is discontinuous, signifying a first-order phase transition. Recalling that the average molar volume is

$$\bar{V} = \frac{\partial \bar{G}}{\partial P} \tag{5.2.4}$$

From the graph, we see that the slopes obey

$$\bar{V}^{(\text{gas})} \gg \bar{V}^{(\text{liquid})} > \bar{V}^{(\text{solid})} \tag{5.2.5}$$

as one might expect for a normal substance like benzene at a temperature above its triple point. Because the temperature is above the triple point, the free energy follows a continuous path (even though it is not everywhere differentiable) from gas to liquid to solid.

On the other hand, for water, we see something a bit different, namely, that

$$\bar{V}^{(\text{gas})} \gg \bar{V}^{(\text{solid})} > \bar{V}^{(\text{liquid})} \tag{5.2.6}$$

at a temperature below the triple point. This, again, indicates, the unusual property of water that its solid phase is less dense than its liquid phase in the coexistence region.

Interestingly, if we look at how the plot of $G(P)$ changes with T, we obtain a plot like that shown below: Below the triple point, it is easy to see from the benzene phase diagram that the system proceeds directly from solid to gas. There is a liquid curve on this plot that is completely disconnected from the gas-solid curve, suggesting that, below the triple point, the liquid state can exist metastably if at all. AT the triple point, the solid can transition into the liquid or gas phases depending on the value of the free energy. Near the critical temperature, we see the liquid-gas transition line, while the solid line is disconnected. Above the critical temperature, the system exists as a supercritical fluid, which is shown on the lower line, and this line now shows derivative discontinuity.

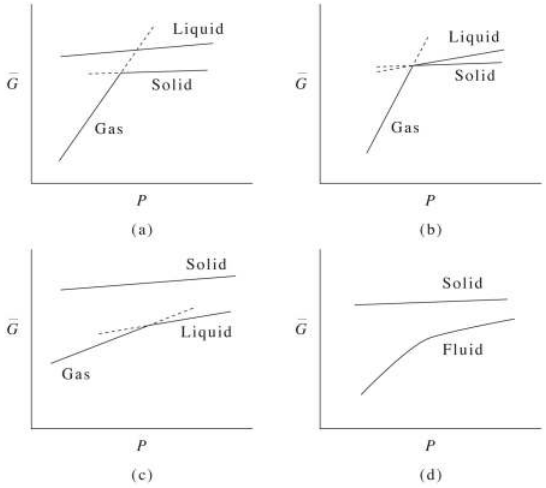


Figure 13.7: Behavior of the Gibbs free energy as a function of P across different phases at different temperatures for benzene. (a): Temperature is less than the triple point; (b): Temperature is equal to the triple point; (c): Temperature is just below the critical temperature; (d): Temperature is greater than the critical temperature.

5.2.3: Conjugate Variables

As discussed before there are many other forms of work possible, such as electrical work, magnetic work or elastic work. These they are commonly incorporated in the formalism of thermodynamics by adding other terms, e.g:

$$dG = -SdT + VdP + \mathcal{E}de + MdH + FdL + \gamma dA$$

1. $\mathcal{E}de$ stands for the electromotoric force $\mathcal{E}$ and de the amount of charge transported against it.
2. MdH stand for magnetization and (change in) magnetic field.
3. F stands for the elastic force of e.g. a rubber band dL for the length it is stretched
4. γ stands for the surface tension (e.g. of a soap bubble), A for its surafce area.

The terms always appear in a pair of what is known as conjugate variables. That is even clearer if we write out the state function rather than its differential form:

$$G = U + PV - TS + \mathcal{E}e + MH + FL + \gamma A + ...$$

The PV term can also be generalized -and needs to be so- for a viscous fluid to a stress-strain conjugate pair. It then involves a stress tensor. We will soon encounter another conjugate pair: μdn that deals with changes in composition (n) and the thermodynamic potential μ.

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5.3: The Chemical Potentials of a Pure Substance in Two Phases in Equilibrium

5.3.1: Chemical Potential of Two Phases in Equilibrium

Equilibrium between two phases, e.g. water ice (ice) and liquid water ($water$), is at constant T and P. Therefore:

$$dG = \cancel{-SdT + VdP} + \mu_{ice}dn_{ice} + \mu_{water}dn_{water}$$

There is a relationship between the amount of ice and water:

$$dn_{ice} = -dn_{water}$$

From this, we get:

$$0 = [\mu_{ice} - \mu_{water}]dn_{water} = \Delta\mu\ dn_{water}$$

As dn_{water} is not zero, this means that $\Delta\mu$ must be zero! This must hold true for any set of points where ice and water are in equilibrium. The statement is not just for liquid and solid water, but for any two phases in equilibrium. That is, any two phases in equilbrium will always have the same chemical potential.

5.3.2: The Clapeyron Equation

That is the almost vertical line in the diagram. Its points are not at the same P and T, but we can find out where they should be by considering the thermodynamic potential μ as a *function* of T and P:

$$d\mu = \left(\frac{\partial\mu}{\partial P}\right)_T dT + \left(\frac{\partial\mu}{\partial T}\right)_P dP$$

Because $\mu = \left(\frac{\partial G}{\partial n}\right)_{T,P} = \bar{G}$, it is not hard to identify the partial derivatives:

$$\left(\frac{\partial\mu}{\partial P}\right) = \left(\frac{\partial\bar{G}}{\partial P}\right) = \bar{V}$$

$$\left(\frac{\partial\mu}{\partial T}\right) = \left(\frac{\partial\bar{G}}{\partial T}\right) = -\bar{S}$$

This is true for both water and ice, or any two phases in equilibrium. As the $\Delta\mu = 0$, we can equate the $d\mu$ expressions for both water and ice:

$$\left(\frac{\partial\mu_{ice}}{\partial P}\right)_T dT + \left(\frac{\partial\mu_{ice}}{\partial T}\right)_P dP = \left(\frac{\partial\mu_{water}}{\partial P}\right)_T dT + \left(\frac{\partial\mu_{water}}{\partial T}\right)_P dP$$

Rearranging and identifying the partials gives:

$$\bar{V}_{ice}dP - \bar{S}_{ice}dT = \bar{V}_{water}dP - \bar{S}_{water}dT$$

Solving for dP/dT we get:

$$\frac{dP}{dT} = \frac{\Delta\bar{S}}{\Delta\bar{V}}$$

As $\Delta\bar{G} = \Delta\bar{H} - T\Delta\bar{S} = 0$, we have:

$$\Delta\bar{S} = \frac{\Delta\bar{H}}{T_m}$$

So:

$$\frac{dP}{dT} = \frac{\Delta\bar{H}}{T\Delta\bar{V}}$$

This expression should be valid for all points along a phase boundary, such as the melt line. In fact, it tells use that the phase boundary is **defined** by $\Delta\bar{H}/T\Delta\bar{V}$. For water and ice, we immediately see why the melt line runs a little to the left: exceptionally

$\Delta\bar{V}$ is negative for ice, because water is actually a little denser that ice.

The above expression(s) are named after ***Clapeyron.*** The values of $\Delta\bar{H}$ and $\Delta\bar{V}$ do not change much with pressure and can often be considered *constants* for the melting line. When gases are involved that is not really true.

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5.4: The Clausius-Clapeyron Equation

5.4.1: Evaporation

In Section 23.3, the Clapeyron Equation was derived for melting points.

$$\frac{dP}{dT} = \frac{\Delta H_{molar}}{T\Delta V_{molar}}$$

However, our argument is actually quite general and should hold for vapor equilibria as well. The only problem is that the molar volume of gases are by no means so nicely constant as they are for condensed phases. (i. e., for condenses phases, both α and κ are pretty small).

We can write:

$$\frac{dP}{dT} = \frac{\Delta H_{molar}}{T\Delta V_{molar}} = \frac{\Delta H_{molar}}{T}\left[V_{molar}^{gas} - V_{molar}^{liquid}\right]$$

as

$$V_{molar}^{gas} \gg V_{molar}^{liquid}$$

we can approximate

$$V_{molar}^{gas} - V_{molar}^{liquid}$$

by just taking V_{molar}^{gas}. Further more if the vapor is considered an ideal gas, then

$$V_{molar}^{gas} = \frac{RT}{P}$$

We get

$$\frac{1}{P}\cdot\frac{dP}{dT} = \frac{d\ln P}{dT} = \frac{\Delta H_{molar}^{vap}}{RT^2} \tag{5.4.1}$$

Equation 5.4.1 is known as the **Clausius-Clapeyron** equation. We can further work our the integration and find the how the equilibrium vapor pressure changes with temperature:

$$\ln\left(\frac{P_2}{P_1}\right) = \frac{-\Delta H_{molar}^{vap}}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

Thus if we know the molar enthalpy of vaporization we can predict the vapor lines in the diagram. Of course the approximations made are likely to lead to deviations if the vapor is not ideal or very dense (e.g., approaching the critical point).

5.4.2: The Clapeyron Equation

The Clapeyron attempts to answer the question of what the shape of a two-phase coexistence line is. In the $P-T$ plane, we see the a function $P(T)$, which gives us the dependence of P on T along a coexistence curve.

Consider two phases, denoted α and β, in equilibrium with each other. These could be solid and liquid, liquid and gas, solid and gas, two solid phases, et. Let $\mu_\alpha(P,T)$ and $\mu_\beta(P,T)$ be the chemical potentials of the two phases. We have just seen that

$$\mu_\alpha(P,T) = \mu_\beta(P,T) \tag{5.4.2}$$

Next, suppose that the pressure and temperature are changed by dP and dT. The changes in the chemical potentials of each phase are

$$d\mu_\alpha(P,T) = d\mu_\beta(P,T) \tag{5.4.3}$$

$$\left(\frac{\partial\mu_\alpha}{\partial P}\right)_T dP + \left(\frac{\partial\mu_\alpha}{\partial T}\right)_P dT = \left(\frac{\partial\mu_\beta}{\partial P}\right)_T dP + \left(\frac{\partial\mu_\beta}{\partial T}\right)_P dT \tag{5.4.4}$$

However, since $G(n,P,T) = n\mu(P,T)$, the *molar* free energy $\bar{G}(P,T)$, which is $G(n,P,T)/n$, is also just equal to the chemical potential

$$\bar{G}(P,T) = \frac{G(n,P,T)}{n} = \mu(P,T) \tag{5.4.5}$$

Moreover, the derivatives of $\bar{G}$ are

$$\left(\frac{\partial \bar{G}}{\partial P}\right)_T = \bar{V}, \qquad \left(\frac{\partial \bar{G}}{\partial T}\right)_P = -\bar{S} \tag{5.4.6}$$

Applying these results to the chemical potential condition in Equation 5.4.4, we obtain

$$\left(\frac{\partial \bar{G}_\alpha}{\partial P}\right)_T dP + \left(\frac{\partial \bar{G}_\alpha}{\partial T}\right)_P dT = \left(\frac{\partial \bar{G}_\beta}{\partial P}\right)_T dP + \left(\frac{\partial \bar{G}_\beta}{\partial T}\right)_P dT \tag{5.4.7}$$

$$\bar{V}_\alpha dP - \bar{S}_\alpha dT = \bar{V}_\beta dP - \bar{S}_\beta dT \tag{5.4.8}$$

Dividing through by dT, we obtain

$$\bar{V}_\alpha \frac{\partial P}{\partial T} - \bar{S}_\alpha = \bar{V}_\beta \frac{\partial P}{\partial T} - \bar{S}_\beta \tag{5.4.9}$$

$$(\bar{V}_\alpha - \bar{V}_\beta)\frac{\partial P}{\partial T} = \bar{S}_\alpha - \bar{S}_\beta \tag{5.4.10}$$

$$\frac{dP}{dT} = \frac{\bar{S}_\alpha - \bar{S}_\beta}{\bar{V}_\alpha - \bar{V}_\beta} \tag{5.4.11}$$

The importance of the quantity dP/dT is that is represents the slope of the coexistence curve on the phase diagram between the two phases. Now, in equilibrium $dG = 0$, and since $G = H - TS$, it follows that $dH = T\,dS$ at fixed T. In the narrow temperature range in which the two phases are in equilibrium, we can assume that H is independent of T, hence, we can write $S = H/T$. Consequently, we can write the molar entropy difference as

$$\bar{S}_\alpha - \bar{S}_\beta = \frac{\bar{H}_\alpha - \bar{H}_\beta}{T} \tag{5.4.12}$$

and the pressure derivative dP/dT becomes

$$\frac{dP}{dT} = \frac{\bar{H}_\alpha - \bar{H}_\beta}{T(\bar{V}_\alpha - \bar{V}_\beta)} = \frac{\Delta_{\alpha\beta}\bar{H}}{T\Delta_{\alpha\beta}\bar{V}} \tag{5.4.13}$$

a result known as the **Clapeyron equation**, which tells us that the slope of the coexistence curve is related to the ratio of the molar enthalpy between the phases to the change in the molar volume between the phases. If the phase equilibrium is between the solid and liquid phases, then $\Delta_{\alpha\beta}\bar{H}$ and $\Delta_{\alpha\beta}\bar{V}$ are $\Delta\bar{H}_{\text{fus}}$ and $\Delta\bar{V}_{\text{fus}}$, respectively. If the phase equilibrium is between the liquid and gas phases, then $\Delta_{\alpha\beta}\bar{H}$ and $\Delta_{\alpha\beta}\bar{V}$ are $\Delta\bar{H}_{\text{vap}}$ and $\Delta\bar{V}_{\text{vap}}$, respectively.

For the liquid-gas equilibrium, some interesting approximations can be made in the use of the Clapeyron equation. For this equilibrium, Equation 5.4.13 becomes

$$\frac{dP}{dT} = \frac{\Delta\bar{H}_{\text{vap}}}{T(\bar{V}_g - \bar{V}_l)} \tag{5.4.14}$$

In this case, $\bar{V}_g \gg \bar{V}_l$, and we can approximate Equation 5.4.14 as

$$\frac{dP}{dT} \approx \frac{\Delta\bar{H}_{\text{vap}}}{T\bar{V}_g} \tag{5.4.15}$$

Suppose that we can treat the vapor phase as an ideal gas. Certainly, this is not a good approximation so close to the vaporization point, but it leads to an example we can integrate. Since $PV_g = nRT$, $P\bar{V}_g = RT$, Equation 5.4.15 becomes

$$\frac{dP}{dT} = \frac{\Delta \bar{H}_{\text{vap}} P}{RT^2} \tag{5.4.16}$$

$$\frac{1}{P}\frac{dP}{dT} = \frac{\Delta \bar{H}_{\text{vap}}}{RT^2} \tag{5.4.17}$$

$$\frac{d \ln P}{dT} = \frac{\Delta \bar{H}_{\text{vap}}}{RT^2} \tag{5.4.18}$$

which is called the ***Clausius-Clapeyron equation***. We now integrate both sides, which yields

$$\ln P = -\frac{\Delta \bar{H}_{\text{vap}}}{RT} + C$$

where C is a constant of integration. Exponentiating both sides, we find

$$P(T) = C' e^{-\Delta \bar{H}_{\text{vap}}/RT}$$

which actually has the wrong curvature for large T, but since the liquid-vapor coexistence line terminates in a critical point, as long as T is not too large, the approximation leading to the above expression is not that bad.

If we, instead, integrate both sides, the left from P_1 to P_2, and the right from T_1 to T_2, we find

$$\int_{P_1}^{P_2} d \ln P = \int_{T_1}^{T_2} \frac{\Delta \bar{H}_{\text{vap}}}{RT^2} dT \tag{5.4.19}$$

$$\ln \left(\frac{P_2}{P_1} \right) = -\frac{\Delta \bar{H}_{\text{vap}}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \tag{5.4.20}$$

$$= \frac{\Delta \bar{H}_{\text{vap}}}{R} \left(\frac{T_1 - T_1}{T_1 T_2} \right) \tag{5.4.21}$$

assuming that $\Delta \bar{H}_{\text{vap}}$ is independent of T. Here P_1 is the pressure of the liquid phase, and P_2 is the pressure of the vapor phase. Suppose we know P_2 at a temperature T_2, and we want to know P_3 at another temperature T_3. The above result can be written as

$$\ln \left(\frac{P_3}{P_1} \right) = -\frac{\Delta \bar{H}_{\text{vap}}}{R} \left(\frac{1}{T_3} - \frac{1}{T_1} \right) \tag{5.4.22}$$

Subtracting the two results, we obtain

$$\ln \left(\frac{P_2}{P_3} \right) = -\frac{\Delta \bar{H}_{\text{vap}}}{R} \left(\frac{1}{T_2} - \frac{1}{T_3} \right) \tag{5.4.23}$$

so that we can determine the vapor pressure at any temperature if it is known as one temperature.

In order to illustrate the use of this result, consider the following example:

Example 23.4.1

At $1\ \text{bar}$, the boiling point of water is $373\ \text{K}$. At what pressure does water boil at $473\ \text{K}$? Take the heat of vaporization of water to be $40.65\ \text{kJ/mol}$.

Solution

Let $P_1 = 1\ \text{bar}$ and $T_1 = 373\ \text{K}$. Take $T_2 = 473\ \text{K}$, and we need to calculate P_2. Substituting in the numbers, we find

$$\ln P_2(\text{bar}) = -\frac{(40.65\ \text{kJ/mol})(1000\ \text{J/kJ})}{8.3145\ \text{J/mol} \cdot \text{K}} \left(\frac{1}{473\ \text{K}} - \frac{1}{373\ \text{K}} \right) = 2.77 \tag{5.4.24}$$

$$P_2(\text{bar}) = (1\ \text{bar})\, e^{2.77} = 16\ \text{bar} \tag{5.4.25}$$

Learning Objectives

- Apply the Clausius-Clapeyron equation to estimate the vapor pressure at any temperature.
- Estimate the heat of phase transition from the vapor pressures measured at two temperatures.

The *vaporization curves* of most liquids have similar shapes with the vapor pressure steadily increasing as the temperature increases (Figure 5.4.1).

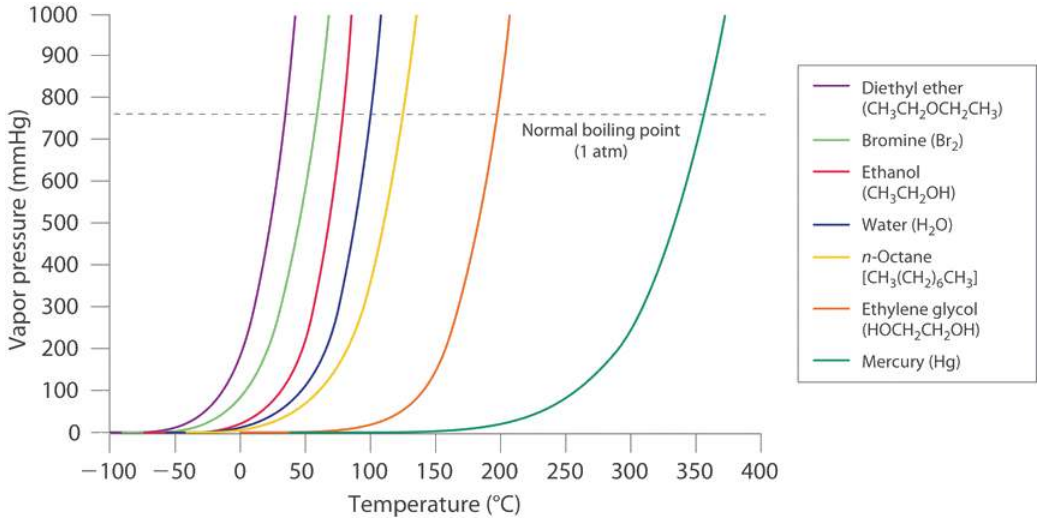


Figure 5.4.1: The Vapor Pressures of Several Liquids as a Function of Temperature. The point at which the vapor pressure curve crosses the P = 1 atm line (dashed) is the normal boiling point of the liquid. (CC BY-SA-NC 3.0; Anonymous)

A good approach is to find a mathematical model for the pressure increase as a function of temperature. Experiments showed that the vapor pressure $\boldsymbol{P}$ and temperature $\boldsymbol{T}$ are related,

$$P \propto \exp\left(-\frac{\Delta H_{vap}}{RT}\right) \tag{5.4.26}$$

where $\Delta \boldsymbol{H_{vap}}$ is the Enthalpy (heat) of Vaporization and $\boldsymbol{R}$ is the gas constant (8.3145 J mol^{-1} K^{-1}).

A simple relationship can be found by integrating Equation 5.4.26 between two pressure-temperature endpoints:

$$\ln\left(\frac{P_1}{P_2}\right) = \frac{\Delta H_{vap}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{5.4.27}$$

where $\boldsymbol{P_1}$ and $\boldsymbol{P_2}$ are the vapor pressures at two temperatures $\boldsymbol{T_1}$ and $\boldsymbol{T_2}$. Equation 5.4.27 is known as the **Clausius-Clapeyron Equation** and allows us to estimate the vapor pressure at another temperature, if the vapor pressure is known at some temperature, and if the enthalpy of vaporization is known.

Alternative Formulation

The order of the temperatures in Equation 5.4.27 matters as the Clausius-Clapeyron Equation is sometimes written with a negative sign (and switched order of temperatures):

$$\ln\left(\frac{P_1}{P_2}\right) = -\frac{\Delta H_{vap}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{5.4.28}$$

Example 5.4.1: Vapor Pressure of Water

The vapor pressure of water is 1.0 atm at 373 K, and the enthalpy of vaporization is 40.7 kJ mol^{-1}. Estimate the vapor pressure at temperature 363 and 383 K respectively.

Solution

Using the Clausius-Clapeyron equation (Equation 5.4.28), we have:

$$P_{363} = 1.0 \exp\left[-\left(\frac{40,700}{8.3145}\right)\left(\frac{1}{363\ K} - \frac{1}{373\ K}\right)\right]$$
$$= 0.697 \text{ atm}$$

$$P_{383} = 1.0 \exp\left[-\left(\frac{40,700}{8.3145}\right)\left(\frac{1}{383\ K} - \frac{1}{373\ K}\right)\right]$$
$$= 1.409 \text{ atm}$$

Note that the increase in vapor pressure from 363 K to 373 K is 0.303 atm, but the increase from 373 to 383 K is 0.409 atm. The increase in vapor pressure is not a linear process.

Discussion

We can use the Clausius-Clapeyron equation to construct the entire vaporization curve. There is a deviation from experimental value, that is because the enthalpy of vaporization varies slightly with temperature.

The Clausius-Clapeyron equation can be also applied to sublimation; the following example shows its application in estimating the heat of sublimation.

✔ Example 5.4.2: Sublimation of Ice

The vapor pressures of ice at 268 K and 273 K are 2.965 and 4.560 torr respectively. Estimate the heat of sublimation of ice.

Solution

The enthalpy of sublimation is ΔH_{sub}. Use a piece of paper and derive the Clausius-Clapeyron equation so that you can get the form:

$$\Delta H_{sub} = \frac{R \ln\left(\frac{P_{273}}{P_{268}}\right)}{\frac{1}{268\ K} - \frac{1}{273\ K}}$$
$$= \frac{8.3145 \ln\left(\frac{4.560}{2.965}\right)}{\frac{1}{268\ \text{K}} - \frac{1}{273\ \text{K}}}$$
$$= 52,370 \text{ J mol}^{-1}$$

Note that the heat of sublimation is the sum of heat of melting (6,006 J/mol at 0°C and 101 kPa) and the heat of vaporization (45,051 J/mol at 0 °C).

? Exercise 5.4.2

Show that the vapor pressure of ice at 274 K is higher than that of water at the same temperature. Note the curve of vaporization is also called the curve of vaporization.

✔ Example 5.4.3: Vaporization of Ethanol

Calculate ΔH_{vap} for ethanol, given vapor pressure at 40 ^{o}C = 150 torr. The normal boiling point for ethanol is 78 ^{o}C.

Solution

Recognize that we have TWO sets of (P, T) data:

- Set 1: (150 torr at 40+273K)
- Set 2: (760 torr at 78+273K)

We then directly use these data in Equation 5.4.28

$$\ln\left(\frac{150}{760}\right) = \frac{-\Delta H_{vap}}{8.314}\left[\frac{1}{313} - \frac{1}{351}\right]$$

$$\ln 150 - \ln 760 = \frac{-\Delta H_{vap}}{8.314}\left[\frac{1}{313} - \frac{1}{351}\right]$$

$$-1.623 = \frac{-\Delta H_{vap}}{8.314}\left[0.0032 - 0.0028\right]$$

Then solving for ΔH_{vap}

$$\Delta H_{vap} = 3.90 \times 10^4 \text{ J/mol}$$
$$= 39.0 \text{ kJ/mol}$$

Advanced Note

It is important to not use the Clausius-Clapeyron equation for the solid to liquid transition. That requires the use of the more general **Clapeyron equation**

$$\frac{dP}{dT} = \frac{\Delta \bar{H}}{T\Delta \bar{V}}$$

where $\Delta \bar{H}$ and $\Delta \bar{V}$ is the molar change in enthalpy (the enthalpy of fusion in this case) and volume respectively between the two phases in the transition.

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5.E: Phase Equilibria (Exercises)

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CHAPTER OVERVIEW

6: Properties of Solutions

6.1: Ideal Solutions

6.2: Real Solutions

6.2.1: Vapor Pressures of Volatile Binary Solutions

6.3: Colligative Properties

6.4: Solutions Exercises

6.4.E: Mixtures and Solutions (Exercises)

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6.1: Ideal Solutions

Liquids tend to be volatile, and as such will enter the vapor phase when the temperature is increased to a high enough value, provided they do not decompose first. A volatile liquid is one that has an appreciable vapor pressure at the specified temperature. An ideal mixture containing at least one volatile liquid can be described using **Raoult's Law:**

$$P_j = x_j P_j^*$$

Raoult's law can be used to predict the total vapor pressure above a mixture of two volatile liquids. As it turns out, the composition of the vapor will be different than that of the two liquids, with the more volatile compound having a larger mole fraction in the vapor phase than in the liquid phase. This is summarized in the following diagram for an ideal mixture of two compounds, water and ethanol at 75 °C. At this temperature, water a pure vapor pressure of 384 Torr and ethanol has a pure vapor pressure of 945 Torr. In Figure 24.4.1, the composition of the liquid phase is represented by the solid line and the composition of the vapor phase is represented by the dashed line.

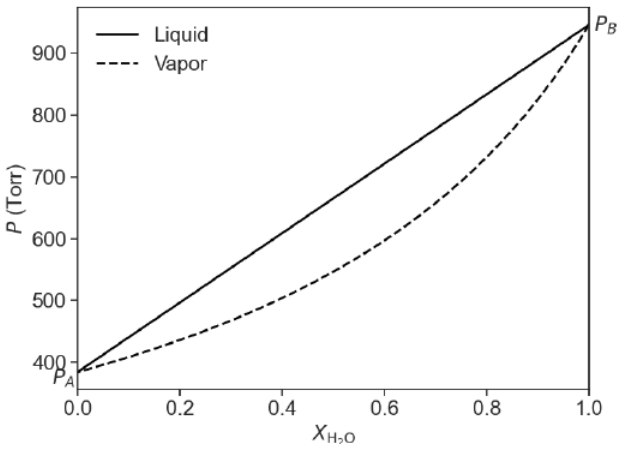


Figure 24.4.1: The composition of the liquid phase (solid line) and the vapor phase (dashed lined) as a function of mole fraction according to Raoult's law. The solution is a mixture of water and ethanol. P_A is the vapor pressure of pure water and P_B is the vapor pressure of pure ethanol at 75 °C

Often, it is desirable to depict the phase diagram at a single pressure so that temperature and composition are the variables included in the graphical representation. In such a diagram, the vapor, which exists at higher temperatures) is indicated at the top of the diagram, while the liquid is at the bottom. A typical temperature vs. composition diagram is depicted in Figure 24.4.2 for an ideal mixture of two volatile liquids.

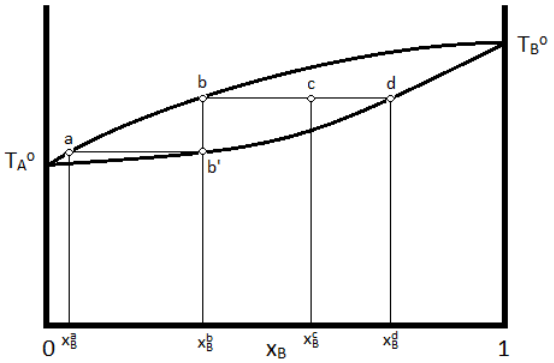


Figure 24.4.2: A typical temperature vs. composition diagram.

In this diagram, T_A and T_B represent the boiling points of pure compounds A and B. If a system having the composition indicated by χ_B^c has its temperature increased to that indicated by point c, The system will consist of two phases, a liquid phase, with a composition indicated by χ_B^d and a vapor phase indicated with a composition indicated by χ_B^b. The relative amounts of material in each phase can be described by the lever rule, as described previously.

Further, if the vapor with composition χ_B^b is condensed (the temperature is lowered to that indicated by point b') and re-vaporized, the new vapor will have the composition consistent with χ_B^a. This demonstrates how the more volatile liquid (the one with the lower boiling temperature, which is A in the case of the above diagram) can be purified from the mixture by collecting and re-evaporating fractions of the vapor. If the liquid was the desired product, one would collect fractions of the residual liquid to achieve the desired result. This process is known as distillation.

6.1.1: The Gibbs energy of mixing is always negative

When we add n_A moles of component A and n_B moles of component B to form an ideal liquid solution, this is generally a spontaneous process. Let us consider the Gibbs free energy change of that process:

$$\Delta_{mix}G = n_1\mu_1^{sln} + n_2\mu_2^{sln} - (n_1\mu_1^* + n_2\mu_2^*)$$

Using:

$$\mu_i^{sln} \equiv \mu_i^* + nRTx_i \ln x_i$$

his expression simplifies to:

$$\Delta_{mix}G = nRTx_A \ln x_A + nRTx_B \ln x_B$$

where n is the total moles. Mole fraction, x_i, is always less than one, so the Gibbs energy of mixing is always negative; mixing is always spontaneous. We can generalize this to mixtures with more than two components:

$$\Delta_{mix}G = nRT\sum_i x_i \ln x_i$$

This expression looks suspiciously familiar. Apart from a factor of $-T$, it is just like the **entropy of mixing**:

$$\Delta_{mix}S = -nR\sum_i x_i \ln x_i$$

Recalling the relationship between Gibbs energy and entropy:

$$\Delta_{mix}G = \Delta_{mix}H - T\Delta_{mix}S$$

This leaves no room at all for an enthalpy effect:

$$\Delta_{mix}H = 0$$

Even though there are strong interactions between neighboring particles in liquids, there is no enthalpy change. This implies that it does not matter what the neighboring molecules are. If we represent the average interaction energy between molecule i and j by U_{ij}, we are assuming that U_{ij} is always the same. In practice, this is *seldom* the case. It usually does matter and then the enthalpy term is not zero. As this affects the thermodynamics of the liquid solution, it should also affect the vapor pressures that are in equilibrium with it.

6.1.2: In the ideal case, volumes are additive

From the change of G in its natural variables, we know that:

$$\left(\frac{\partial G}{\partial P}\right)_T = V$$

This means that if we take

$$\left(\frac{\partial \Delta G}{\partial P}\right)_T = \Delta V_{mix}$$

In the ideal case we get:

$$\left(\frac{\partial \Delta G^{ideal}}{\partial P}\right)_T = \Delta V_{mix}^{ideal}$$

$$\left(\frac{\partial RT(n_1 \ln x_1 + n_2 \ln x_2)}{\partial P}\right)_T = \Delta V_{mix}^{ideal} = 0$$

In the ideal case, volumes are *additive* and we need not worry about how the partial molar volumes change with composition.

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- **24.9: Gibbs Energy of Mixing of Binary Solutions in Terms of the Activity Coefficient** is licensed CC BY-NC-SA 4.0.

6.2: Real Solutions

If we plot the partial pressure of one component, P_1, above a mixture with a mole fraction x_1, we should get a straight line with a slope of P_1^* (Raoult's law). Above non-ideal solutions the graph will no longer be a straight line but a curve. However towards $x_1 = 1$ the curve typically approaches the Raoult line. On the other extreme, there often is a more or less linear region as well, ***but with a different slope*** (Figure 24.5.1). This means that we can identify two *limiting* laws:

- For $x \to 0$: **Henry's law**:

$$P_1 = K_H x_1$$

- For $x \to 1$: **Raoult's law**:

$$P_1 = P_1^* x_1$$

This implies that the straight line that indicates the Henry expression will intersect the y-axis at $x = 1$ (pure compound) at a ***different*** point than P^*. For $x \to 0$ (low concentrations) we can speak of component 1 being the *solute* (the minority component). At the other end $x \to 1$ it plays the role of the *solvent* (majority component).

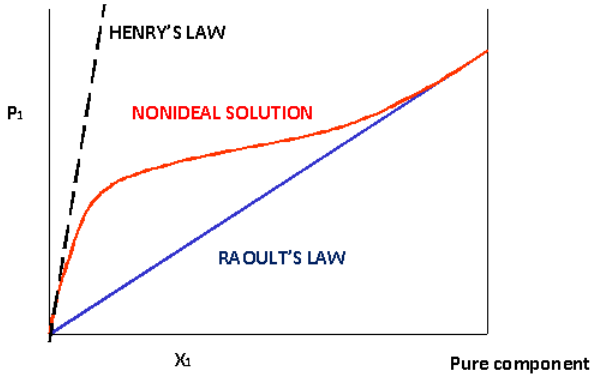


Figure 24.5.1 : Vapor pressure above an ideal and a non-ideal solution

> Another thing to note is that P^* is a property of *one pure component*, the value of K_H by contrast is a property of the *combination of two components*, so it needs to be measured for each solute-solvent combination.

As you can see we have a description for both the high and the low end, but not in the middle. In general, the more modest the deviations from ideality the larger the range of validity of the two limiting laws. The way to determine K_H would be to actually determine vapor pressures. How about the other component? Do we need to measure them too? Fortunately we can use thermodynamics to answer this question with no. There is a handy expression that saves us the trouble.

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- **24.5: Most Solutions are Not Ideal** by Jerry LaRue is licensed CC BY-NC-SA 4.0.

6.2.1: Vapor Pressures of Volatile Binary Solutions

The behaviors of ideal solutions of volatile compounds follow Raoult's Law. Henry's Law can be used to describe the deviations from ideality. Henry's law states:

$$P_B = k_H P_B^o$$

For which the Henry's Law constant (k_H) is determined for the specific compound. Henry's Law is often used to describe the solubilities of gases in liquids. The relationship to Raoult's Law is summarized in Figure **6.2.1.1**.

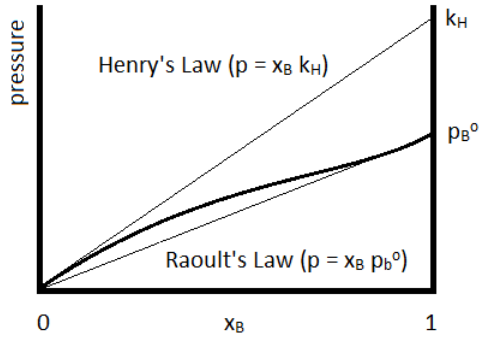


Figure **6.2.1.1**: The relationship between Raoult's Law and Henry's Law for a binary mixture.

Henry's Law is depicted by the upper straight line and Raoult's Law by the lower.

Example 6.2.1.1: Solubility of Carbon Dioxide in Water

The solubility of $CO_2(g)$ in water at 25 °C is 3.32 x 10^{-2} M with a partial pressure of CO_2 over the solution of 1 bar. Assuming the density of a saturated solution to be 1 kg/L, calculate the Henry's Law constant for CO_2.

Solution:

In one L of solution, there is 1000 g of water (assuming the mass of CO_2 dissolved is negligible.)

$$(1000\,g)\left(\frac{1\,mol}{18.02\,g}\right) = 55\,mol\,H_2O$$

The solubility of CO_2 can be used to find the number of moles of CO_2 dissolved in 1 L of solution also:

$$\frac{3.32\times10^{-2}mol}{L}\cdot 1\,L = 3.32\times10^{-2}mol\,CO_2$$

and so the mol fraction of CO_2 is

$$\chi_b = \frac{3.32\times10^{-2}mol}{55.5\,mol} = 5.98\times10^{-4}$$

And so

$$10^5\,Pa = 5.98\times10^{-4}k_H$$

or

$$k_H = 1.67\times10^9\,Pa$$

6.2.1.1: Azeotropes

An azeotrope is defined as the common composition of vapor and liquid when they have the same composition.

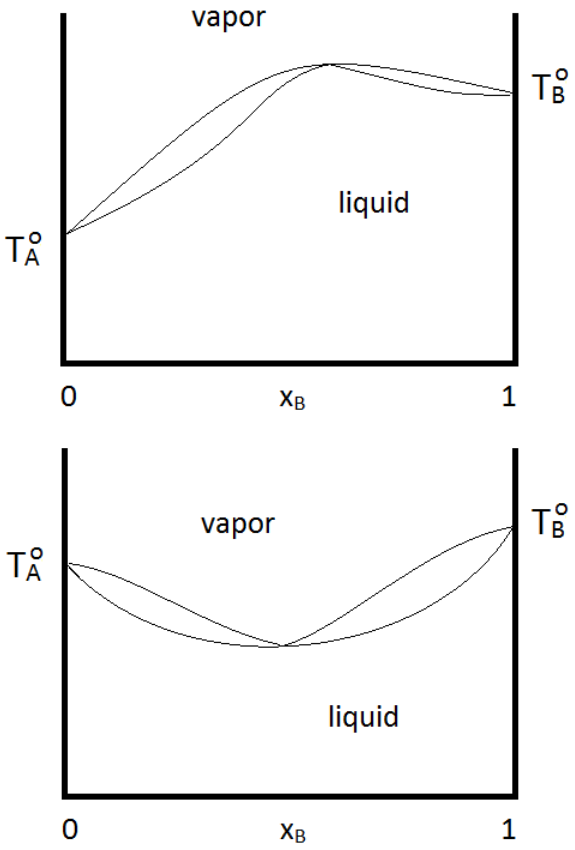


Figure **6.2.1.2**: Phase diagrams for (left) a maximum boiling point azeotrope and (right) Ta maximum boiling point azeotrope.

Azeotropes can be either maximum boiling or minimum boiling, as show in Figure **6.2.1.2;**. Regardless, distillation cannot purify past the azeotrope point, since the vapor and the liquid phases have the same composition. If a system forms a minimum boiling azeotrope and has a range of compositions and temperatures at which two liquid phases exist, the phase diagram might look like Figure **6.2.1.2;**:

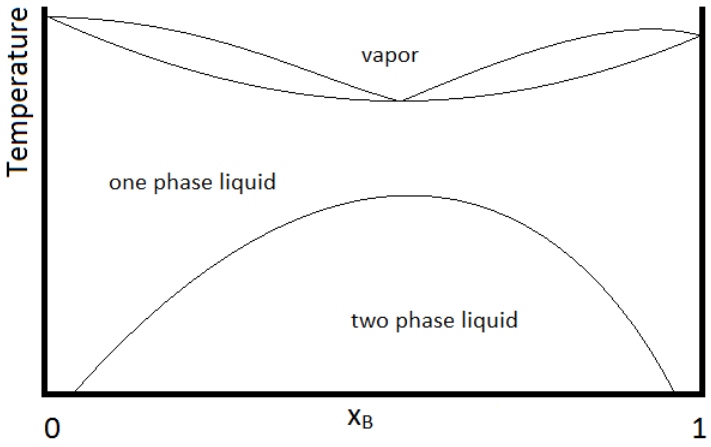
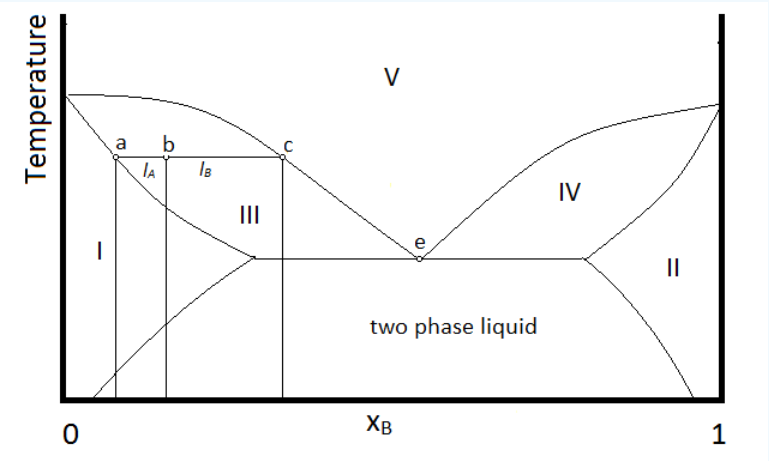


Figure **6.2.1.3**: *Phase diagram for a binary solution with the boiling point of a minimum boiling azeotrope that is higher that when components are miscible (single phase).*

Another possibility that is common is for two substances to form a two-phase liquid, form a minimum boiling azeotrope, but for the azeotrope to boil at a temperature below which the two liquid phases become miscible. In this case, the phase diagram will look like Figure **6.2.1.3**.

Example 6.2.1.1:

In the diagram, make up of a system in each region is summarized below the diagram. The point e indicates the azeotrope composition and boiling temperature.



I. Single phase liquid (mostly compound A)
II. Single phase liquid (mostly compound B)
III. Single phase liquid (mostly A) and vapor
IV. Single phase liquid (mostly B) and vapor
V. Vapor (miscible at all mole fractions since it is a gas)

Solution

Within each two-phase region (III, IV, and the two-phase liquid region, the lever rule will apply to describe the composition of each phase present. So, for example, the system with the composition and temperature represented by point b (a single-phase liquid which is mostly compound A, designated by the composition at point a, and vapor with a composition designated by that at point c), will be described by the lever rule using the lengths of tie lines l_A and l_B.

6.2.1.1.1: Gibbs-Duhem and Henry's law

What happens when Raoult does *not* hold over the whole range? Recall that in a gas:

$$\mu_j = \mu_j^o + RT \ln \frac{P_j}{P^o} \tag{6.2.1.1}$$

or

$$\mu_j = \mu_j^o + RT \ln P_j$$

after dropping $P^o = 1\ bar$ out of the notation. Note that numerically this does not matter, since P_j is now *assumed* to be dimensionless.

Let's consider $d\mu_1$ at constant temperature:

$$d\mu_1 = RT \left(\frac{\partial \ln P_1}{\partial x_1} \right) dx_1$$

likewise:

$$d\mu_2 = RT \left(\frac{\partial \ln P_2}{\partial x_2} \right) dx_2$$

If we substitute into the Gibbs-Duhem expression we get:

$$x_1\left(\frac{\partial \ln P_1}{\partial x_1}\right)dx_1 + x_2\left(\frac{\partial \ln P_2}{\partial x_2}\right)dx_2 = 0$$

Because $dx_1 = -dx_2$:

$$x_1\left(\frac{\partial \ln P_1}{\partial x_1}\right) = x_2\left(\frac{\partial \ln P_2}{\partial x_2}\right)$$

(This is an alternative way of writing Gibbs-Duhem).

If in the limit for $x_1 \to 1$ Raoult Law holds then

$$P_1 \to x_1 P_1^*$$

Thus:

$$\frac{\partial \ln P_1}{\partial x_1} = \frac{1}{x_1}$$

and

$$\frac{x_1}{x_1} = x_2\frac{\partial \ln P_2}{\partial x_2}$$

$$1 = x_2\frac{\partial \ln P_2}{\partial x_2}$$

$$\frac{1}{x_2} = \frac{\partial \ln P_2}{\partial x_2} \tag{6.2.1.2}$$

We can integrate Equation 6.2.1.2 to form a logarithmic impression, but it will have an integration constant:

$$\ln P_2 = \ln x_2 + constant$$

This constant of integration can be folded into the logarithm as a multiplicative constant, K

$$\ln P_2 = \ln (K x_2)$$

So for $x_1 \to 1$ (i.e., $x_2 \to 0$), we get that

$$P_2 = K x_2$$

where K is *some* constant, but not necessarily P^*. What this shows is that when one component follows Raoult the other *must* follow Henry and vice versa. (Note that the ideal case is a subset of this case, in that the value of K then becomes P^* and the linearity must hold over the whole range.)

6.2.1.2: Margules Functions

Of course a big drawback of the Henry law is that it only describes what happens at the two extremes of the phase diagram and not in the middle. In cases of moderate non-ideality, it is possible to describe the whole range (at least in good approximation) using a **Margules function**:

$$P_1 = (x_1 P_1^*)\, f_{Mar}$$

The function f_{Mar} has the shape:

$$f_{Mar} = \exp\left[\alpha x_2^2 + \beta x_2^3 + \delta x_2^3 + ...\right]$$

Notice that the Margules function involves the mole fraction of the *opposite* component. It is an exponential with a series expansion. with the constant and linear term missing. As you can see the function has a number of parameters α, β, δ etc. that need to be determined by experiment. In general, the more the system diverges from ideality, the more parameters you need. Using Gibbs-Duhem is is possible to translate the expression for P_1 into the corresponding one for P_2.

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6.3: Colligative Properties

Colligative properties are important properties of **solutions** as they describe how the properties of the **solvent** will change as **solute** (or solutes) is (are) added. Before discussing these important properties, let us first review some definitions.

- **Solution** – a homogeneous mixture.
- **Solvent** – The component of a solution with the largest mole fraction
- **Solute** – Any component of a solution that is not the solvent.

Solutions can exist in solid (alloys of metals are an example of solid-phase solutions), liquid, or gaseous forms. For the most part, this discussion will focus on liquid-phase solutions.

Freezing Point Depression

In general (and as will be discussed in Chapter 8 in more detail) a liquid will freeze when

$$\mu_{solid} \leq \mu_{liquid}$$

As such, the freezing point of the solvent in a solution will be affected by anything that changes the chemical potential of the solvent. As it turns out, the chemical potential of the solvent is reduced by the presence of a solute.

In a mixture, the chemical potential of component A can be calculated by

$$\mu_A = \mu_A^o + RT \ln \chi_A \tag{6.3.1}$$

And because χ_A is always less than (or equal to) 1, the chemical potential is always reduced by the addition of another component.

The condition under which the solvent will freeze is

$$\mu_{A,solid} = \mu_{A,liquid}$$

where the chemical potential of the liquid is given by Equation 6.3.1, which rearrangement to

$$\frac{\mu_A - \mu_A^o}{RT} = \ln \chi_A$$

To evaluate the temperature dependence of the chemical potential, it is useful to consider the temperature derivative at constant pressure.

$$\left[\frac{\partial}{\partial T}\left(\frac{\mu_A - \mu_A^o}{RT}\right)\right]_p = \left(\frac{\partial \ln \chi_A}{\partial T}\right)_p$$

$$-\frac{\mu_A - \mu_A^o}{RT^2} + \frac{1}{RT}\left[\left(\frac{\partial \mu_A}{\partial T}\right)_p - \left(\frac{\partial \mu_A^o}{\partial T}\right)_p\right] = \left(\frac{\partial \ln \chi_A}{\partial T}\right)_p \tag{6.3.2}$$

Recalling that

$$\mu = H = TS$$

and

$$\left(\frac{\partial \mu}{\partial T}\right)_p = -S$$

Equation 6.3.2 becomes

$$-\frac{(H_A - TS_A - H_A^o + TS_A^o)}{RT^2} + \frac{1}{RT}\left[-S_A + S_A^o\right] = \left(\frac{\partial \ln \chi_A}{\partial T}\right)_p \tag{6.3.3}$$

And noting that in the case of the solvent freezing, H_A^o is the enthalpy of the pure solvent in solid form, and H_A is the enthalpy of the solvent in the liquid solution. So

$$H_A^o - H_a = \Delta H_{fus}$$

Equation 6.3.3 then becomes

$$\frac{\Delta H_{fus}}{RT^2} - \cancel{\frac{-S_A + S_A^o}{RT}} + \cancel{\frac{-S_A + S_A^o}{RT}} = \left(\frac{\partial \ln \chi_A}{\partial T}\right)_p$$

or

$$\frac{\Delta H_{fus}}{RT^2} = \left(\frac{\partial \ln \chi_A}{\partial T}\right)_p$$

Separating the variables puts the equation into an integrable form.

$$\int_{T^o}^{T} \frac{\Delta H_{fus}}{RT^2} dT = \int d \ln \chi_A \tag{6.3.4}$$

where T^o is the freezing point of the pure solvent and T is the temperature at which the solvent will begin to solidify in the solution. After integration of Equation 6.3.4:

$$-\frac{\Delta H_{fus}}{R}\left(\frac{1}{T} - \frac{1}{T^o}\right) = \ln \chi_A \tag{6.3.5}$$

This can be simplified further by noting that

$$\frac{1}{T} - \frac{1}{T^o} = \frac{T^o - T}{TT^o} = \frac{\Delta T}{TT^o}$$

where ΔT is the difference between the freezing temperature of the pure solvent and that of the solvent in the solution. Also, for small deviations from the pure freezing point, TT^o can be replaced by the approximate value $(T^o)^2$. So the Equation 6.3.5 becomes

$$-\frac{\Delta H_{fus}}{R(T^o)^2}\Delta T = \ln \chi_A \tag{6.3.6}$$

Further, for dilute solutions, for which χ_A, the mole fraction of the solvent is very nearly 1, then

$$\ln \chi_A \approx -(1 - \chi_A) = -\chi_B$$

where χ_B is the mole fraction of the solute. After a small bit of rearrangement, this results in an expression for freezing point depression of

$$\Delta T = \left(\frac{R(T^o)^2}{\Delta H_{fus}}\right)\chi_B$$

The first factor can be replaced by K_f:

$$\frac{R(T^o)^2}{\Delta H_{fus}} = K_f$$

which is the **cryoscopic constant** for the solvent.

ΔT gives the magnitude of the reduction of freezing point for the solution. Since ΔH_{fus} and T^o are properties of the solvent, the freezing point depression property is independent of the solute and is a property based solely on the nature of the solvent. Further, since χ_B was introduced as $(1 - \chi_A)$, it represents the sum of the mole fractions of all solutes present in the solution.

It is important to keep in mind that for a real solution, freezing of the solvent changes the composition of the solution by decreasing the mole fraction of the solvent and increasing that of the solute. As such, the magnitude of ΔT will change as the freezing process continually removes solvent from the liquid phase of the solution.

Boiling Point Elevation

The derivation of an expression describing boiling point elevation is similar to that for freezing point depression. In short, the introduction of a solute into a liquid solvent lowers the chemical potential of the solvent, cause it to favor the liquid phase over the vapor phase. As sch, the temperature must be increased to increase the chemical potential of the solvent in the liquid solution until it is equal to that of the vapor-phase solvent. The increase in the boiling point can be expressed as

$$\Delta T = K_b \chi_B$$

where

$$\frac{R(T^o)^2}{\Delta H_{vap}} = K_b$$

is called the **ebullioscopic constant** and, like the cryoscopic constant, is a property of the solvent that is independent of the solute or solutes. A very elegant derivation of the form of the models for freezing point depression and boiling point elevation has been shared by F. E. Schubert (Schubert, 1983).

Cryoscopic and ebullioscopic constants are generally tabulated using molality as the unit of solute concentration rather than mole fraction. In this form, the equation for calculating the magnitude of the freezing point decrease or the boiling point increase is

$$\Delta T = K_f m$$

or

$$\Delta T = K_b m$$

where m is the concentration of the solute in moles per kg of solvent. Some values of K_f and K_b are shown in the table below.

Substance	K_f (°C kg mol-1)	T_f^o (°C)	K_b (°C kg mol-1)	T_b^o (°C)
Water	1.86	0.0	0.51	100.0
Benzene	5.12	5.5	2.53	80.1
Ethanol	1.99	-114.6	1.22	78.4
CCl_4	29.8	-22.3	5.02	76.8

Example 6.3.1:

The boiling point of a solution of 3.00 g of an unknown compound in 25.0 g of CCl_4 raises the boiling point to 81.5 °C. What is the molar mass of the compound?

Solution

The approach here is to find the number of moles of solute in the solution. First, find the concentration of the solution:

$$(85.5\,°C - 76.8\,°C) = (5.02\,°C\,Kg/mol)\,m$$

$$m = 0.936\,mol/kg$$

Using the number of kg of solvent, one finds the number for moles of solute:

$$\left(0.936\,mol/\cancel{kg}\right)(0.02\,\cancel{kg}) = 0.0234\,mol$$

The ratio of mass to moles yields the final answer:

$$\frac{3.00\,g}{0.0234} = 128 g/mol$$

Vapor Pressure Lowering

For much the same reason as the lowering of freezing points and the elevation of boiling points for solvents into which a solute has been introduced, the vapor pressure of a volatile solvent will be decreased due to the introduction of a solute. The magnitude of this decrease can be quantified by examining the effect the solute has on the chemical potential of the solvent.

In order to establish equilibrium between the solvent in the solution and the solvent in the vapor phase above the solution, the chemical potentials of the two phases must be equal.

$$\mu_{vapor} = \mu_{solvent}$$

If the solute is not volatile, the vapor will be pure, so (assuming ideal behavior)

$$\mu^o_{vap} + RT \ln \frac{p'}{p^o} = \mu^o_A + RT \ln \chi_A \tag{6.3.7}$$

Where p' is the vapor pressure of the solvent over the solution. Similarly, for the pure solvent in equilibrium with its vapor

$$\mu^o_A = \mu^o_{vap} + RT \ln \frac{p_A}{p^o} \tag{6.3.8}$$

where p^o is the standard pressure of 1 atm, and p_A is the vapor pressure of the pure solvent. Substituting Equation 6.3.8 into Equation 6.3.7 yields

$$\cancel{\mu^o_{vap}} + RT \ln \frac{p'}{p^o} = \left(\cancel{\mu^o_{vap}} + RT \ln \frac{p_A}{p^o} \right) + RT \ln \chi_A$$

The terms for μ^o_{vap} cancel, leaving

$$RT \ln \frac{p'}{p^o} = RT \ln \frac{p_A}{p^o} + RT \ln \chi_A$$

Subtracting $RT \ln(P_A/P^o)$ from both side produces

$$RT \ln \frac{p'}{p^o} - RT \ln \frac{p_A}{p^o} = RT \ln \chi_A$$

which rearranges to

$$RT \ln \frac{p'}{p_A} = RT \ln \chi_A$$

Dividing both sides by RT and then exponentiating yields

$$\frac{p'}{p_A} = \chi_A$$

or

$$p' = \chi_A p_A \tag{6.3.9}$$

This last result is Raoult's Law. A more formal derivation would use the fugacities of the vapor phases, but would look essentially the same. Also, as in the case of freezing point depression and boiling point elevations, this derivation did not rely on the nature of the solute! However, unlike freezing point depression and boiling point elevation, this derivation did not rely on the solute being dilute, so the result should apply the entire range of concentrations of the solution.

Example 6.3.2:

Consider a mixture of two volatile liquids A and B. The vapor pressure of pure A is 150 Torr at some temperature, and that of pure B is 300 Torr at the same temperature. What is the total vapor pressure above a mixture of these compounds with the mole fraction of B of 0.600. What is the mole fraction of B in the vapor that is in equilibrium with the liquid mixture?

Solution

Using Raoult's Law (Equation 6.3.9)

$$p_A = (0.400)(150\,Toor) = 60.0\,Torr$$

$$p_B = (0.600)(300\,Toor) = 180.0\,Torr$$

$$p_{tot} = p_A + p_B = 240\,Torr$$

To get the mole fractions in the gas phase, one can use Dalton's Law of partial pressures.

$$\chi_A = \frac{p_A}{p_{tot}} = \frac{60.0\,Torr}{240\,Torr} = 0.250$$

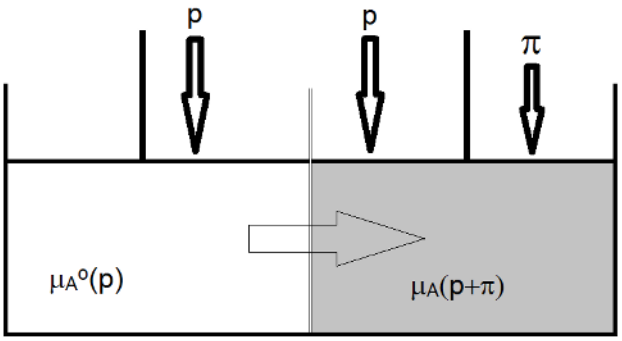
$$\chi_B = \frac{p_B}{p_{tot}} = \frac{180.0\,Torr}{240\,Torr} = 0.750$$

And, of course, it is also useful to note that the sum of the mole fractions is 1 (as it must be!)

$$\chi_A + \chi_B = 1$$

Osmotic Pressure

Osmosis is a process by which solvent can pass through a semi-permeable membrane (a membrane through which solvent can pass, but not solute) from an area of low solute concentration to a region of high solute concentration. The **osmotic pressure** is the pressure that when exerted on the region of high solute concentration will halt the process of osmosis.



The nature of osmosis and the magnitude of the osmotic pressure can be understood by examining the chemical potential of a pure solvent and that of the solvent in a solution. The chemical potential of the solvent in the solution (before any extra pressure is applied) is given by

$$\mu_A = \mu_A^o + RT \ln \chi_A$$

And since $x_A < 1$, the chemical potential is of the solvent in a solution is always lower than that of the pure solvent. So, to prevent osmosis from occurring, something needs to be done to raise the chemical potential of the solvent in the solution. This can be accomplished by applying pressure to the solution. Specifically, the process of osmosis will stop when the chemical potential solvent in the solution is increased to the point of being equal to that of the pure solvent. The criterion, therefore, for osmosis to cease is

$$\mu_A^o(p) = \mu_A(\chi_b, +\pi)$$

To solve the problem to determine the magnitude of p, the pressure dependence of the chemical potential is needed in addition to understanding the effect the solute has on lowering the chemical potential of the solvent in the solution. The magnitude, therefore, of the increase in chemical potential due to the application of excess pressure p must be equal to the magnitude of the reduction of chemical potential by the reduced mole fraction of the solvent in the solution. We already know that the chemical potential of the solvent in the solution is reduced by an amount given by

$$\mu_A^o - \mu_A = RT \ln \chi_A$$

And the increase in chemical potential due to the application of excess pressure is given by

$$\mu(p+\pi) = \mu(p) + \int_p^\pi \left(\frac{\partial \mu}{\partial p}\right)_T dp$$

The integrals on the right can be evaluated by recognizing

$$\left(\frac{\partial \mu}{\partial p}\right)_T = V$$

where V is the molar volume of the substance. Combining these expressions results in

$$-RT\ln\chi_A = \int_p^{p+\pi} V\,dp$$

If the molar volume of the solvent is independent of pressure (has a very small value of κ_T – which is the case for most liquids) the term on the right becomes.

$$\int_p^{\pi} V\,dP = Vp\Big|_p^{p+\pi} = V\pi$$

Also, for values of χ_A very close to 1

$$\ln\chi_A \approx -(1-\chi_A) = -\chi_B$$

So, for dilute solutions

$$\chi_B RT = V\pi$$

Or after rearrangement

$$\pi\frac{\chi_B RT}{V}$$

again, where V is the molar volume of the solvent. And finally, since χ_B/V is the concentration of the solute B for cases where $n_B \ll n_A$. This allows one to write a simplified version of the expression which can be used in the case of very dilute solutions

$$\pi = [B]RT$$

When a pressure exceeding the osmotic pressure π is applied to the solution, the chemical potential of the solvent in the solution can be made to exceed that of the pure solvent on the other side of the membrane, causing reverse osmosis to occur. This is a very effective method, for example, for recovering pure water from a mixture such as a salt/water solution.

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6.4: Solutions Exercises

TBA

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6.4.E: Mixtures and Solutions (Exercises)

Q7.1

The compression factor (Z) for O_2 at 200 K is measured to have the following values:

p (atm)	Z
1.000	0.9970
4.000	0.9880
7.000	0.9788
10.000	0.9700

Using numerical integration, calculate the fugacity constant for O_2 at 200 K from these data.

Q7.2

The normal boiling point of ethanol is 78.4 ^oC. Its enthalpy of vaporization is 38.6 kJ/mol. Estimate the vapor pressure of ethanol at 24.4 ^oC.

Q7.3

When 20.0 grams of an unknown nonelectrolyte compound are dissolved in 500.0 grams of benzene, the freezing point of the resulting solution is 3.77 °C. The freezing point of pure benzene is 5.444 °C and the cryoscopic constant (K_f) for benzene is 5.12 °C/m. What is the molar mass of the unknown compound?

Q7.4

Consider a mixture of two volatile liquids, A and B. The vapor pressure of pure liquid A is 324.3 Torr and that of pure liquid B is 502.3 Torr. What is the total vapor pressure over a mixture of the two liquids for which x_B = 0.675?

Q7.5

Consider the following expression for osmotic pressure

$$\pi V = \chi_B RT \tag{6.4.E.1}$$

where π is the osmotic pressure, V is the molar volume of the solvent, χ_B is the mole fraction of the solute, R is the gas law constant, and T is the temperature (in Kelvin).

The molar volume of a particular solvent is 0.0180 L/mol. 0.200 g of a solute (B) is dissolved in 1.00 mol of the solvent. The osmotic pressure of the solvent is then measured to be 0.640 atm at 298 K. Calculate the molar mass of the solute.

Q7.6

At 300 K, the vapor pressure of HCl(g) over a solution of HCl in $GeCl_4$ are summarized in the following table. Calculate the Henry's Law constant for HCl based on these data.

χ_{HCl}	P_{HCl} (kPa)
0.005	32.0
0.012	76.9
0.019	121.8

Q7.7

Consider the mixing of 1.00 mol of hexane (C_6H_{12}) with 1.00 mole of benzene (C_6H_6). Calculate \(\Delta H\), \(\Delta S\), and \(\Delta G\) of mixing, of the mixing occurs ideally at 298 K.

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CHAPTER OVERVIEW

7: The Development of Quantum Mechanics

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7.1.1: Quantum Hypothesis Used for Blackbody Radiation Law

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7.3.1: The Rydberg Formula and the Hydrogen Atomic Spectrum

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7.5: The Heisenberg Uncertainty Principle

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7.1: Blackbody Radiation

Learning Objectives

One experimental phenomenon that could not be adequately explained by classical physics was blackbody radiation. Objectives for this section include

- Be familiar with black-body radiators
- Understand the Rayleigh-Jeans Law and how it fails to properly model black-body radiation

All normal matter at temperatures above absolute zero emits electromagnetic radiation, which represents a conversion of a body's internal thermal energy into electromagnetic energy, and is therefore called *thermal radiation*. Conversely, all normal matter *absorbs* electromagnetic radiation to some degree. An object that absorbs ALL radiation falling on it, at all wavelengths, is called a blackbody. When a blackbody is at a uniform temperature, its emission has a characteristic frequency distribution that depends on the temperature. This emission is called *blackbody radiation*.

A room temperature blackbody appears black, as most of the energy it radiates is infra-red and cannot be perceived by the human eye. Because the human eye cannot perceive light waves at lower frequencies, a black body, viewed in the dark at the lowest just faintly visible temperature, subjectively appears grey, even though its objective physical spectrum peaks in the infrared range. When it becomes a little hotter, it appears dull red. As its temperature increases further it becomes yellow, white, and ultimately blue-white.



Figure 7.1.1 : Blackbody Radiation. When heated, all objects emit electromagnetic radiation whose wavelength (and color) depends on the temperature of the object. A relatively low-temperature object, such as a horseshoe forged by a blacksmith, appears red, whereas a higher-temperature object, such as the surface of the sun, appears yellow or white. Images used with permission from Wikipedia.

Blackbody radiation has a characteristic, continuous frequency spectrum that experimentally depends only on the body's temperature. In fact, we can be much more precise:

> *A body emits radiation at a given temperature and frequency exactly as well as it absorbs the same radiation.*

This statement was proved by Gustav Kirchhoff: the essential point is that if we *instead* suppose a particular body can absorb better than it emits, then in a room full of objects all at the same temperature, it will absorb radiation from the other bodies better than it radiates energy back to them. This means it will get hotter, and the rest of the room will grow colder, contradicting the second law of thermodynamics. *Thus, a body must emit radiation exactly as well as it absorbs the same radiation at a given temperature and frequency in order to not violate the second law of thermodynamics.*

Any body at any temperature above absolute zero **will** radiate to some extent, the intensity and frequency distribution of the radiation depending on the detailed structure of the body. To begin analyzing heat radiation, we need to be specific about the body doing the radiating: *the simplest possible case is an idealized body which is a perfect absorber, and therefore also (from the above argument) a perfect emitter.* So how do we construct a perfect absorber in the laboratory? In 1859 Kirchhoff had a good idea: a small hole in the side of a large box is an excellent absorber, since any radiation that goes through the hole bounces around inside, a lot getting absorbed on each bounce, and has little chance of ever getting out again. So, we can do this *in reverse*: have an oven

with a tiny hole in the side, and presumably the radiation coming out the hole is as good a representation of a perfect emitter as we're going to find (Figure 7.1.2).

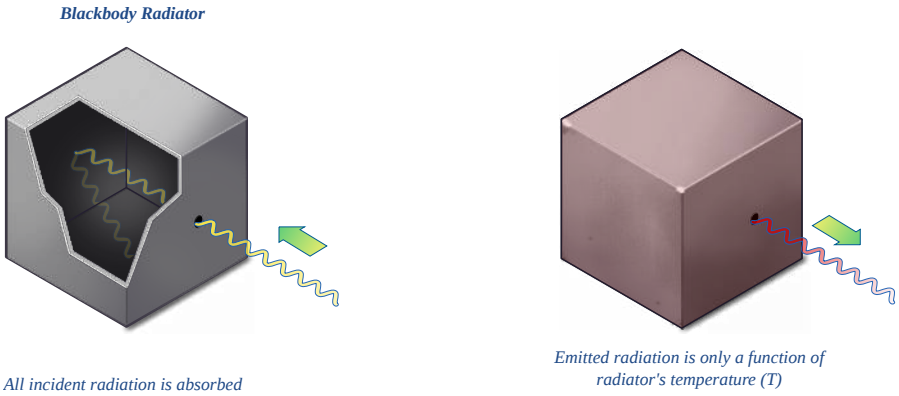


Figure 7.1.2 : Blackbody radiator is any object that is a perfect emitter and a perfect absorber of radiation. (CC BY-NC; Ümit Kaya via LibreTexts)

By the 1890's, experimental techniques had improved sufficiently that it was possible to make fairly precise measurements of the energy distribution of blackbody radiation. In 1895, at the University of Berlin, Wien and Lummer punched a small hole in the side of an otherwise completely closed oven, and began to measure the radiation coming out. The beam coming out of the hole was passed through a diffraction grating, which sent the different wavelengths/frequencies in different directions, all towards a screen. A detector was moved up and down along the screen to find how much radiant energy was being emitted in each frequency range. They found a radiation intensity/frequency curve close to the distributions in Figure 7.1.3 .

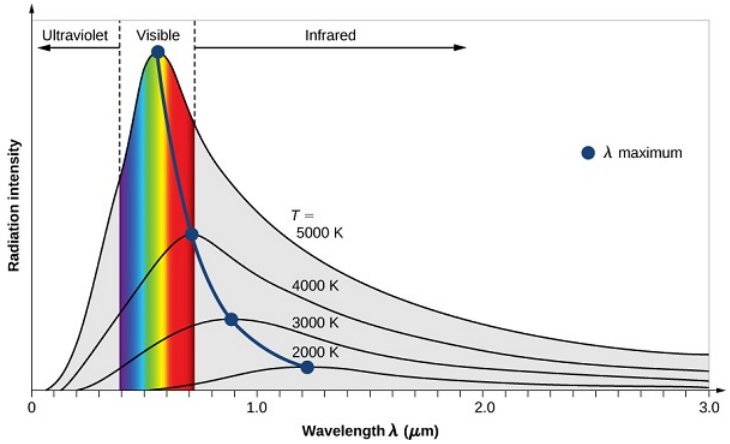
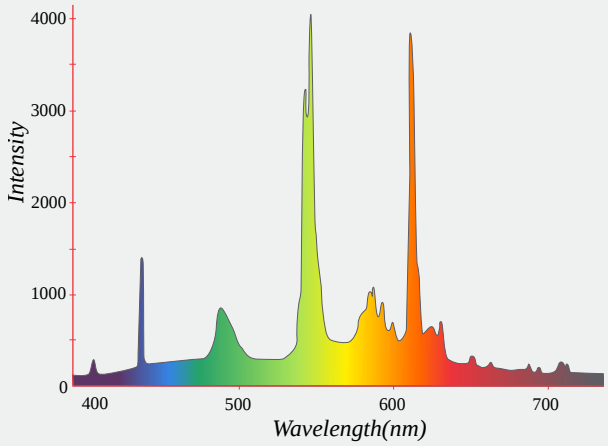


Figure 7.1.3 : Graphic representation of spectral distribution of blackbody radiation at different temperatures. The Stefan-Boltzmann's Law is observed as the increase in the emission amplitude with increasing temperature and the Wien's Displacement Law is observed as the shift to smaller wavelength with increasing temperature. (CC-BY 4.0; OpenStax)

Not all radiators are blackbody radiators

The radiation of a blackbody radiator is produced by the thermal activity of the material, not the nature of the material, nor how it got thermally excited. Some examples of blackbodies include incandescent light bulbs, stars, and hot stove tops. The emission appears as a continuous spectrum (Figure 7.1.3) with multiple coexisting colors. However, not every radiator is a blackbody radiator. For example, the emission of a fluorescence bulb is not one. The following spectrum show the distribution of light from a fluoresce light tube and is a mixture of discrete bands at different wavelengths of light in contrast to the continuous spectra in Figure 7.1.3 for blackbody radiators.



Fluorescent lighting spectrum with emission peaks. Graph of Intensity (counts) vs. Wavelength (nm) in the visible spectrum. (CC BY-NC; Ümit Kaya via LibreTexts).

Fluorescent light bulbs contain a mixture of inert gases (usually argon and neon) together with a drop of mercury at low pressure. A different mix of visible colors blend to produce a light that appears to us white with different shadings.

7.1.1: The Rayleigh-Jeans Law

Lord Rayleigh and J. H. Jeans developed an equation which explained blackbody radiation at low frequencies. The equation which seemed to express blackbody radiation was built upon all the known assumptions of physics at the time. *The big assumption which Rayleigh and Jean implied was that infinitesimal amounts of energy were continuously added to the system when the frequency was increased*. Classical physics assumed that energy emitted by atomic oscillations could have any continuous value. This was true for anything that had been studied up until that point, including things like acceleration, position, or energy. Their resulting **Rayleigh-Jeans Law** was

$$d\rho\left(\nu, T\right) = \rho_{\nu}\left(T\right) d\nu \tag{7.1.1}$$

$$= \frac{8\pi k_B T}{c^3}\nu^2 d\nu \tag{7.1.2}$$

Experimental data performed on the black box showed slightly different results than what was expected by the Rayleigh-Jeans law (Figure 7.1.5). The law had been studied and widely accepted by many physicists of the day, but the experimental results did not lie, something was different between what was theorized and what actually happens. The experimental results showed a bell type of curve, but according to the Rayleigh-Jeans law the frequency diverged as it neared the ultraviolet region (Equation 7.1.2). Ehrenfest later dubbed this the "ultraviolet catastrophe". It is important to emphasizing that Equation 7.1.2 is a **classical** result: the only inputs are classical dynamics and Maxwell's electromagnetic theory.

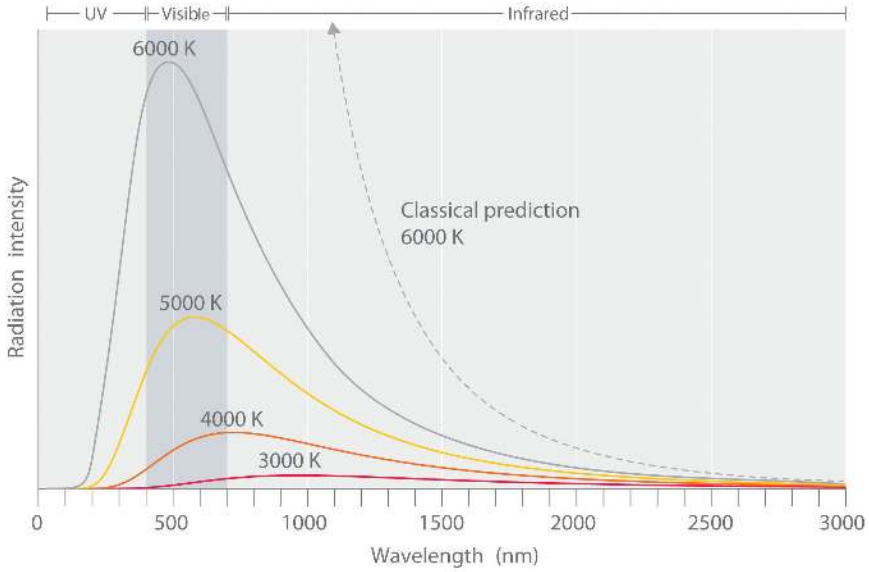


Figure 7.1.5 : Relationship between the temperature of an object and the spectrum of blackbody radiation it emits. At relatively low temperatures, most radiation is emitted at wavelengths longer than 700 nm, which is in the infrared portion of the spectrum. The dull red glow of the hot metalwork in Figure 7.1.5 is due to the small amount of radiation emitted at wavelengths less than 700 nm, which the eye can detect. As the temperature of the object increases, the maximum intensity shifts to shorter wavelengths, successively resulting in orange, yellow, and finally white light. At high temperatures, all wavelengths of visible light are emitted with approximately equal intensities. (CC BY-SA-NC; anonymous)

Differential vs. Integral Representation of the Distribution

Radiation is understood as a continuous distribution of amplitude vs. wavelength or, equivalently, amplitude vs. frequency (Figure 7.1.5). According to Rayleigh-Jeans law, the intensity at a specific frequency ν and temperature is

$$\rho(\nu, T) = \frac{8\pi k_b T \nu^2}{c^3}.$$

However, in practice, we are more interested in frequency intervals. An exact frequency is the limit of a sequence of smaller and smaller intervals. If we make the assumption that, for a sufficiently small interval, $\rho(\nu, T)$ does not vary, we get your definition for the differential $d\rho(\nu, T)$ in Equation 7.1.2:

The assumption is fair due to the continuity of $\rho(\nu, T)$. This is the approximation of an integral on a very small interval $d\nu$ by the height of a point inside this interval ($\frac{8\pi k_b T \nu^2}{c^3}$) times its length ($d\nu$). So, if we sum an infinite amount of small intervals like the one above we get an integral. The total radiation between ν_1 and ν_2 will be:

$$\begin{aligned}\int_{\nu_1}^{\nu_2} \mathrm{d}\rho(\nu, T) &= \int_{\nu_1}^{\nu_2} \rho(\nu, T)\, \mathrm{d}\nu \\ &= \int_{\nu_1}^{\nu_2} \frac{8\pi k_b T \nu^2}{c^3} \mathrm{d}\nu \\ &= 8\pi k_b T \frac{v_2^3 - v_1^3}{3c^3}.\end{aligned}$$

Observe that $\rho(\nu, T)$ is quadratic in ν.

Example 7.1.4 : The Ultraviolet Catastrophe

What is the total spectral radiance of a radiator that follows the Rayleigh-Jeans law for its emission spectrum?

Solution

The total spectral radiance $\rho_{tot}(T)$ is the combined emission over all possible wavelengths (or equivalently, frequencies), which is an integral over the relevant distribution (Equation 7.1.2 for the Rayleigh-Jeans Law).

$$\rho_{tot}(T) = \int_0^\infty d\rho\,(\nu, T)$$
$$= \int_0^\infty \frac{8\pi k_B T}{c^3}\nu^2 d\nu$$

but the integral

$$\int_0^\infty x^2 \mathrm{d}x$$

does not converge. Worse, it is infinite,

$$\lim_{k\to\infty}\int_0^k x^2 \mathrm{d}x = \infty$$

Hence, the classically derived Rayleigh-Jeans law predicts that the radiance of a blackbody is **infinite**. Since radiance is power per angle and unit area, this also implies that the total power and hence the energy a blackbody emitter gives off is infinite, which is patently absurd. This is called the ultraviolet catastrophe because the absurd prediction is caused by the classical law not predicting the behavior at high frequencies/small wavelengths correctly (Figure 7.1.5).

Contributors and Attributions

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7.1.1: Quantum Hypothesis Used for Blackbody Radiation Law

Learning Objectives

- To understand how energy is quantized in blackbody radiation

By the late 19th century, many physicists thought their discipline was well on the way to explaining most natural phenomena. They could calculate the motions of material objects using Newton's laws of classical mechanics, and they could describe the properties of radiant energy using mathematical relationships known as Maxwell's equations, developed in 1873 by James Clerk Maxwell, a Scottish physicist. The universe appeared to be a simple and orderly place, containing matter, which consisted of particles that had mass and whose location and motion could be accurately described, and electromagnetic radiation, which was viewed as having no mass and whose exact position in space could not be fixed. Thus matter and energy were considered distinct and unrelated phenomena. Soon, however, scientists began to look more closely at a few inconvenient phenomena that could not be explained by the theories available at the time.

One experimental phenomenon that could not be adequately explained by classical physics was blackbody radiation (Figure 1.2.1). Attempts to explain or calculate this spectral distribution from classical theory were complete failures. A theory developed by Rayleigh and Jeans predicted that the intensity should go to infinity at short wavelengths. Since the intensity actually drops to zero at short wavelengths, the Rayleigh-Jeans result was called the **ultraviolet catastrophe** (Figure 1.2.1 dashed line). There was no agreement between theory and experiment in the ultraviolet region of the blackbody spectrum.

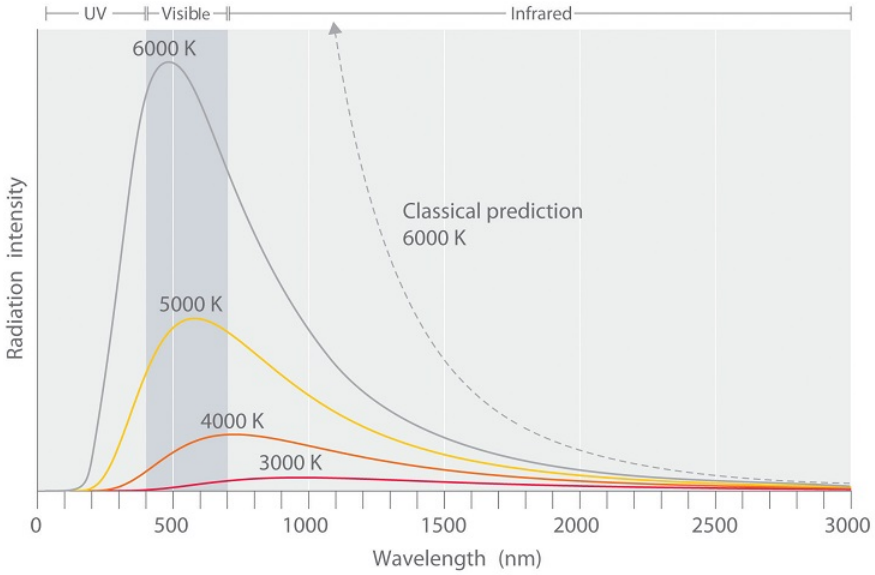


Figure 1.2.1 : Relationship between the temperature of an object and the spectrum of blackbody radiation it emits. At relatively low temperatures, most radiation is emitted at wavelengths longer than 700 nm, which is in the infrared portion of the spectrum. As the temperature of the object increases, the maximum intensity shifts to shorter wavelengths, successively resulting in orange, yellow, and finally white light. At high temperatures, all wavelengths of visible light are emitted with approximately equal intensities. The white light spectrum shown for an object at 6000 K closely approximates the spectrum of light emitted by the sun. Note the sharp decrease in the intensity of radiation emitted at wavelengths below 400 nm, which constituted the ultraviolet catastrophe. The classical prediction fails to fit the experimental curves entirely and does not have a maximum intensity. (CC BY-SA-NC; anonymous).

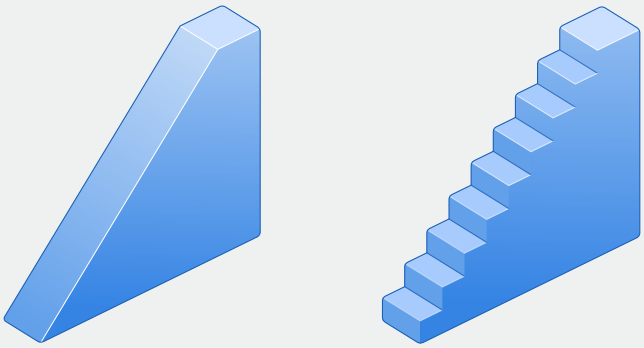
7.1.1.1: Quantizing Electrons in the Radiator

In 1900, the German physicist Max Planck (1858–1947) explained the ultraviolet catastrophe by proposing that the energy of electromagnetic waves is *quantized* rather than continuous. This means that for each temperature, there is a maximum intensity of radiation that is emitted in a blackbody object, corresponding to the peaks in Figure 1.2.1 , so the intensity does not follow a smooth curve as the temperature increases, as predicted by classical physics. Thus energy could be gained or lost only in integral

multiples of some smallest unit of energy, a quantum (the smallest possible unit of energy). Energy can be gained or lost only in integral multiples of a quantum.

Quantization

Although quantization may seem to be an unfamiliar concept, we encounter it frequently in quantum mechanics (hence the name). For example, US money is integral multiples of pennies. Similarly, musical instruments like a piano or a trumpet can produce only certain musical notes, such as C or F sharp. Because these instruments cannot produce a continuous range of frequencies, their frequencies are quantized. It is also similar to going up and down a hill using discrete stair steps rather than being able to move up and down a continuous slope. Your potential energy takes on discrete values as you move from step to step. Even electrical charge is quantized: an ion may have a charge of −1 or −2, but *not* −1.33 electron charges.



A continuous vs. a quantized (gravitationaly) potential energy system. In the continuous case (left) a system can have any potential energy, but in the quantized case (right), a system can only have certain values (other values are not allowed). (CC BY-NC; Ümit Kaya via LibreTexts)

Planck's quantization of energy is described by the his famous equation:

$$E = h\nu \tag{7.1.1.1}$$

where the proportionality constant h is called **Planck's constant**, one of the most accurately known fundamental constants in science

$$h = 6.626070040(81) \times 10^{-34}\, J \cdot s$$

However, for our purposes, its value to four significant figures is sufficient:

$$h = 6.626 \times 10^{-34}\, J \cdot s$$

As the frequency of electromagnetic radiation increases, the magnitude of the associated quantum of radiant energy increases. By assuming that energy can be emitted by an object only in integral multiples of $h\nu$, Planck devised an equation that fit the experimental data shown in Figure 1.2.1 . We can understand Planck's explanation of the ultraviolet catastrophe qualitatively as follows: At low temperatures, radiation with only relatively low frequencies is emitted, corresponding to low-energy quanta. As the temperature of an object increases, there is an increased probability of emitting radiation with higher frequencies, corresponding to higher-energy quanta. At any temperature, however, it is simply more probable for an object to lose energy by emitting a large number of lower-energy quanta than a single very high-energy quantum that corresponds to ultraviolet radiation. The result is a maximum in the plot of intensity of emitted radiation versus wavelength, as shown in Figure 1.2.1 , and a shift in the position of the maximum to lower wavelength (higher frequency) with increasing temperature.

At the time he proposed his radical hypothesis, Planck could not explain *why* energies should be quantized. Initially, his hypothesis explained only one set of experimental data—blackbody radiation. If quantization were observed for a large number of different phenomena, then quantization would become a law. In time, a theory might be developed to explain that law. As things turned out, Planck's hypothesis was the seed from which modern physics grew.

Max Planck explain the spectral distribution of blackbody radiation as result from oscillations of electrons. Similarly, oscillations of electrons in an antenna produce radio waves. Max Planck concentrated on modeling the oscillating charges that must exist in the oven walls, radiating heat inwards and—in thermodynamic equilibrium—themselves being driven by the radiation field. He found he could account for the observed curve if he required these oscillators not to radiate energy continuously, as the classical theory would demand, but they could **only** lose or gain energy in chunks, called **quanta**, of size $h\nu$, for an oscillator of frequency ν (Equation 7.1.1.1).

With that assumption, Planck calculated the following formula for the radiation energy density inside the oven:

$$d\rho(\nu,T) = \rho_\nu(T)d\nu \tag{7.1.1.2}$$

$$= \frac{8\pi h\nu^3}{c^3} \cdot \frac{1}{\exp\left(\frac{h\nu}{k_BT}\right)-1}d\nu \tag{7.1.1.3}$$

with

- $\pi = 3.14159$
- $h = 6.626 \times 10^{-34} J \cdot s$
- $c = 3.00 \times 10^8 m/s$
- $\nu = 1/s$
- $k_B = 1.38 \times 10^{-23} J/K$
- T is absolute temperature (in Kelvin)

Planck's radiation energy density (Equation 7.1.1.3) can also be expressed in terms of wavelength λ.

$$\rho(\lambda,T) = \frac{8\pi hc}{\lambda^5}\left(\frac{1}{e^{hc/\lambda k_BT}-1}\right) \tag{7.1.1.4}$$

With a wavelength of maximum energy density at:

$$\lambda_{max} = \frac{hc}{4.965kT}$$

This can be used to calculate the radiance emitted from surface per unit frequency

$$dB_\nu(\nu,T) = \rho_\nu(T)d\nu$$

$$= \frac{2h\nu^3}{c^2} \cdot \frac{1}{\exp\left(\frac{h\nu}{k_BT}\right)-1}d\nu \tag{7.1.1.5}$$

or

$$B_\lambda(\lambda,T) = \frac{2hc^2}{\lambda^5}\frac{1}{e^{hc/(\lambda k_BT)}-1} \tag{7.1.1.6}$$

Planck's equation (Equation 7.1.1.4) gave an excellent agreement with the experimental observations for all temperatures (Figure 1.2.2).

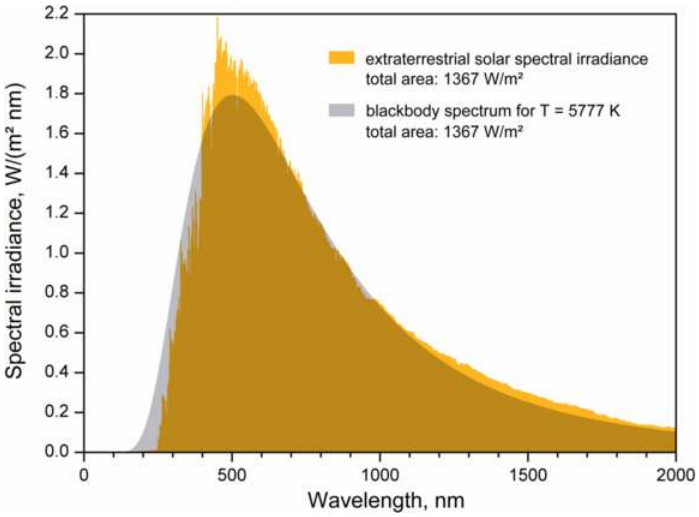
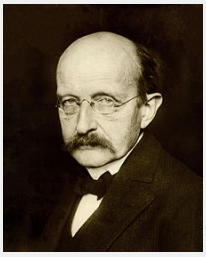


Figure 1.2.2 : The Sun is an excellent approximation of a blackbody. Its effective temperature is ~5777 K. (CC-SA-BY 3.0; Sch).

Max Planck (1858–1947)

Planck made many substantial contributions to theoretical physics, but his fame as a physicist rests primarily on his role as the originator of quantum theory. In addition to being a physicist, Planck was a gifted pianist, who at one time considered music as a career. During the 1930s, Planck felt it was his duty to remain in Germany, despite his open opposition to the policies of the Nazi government.



MAX-PLANCK-GESELLSCHAFT

(left) The German physicist Max Planck had a major influence on the early development of quantum mechanics, being the first to recognize that energy is sometimes quantized. Planck also made important contributions to special relativity and classical physics. (Public Domain; Library of Congress via Wikimedia) (left) The society's logo features Minerva, the Roman goddess of wisdom. (Fair use)

One of his sons was executed in 1944 for his part in an unsuccessful attempt to assassinate Hitler and bombing during the last weeks of World War II destroyed Planck's home. After WWII, the major German scientific research organization was renamed the Max Planck Society.

Exercise 1.2.1

Use Equation 7.1.1.4 to show that the units of $\rho(\lambda, T)\, d\lambda$ are J/m^3 as expected for an energy density.

The near perfect agreement of this formula with precise experiments (e.g., Figure 1.2.3), and the consequent necessity of energy quantization, was the most important advance in physics in the century. His blackbody curve was completely accepted as the correct one: more and more accurate experiments confirmed it time and again, yet the radical nature of the quantum assumption did not sink in. Planck was not too upset—he didn't believe it either, he saw it as a technical fix that (he hoped) would eventually prove unnecessary.

> *Part of the problem was that Planck's route to the formula was long, difficult and implausible—he even made contradictory assumptions at different stages, as Einstein pointed out later. However, the result was correct anyway!*

The mathematics implied that the energy given off by a blackbody was not continuous, but given off at certain specific wavelengths, in regular increments. If Planck assumed that the energy of blackbody radiation was in the form

$$E = nh\nu$$

where n is an integer, then he could explain what the mathematics represented. This was indeed difficult for Planck to accept, because at the time, there was no reason to presume that the energy should only be radiated at specific frequencies. Nothing in Maxwell's laws suggested such a thing. It was as if the vibrations of a mass on the end of a spring could only occur at specific energies. Imagine the mass slowly coming to rest due to friction, but not in a continuous manner. Instead, the mass jumps from one fixed quantity of energy to another without passing through the intermediate energies.

> *To use a different analogy, it is as if what we had always imagined as smooth inclined planes were, in fact, a series of closely spaced steps that only presented the illusion of continuity.*

7.1.1.2: Summary

The agreement between Planck's theory and the experimental observation provided strong evidence that the energy of electron motion in matter is quantized. In the next two sections, we will see that the energy carried by light also is quantized in units of $h\bar{\nu}$. These packets of energy are called "photons."

Contributors and Attributions

- Michael Fowler (Beams Professor, Department of Physics, University of Virginia)
- David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski ("Quantum States of Atoms and Molecules")

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7.2: The Photoelectric Effect

Learning Objectives

- To be familiar with the photoelectron effect for bulk materials
- Understand how the photoelectron kinetic energy and intensity vary as a function of incident light wavelength
- Understand how the photoelectron kinetic energy and intensity vary as a function of incident light intensity
- Describe what a workfunction is and relate it to ionization energy
- Describe the photoelectric effect with Einstein's quantized photon model of light

Nature, it seemed, was quantized (non-continuous, or discrete). If this was so, how could Maxwell's equations correctly predict the result of the blackbody radiator? Planck spent a good deal of time attempting to reconcile the behavior of electromagnetic waves with the discrete nature of the blackbody radiation, to no avail. It was not until 1905, with yet another paper published by Albert Einstein, that the wave nature of light was expanded to include the particle interpretation of light which adequately explained Planck's equation.

The photoelectric effect was first documented in 1887 by the German physicist Heinrich Hertz and is therefore sometimes referred to as the Hertz effect. While working with a spark-gap transmitter (a primitive radio-broadcasting device), Hertz discovered that upon absorption of certain frequencies of light, substances would give off a visible spark. In 1899, this spark was identified as light-excited electrons (called **photoelectrons**) leaving the metal's surface by J.J. Thomson (Figure 1.3.1).

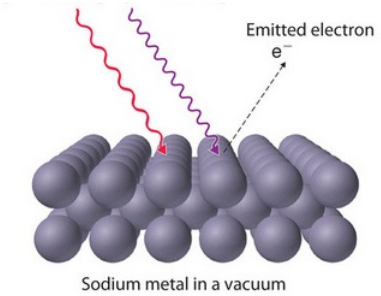


Figure 1.3.1 : The photoelectric effect involves irradiating a metal surface with photons of sufficiently high energy to cause the electrons to be ejected from the metal. (CC BY-SA-NC; anonymous)

The classical picture underlying the photoelectron effect was that the atoms in the metal contained electrons, that were shaken and caused to vibrate by the oscillating electric field of the incident radiation. Eventually some of them would be shaken loose, and would be ejected from the cathode. It is worthwhile considering carefully how the *number* and *speed* of electrons emitted would be expected to vary with the *intensity* and *color* of the incident radiation along with the time needed to observe the photoelectrons.

- Increasing the intensity of radiation would shake the electrons more violently, so one would expect more to be emitted, and they would shoot out at greater speed, on average.
- Increasing the frequency of the radiation would shake the electrons faster, so it might cause the electrons to come out faster. For very dim light, it would take some time for an electron to work up to a sufficient amplitude of vibration to shake loose.

7.2.1: Lenard's Experimental Results (Intensity Dependence)

In 1902, Hertz's student, Philipp Lenard, studied how the energy of the emitted photoelectrons varied with the intensity of the light. He used a carbon arc light and could increase the intensity a thousand-fold. The ejected electrons hit another metal plate, the collector, which was connected to the cathode by a wire with a sensitive ammeter, to measure the current produced by the illumination (Figure 1.3.2). To measure the energy of the ejected electrons, Lenard charged the collector plate negatively, to repel the electrons coming towards it. Thus, only electrons ejected with enough kinetic energy to get up this potential hill would contribute to the current.

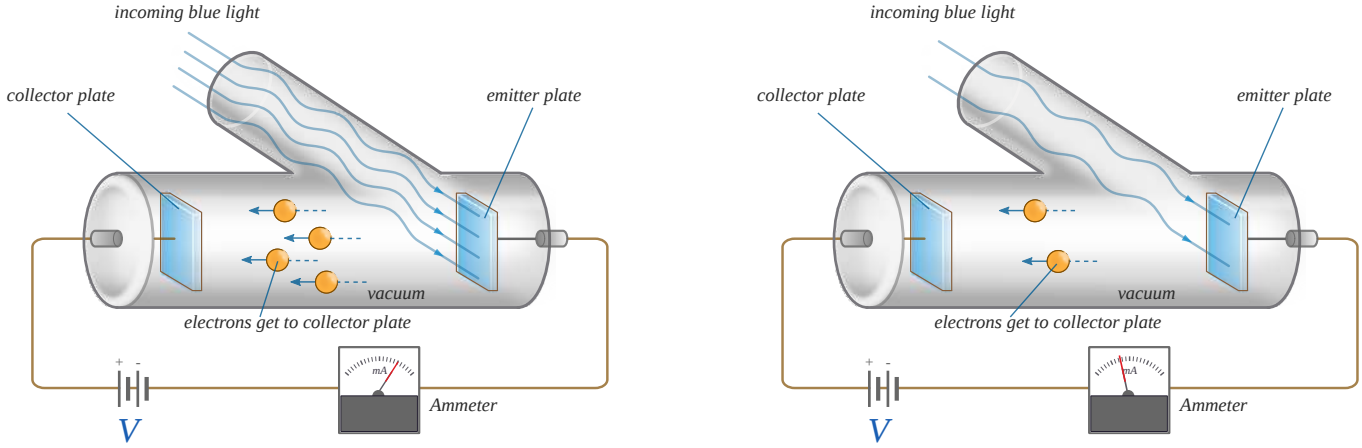


Figure **7.2.2**: Lenard's photoelectric experiment. (left) High light intensity increase photocurrent (number of collected photoelectrons). (right) Low light intensity has reduced photocurrent. However, the kinetic energy of the ejected electrons is independent of incident light intensity. (CC BY-NC; Ümit Kaya via LibreTexts)

Lenard discovered that there was a well defined minimum voltage that stopped any electrons getting through (V_{stop}). To Lenard's surprise, he found that V_{stop} did not depend at all on the intensity of the light! Doubling the light intensity doubled the *number* of electrons emitted, but did not affect the *kinetic energies* of the emitted electrons. The more powerful oscillating field ejected more electrons, but the maximum individual energy of the ejected electrons was the same as for the weaker field (Figure 1.3.2).

7.2.2: Millikan's Experimental Results (Wavelength Dependence)

The American experimental physicist Robert Millikan followed up on Lenard's experiments and using a powerful arc lamp, he was able to generate sufficient light intensity to separate out the colors and check the photoelectric effect using light of different colors. He found that the maximum energy of the ejected electrons *did* depend on the color - the shorter wavelength, higher frequency light eject photoelectrons with greater kinetic energy (Figures 1.3.3).

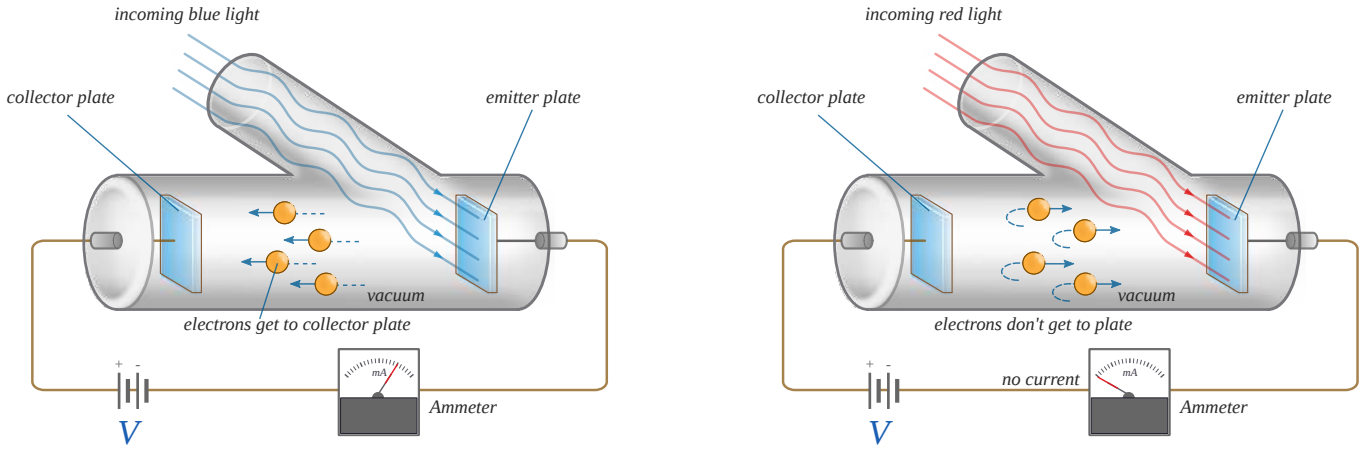


Figure 1.3.3 : Millikan's photoelectric experiment. (left) Incident high-energy blue light. The battery represents the potential Lenard used to charge the collector plate negatively, which would actually be a variable voltage source. Since the electrons ejected by the blue light are getting to the collector plate, the potential supplied by the battery is less than V_{stop}, for blue light. (right) Indicent low-energy red light. Since the electrons ejected by the red light are not getting to the collector plate, the potential supplied by the battery exceeds V_{stop} for red light. (CC BY-NC; Ümit Kaya via LibreTexts)

As shown in Figure 1.3.4 , just the opposite behavior from classical is observed from Lenard's and Millikan's experiments. The intensity affects the number of electrons, and the frequency affects the kinetic energy of the emitted electrons. From these sketches, we see that

- the kinetic energy of the electrons is linearly proportional to the frequency of the incident radiation above a threshold value of ν_0 (no current is observed below ν_0), and the kinetic energy is independent of the intensity of the radiation, and
- the number of electrons (i.e. the electric current) is proportional to the intensity and independent of the frequency of the incident radiation above the threshold value of ν_0 (i.e., no current is observed below ν_0).

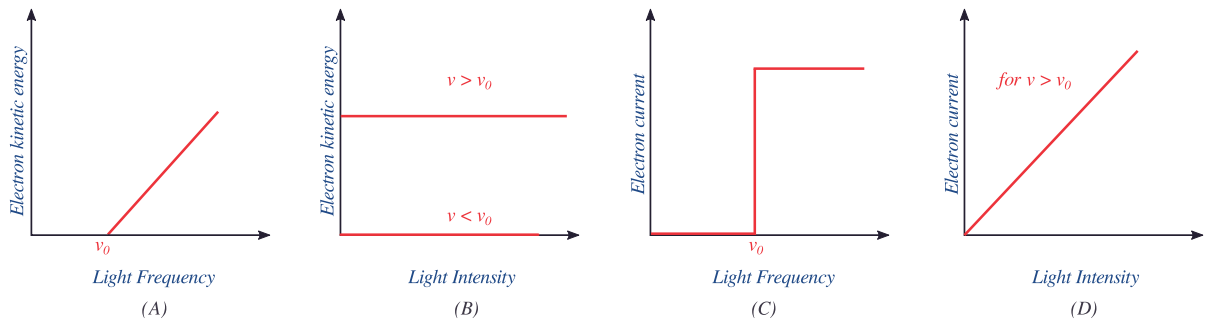


Figure 1.3.4 : Schematic drawings showing the characteristics of the photoelectric effect from Lenard's and Millikan's experiments. (A) The kinetic energy of any single emitted electron increases linearly with frequency above some threshold value (B) The electron kinetic energy is independent of the light intensity above the threshold frequency and zero below. (C) The number of electrons emitted per second (i.e. the electric current) is independent of light frequency above the threshhold frequency and zero below. (D) The number of electrons increases linearly with the light intensity. (CC BY-NC; Ümit Kaya via LibreTexts)

Classical Theory does not Describe Experiment

Classical theory predicts that energy carried by light is proportional to its amplitude independent of its frequency, and this fails to correctly explain the observed wavelength dependence in Lenard's and Millikan's observations.

As with most of the experimental results we discuss in this text, the behavior described above is a simplification of the true experimental results observed in the laboratory. A more complex description involves a greater introduction of more complex physics and instrumentation, which will be ignored for now.

7.2.3: Einstein's Quantum Picture

In 1905 Einstein gave a very simple interpretation of Lenard's results and borrowed Planck's hypothesis about the quantized energy from his blackbody research and assumed that the incoming radiation should be thought of as quanta of energy $h\nu$, with ν the frequency. In photoemission, one such quantum is absorbed by one electron. If the electron is some distance into the material of the cathode, some energy will be lost as it moves towards the surface. There will always be some electrostatic cost as the electron leaves the surface, which is the workfunction, Φ. The most energetic electrons emitted will be those very close to the surface, and they will leave the cathode with kinetic energy

$$KE = h\nu - \Phi \tag{7.2.1}$$

On cranking up the negative voltage on the collector plate until the current just stops, that is, to V_{stop}, the highest kinetic energy electrons (KE_e) must have had energy eV_{stop} upon leaving the cathode. Thus,

$$eV_{stop} = h\nu - \Phi \tag{7.2.2}$$

Thus, Einstein's theory makes a very definite quantitative prediction: if the frequency of the incident light is varied, and V_{stop} plotted as a function of frequency, the slope of the line should be $\frac{h}{e}$ (Figure 7.2.4*A*). It is also clear that there is a minimum light frequency for a given metal ν_o, that for which the quantum of energy is equal to Φ (Equation 7.2.1). Light below that frequency, no matter how bright, will not eject electrons.

> *According to both Planck and Einstein, the energy of light is proportional to its frequency rather than its amplitude, there will be a minimum frequency ν_0 needed to eject an electron with no residual energy.*

Since every photon of sufficient energy excites only one electron, increasing the light's intensity (i.e. the number of photons/sec) only increases the *number* of released electrons and not their kinetic energy. In addition, no time is necessary for the atom to be heated to a critical temperature and therefore the release of the electron is nearly instantaneous upon absorption of the light. Finally, because the photons must be above a certain energy to satisfy the workfunction, a threshold frequency exists below which no

photoelectrons are observed. This frequency is measured in units of Hertz (1/second) in honor of the discoverer of the photoelectric effect.

Einstein's Equation 7.2.1 explains the properties of the photoelectric effect quantitatively. A strange implication of this experiment is that light can behave as a kind of massless "particle" now known as a *photon* whose energy $E = h\nu$ can be transferred to an actual particle (an electron), imparting kinetic energy to it, just as in an elastic collision between to massive particles such as billiard balls.

> Robert Millikan initially did not accept Einstein's theory, which he saw as an attack on the wave theory of light, and worked for ten years until 1916, on the photoelectric effect. He even devised techniques for scraping clean the metal surfaces inside the vacuum tube. For all his efforts he found disappointing results: he confirmed Einstein's theory after ten years. In what he writes in his paper, Millikan is still desperately struggling to avoid this conclusion. However, by the time of his Nobel Prize acceptance speech, he has changed his mind rather drastically!

Einstein's simple explanation (Equation 7.2.1) completely accounted for the observed phenomena in Lenard's and Millikan's experiments (Figure 1.3.4) and began an investigation into the field we now call *quantum mechanics*. This new field seeks to provide a quantum explanation for classical mechanics and create a more unified theory of physics and thermodynamics. The study of the photoelectric effect has also lead to the creation of new field of photoelectron spectroscopy. Einstein's theory of the photoelectron presented a completely different way to measure Planck's constant than from black-body radiation.

7.2.4: The Workfunction (Φ)

The **workfunction** is an intrinsic property of the metal. While the workfunctions and ionization energies appear as similar concepts, they are independent. The workfunction of a metal is the minimum amount of energy (**E**) necessary to remove an electron from the surface of the bulk (*solid*) metal (sometimes referred to as **binding energy**).

$$\mathrm{M(s) + \Phi \rightarrow M^{+}(s) + e^{-}(\text{free with no kinetic energy})}$$

The workfunction is qualitatively similar to ionization energy (**IE**), which is the amount of energy required to remove an electron from an atom or molecule in the *gaseous* state.

$$\mathrm{M(g) + IE \rightarrow M^{+}(g) + e^{-}(\text{free with no kinetic energy})}$$

However, these two energies differ in magnitude (Table 1.3.1). For instance, copper has a workfunction of about 4.7 eV, but has a higher ionization energy of 7.7 eV. Generally, the ionization energies for metals are greater than the corresponding workfunctions (i.e., the electrons are less tightly bound in bulk metal).

Table 1.3.1 : Workfunctions and Ionization Energies of Select Elements

Element	Workfunction Φ (eV)	Ionization Energy (eV)
Lithium (Li)	2.93	5.39
Beryllium (Be)	4.98	9.32
Boron (B)	4.45	8.298
Carbon (C)	5.0	11.26
Sodium (Na)	2.36	5.13
Aluminum (Al)	4.20	5.98
Silicon (Si)	4.85	8.15
Potassium (K)	2.3	4.34
Iron (Fe)	4.67	7.87
Cobalt (Co)	4.89	7.88
Copper (Cu)	4.7	7.7
Gallium (Ga)	4.32	5.99
Germanium (Ge)	5.0	7.89
Arsenic (As)	3.75	9.81
Selenium (Se)	5.9	9.75
Silver (Ag)	4.72	7.57
Tin (Sn)	4.42	7.34
Cesium (Cs)	1.95	3.89
Gold (Au)	5.17	9.22
Mercury $(Hg)_{liquid}$	4.47	10.43
Bismuth (Bi)	4.34	7.29

Example 1.3.1 : Calcium

a. What is the energy in joules and electron volts of a photon of 420-nm violet light?
b. What is the maximum kinetic energy of electrons ejected from calcium by 420-nm violet light, given that the workfunction for calcium metal is 2.71 eV?

Strategy

To solve part (a), note that the energy of a photon is given by $E = h\nu$. For part (b), once the energy of the photon is calculated, it is a straightforward application of Equation 7.2.1 to find the ejected electron's maximum kinetic energy, since Φ is given.

Solution for (a)

Photon energy is given by

$$E = h\nu$$

Since we are given the wavelength rather than the frequency, we solve the familiar relationship $c = \nu\lambda$ for the frequency, yielding

$$\nu = \frac{c}{\lambda}$$

Combining these two equations gives the useful relationship

$$E = \frac{hc}{\lambda}$$

Now substituting known values yields

$$\begin{aligned} E &= \frac{(6.63 \times 10^{-34}\ J \cdot s)(3.00 \times 10^{8} m/s)}{420 \times 10^{-9}\ m} \\ &= 4.74 \times 10^{-19}\ J \end{aligned}$$

Converting to eV, the energy of the photon is

$$\begin{aligned} E &= (4.74 \times 10^{-19}\ J)\left(\frac{1\ eV}{1.6 \times 10^{-19}\ J}\right) \\ &= 2.96\ eV. \end{aligned}$$

Solution for (b)

Finding the kinetic energy of the ejected electron is now a simple application of Equation 7.2.1. Substituting the photon energy and binding energy yields

$$\begin{aligned} KE_e &= h\nu – \Phi \\ &= 2.96\ eV – 2.71\ eV \\ &= 0.246\ eV. \end{aligned}$$

Discussion

The energy of this 420-nm photon of violet light is a tiny fraction of a joule, and so it is no wonder that a single photon would be difficult for us to sense directly—humans are more attuned to energies on the order of joules. But looking at the energy in electron volts, we can see that this photon has enough energy to affect atoms and molecules. A DNA molecule can be broken with about 1 eV of energy, for example, and typical atomic and molecular energies are on the order of eV, so that the UV photon in this example could have biological effects.

The ejected electron (called a photoelectron) has a rather low energy, and it would not travel far, except in a vacuum. The electron would be stopped by a retarding potential of 0.26 eV. In fact, if the photon wavelength were longer and its energy less than 2.71 eV, then the formula would give a negative kinetic energy, an impossibility. This simply means that the 420-nm photons with their 2.96-eV energy are not much above the frequency threshold. You can show for yourself that the threshold wavelength is 459 nm (blue light). This means that if calcium metal is used in a light meter, the meter will be insensitive to wavelengths longer than those of blue light. Such a light meter would be insensitive to red light, for example.

? Exercise 1.3.1 : Silver

What is the longest-wavelength electromagnetic radiation that can eject a photoelectron from silver? Is this in the visible range?

Answer

Given that the workfunction is 4.72 eV from Table 1.3.1 , then only photons with wavelengths lower than 263 nm will induce photoelectrons (calculated via $E = h\nu$). This is ultraviolet and not in the visible range.

? Exercise 1.3.2

Why is the workfunction of an element generally lower than the ionization energy of that element?

Answer

The workfunction of a metal refers to the minimum energy required to extract an electron from the surface of a (**bulk**) metal by the absorption a photon of light. The workfunction will vary from metal to metal. In contrast, ionization energy is

the energy needed to detach electrons from **atoms** and also varies with each particular atom, with the valence electrons require less energy to extract than core electrons (i.e., from lower shells) that are more closely bound to the nuclei. The electrons in the metal lattice there less bound (i.e., free to move within the metal) and removing one of these electrons is much easier than removing an electron from an atom because the metallic bonds of the bulk metal reduces their binding energy. As we will show in subsequent chapters, the more delocalized a particle is, the lower its energy.

7.2.5: Summary

Although Hertz discovered the photoelectron in 1887, it was not until 1905 that a theory was proposed that explained the effect completely. The theory was proposed by Einstein and it made the claim that electromagnetic radiation had to be thought of as a series of particles, called photons, which collide with the electrons on the surface and emit them. This theory ran contrary to the belief that electromagnetic radiation was a wave and thus it was not recognized as correct until 1916 when Robert Millikan experimentally confirmed the theory

The photoelectric effect is the process in which electromagnetic radiation ejects electrons from a material. Einstein proposed photons to be quanta of electromagnetic radiation having energy $E = h\nu$ is the frequency of the radiation. All electromagnetic radiation is composed of photons. As Einstein explained, all characteristics of the photoelectric effect are due to the interaction of individual photons with individual electrons. The maximum kinetic energy KE_e of ejected electrons (photoelectrons) is given by $KE_e = h\nu - \Phi$, where $h\nu$ is the photon energy and Φ is the workfunction (or binding energy) of the electron to the particular material.

7.2.6: Conceptual Questions

1. Is visible light the only type of electromagnetic radiation that can cause the photoelectric effect?
2. Which aspects of the photoelectric effect cannot be explained without photons? Which can be explained without photons? Are the latter inconsistent with the existence of photons?
3. Is the photoelectric effect a direct consequence of the wave character of electromagnetic radiation or of the particle character of electromagnetic radiation? Explain briefly.
4. Insulators (nonmetals) have a higher Φ than metals, and it is more difficult for photons to eject electrons from insulators. Discuss how this relates to the free charges in metals that make them good conductors.
5. If you pick up and shake a piece of metal that has electrons in it free to move as a current, no electrons fall out. Yet if you heat the metal, electrons can be boiled off. Explain both of these facts as they relate to the amount and distribution of energy involved with shaking the object as compared with heating it.

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7.3: Atomic Emission Spectra

Overview

- To introduce the concept of absorption and emission line spectra and describe the Balmer equation to describe the visible lines of atomic hydrogen.

The first person to realize that white light was made up of the colors of the rainbow was Isaac Newton, who in 1666 passed sunlight through a narrow slit, then a prism, to project the colored spectrum on to a wall. This effect had been noticed previously, of course, not least in the sky, but previous attempts to explain it, by Descartes and others, had suggested that the white light became colored when it was refracted, the color depending on the angle of refraction. Newton clarified the situation by using a second prism to reconstitute the white light, making much more plausible the idea that the white light was composed of the separate colors. He then took a monochromatic component from the spectrum generated by one prism and passed it through a second prism, establishing that no further colors were generated. That is, light of a single color did not change color on refraction. He concluded that white light was made up of all the colors of the rainbow, and that on passing through a prism, these different colors were refracted through slightly different angles, thus separating them into the observed spectrum.

7.3.1: Atomic Line Spectra

The spectrum of hydrogen *atoms*, which turned out to be crucial in providing the first insight into atomic structure over half a century later, was first observed by Anders Ångström in Uppsala, Sweden, in 1853. His communication was translated into English in 1855. Ångström, the son of a country minister, was a reserved person, not interested in the social life that centered around the court. Consequently, it was many years before his achievements were recognized, at home or abroad (most of his results were published in Swedish).

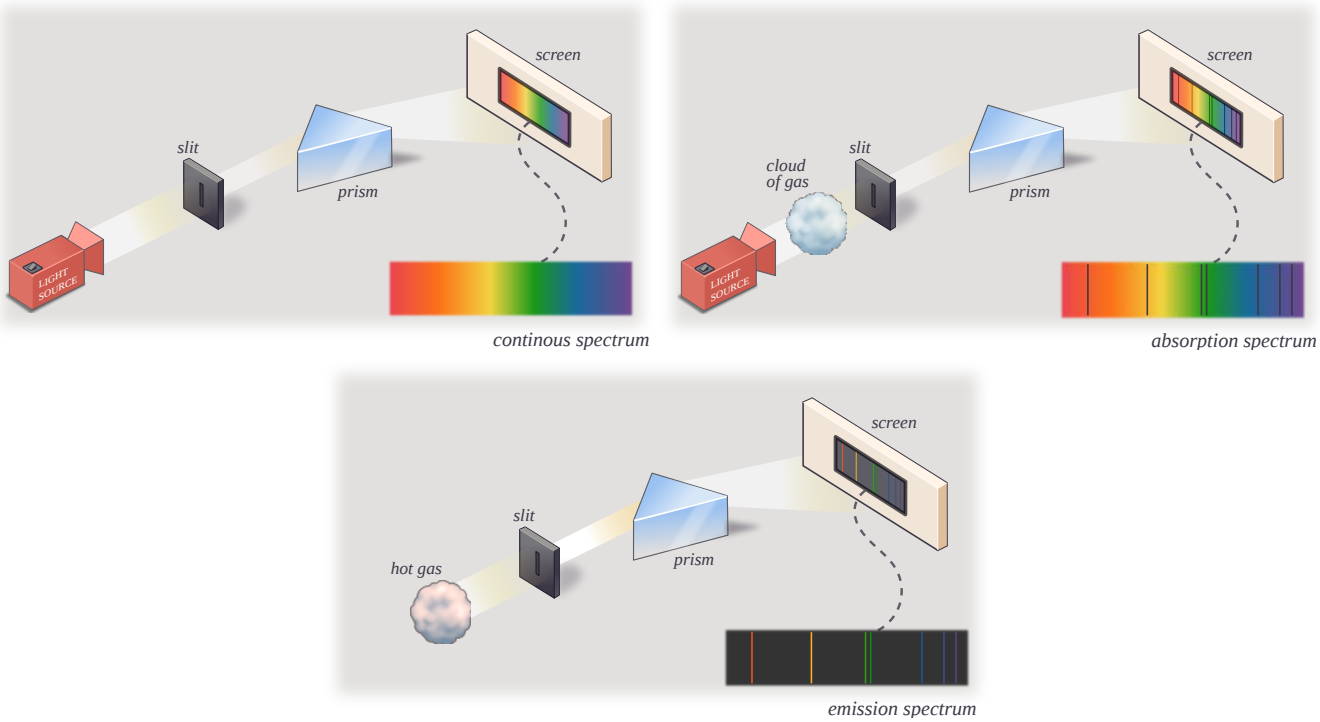


Figure 1.4.1 : Three Kinds of Spectra. When we see a lightbulb or other source of continuous radiation, all the colors are present. When the continuous spectrum is seen through a thinner gas cloud, the cloud's atoms produce absorption lines in the continuous spectrum. When the excited cloud is seen without the continuous source behind it, its atoms produce emission lines. We can learn which types of atoms are in the gas cloud from the pattern of absorption or emission lines. (CC BY-NC; Ümit Kaya via LibreTexts).

Most of what is known about atomic (and molecular) structure and mechanics has been deduced from spectroscopy. Figure 1.4.1 shows two different types of spectra. A continuous spectrum can be produced by an incandescent solid or gas at high pressure (e.g., blackbody radiation is a continuum). An emission spectrum can be produced by a gas at low pressure excited by heat or by collisions with electrons. An absorption spectrum results when light from a continuous source passes through a cooler gas, consisting of a series of dark lines characteristic of the composition of the gas.

Fraunhofer Lines

In 1802, William Wollaston in England had discovered that the solar spectrum had tiny gaps - there were many thin dark lines in the rainbow of colors. These were investigated much more systematically by Joseph von Fraunhofer, beginning in 1814. He increased the dispersion by using more than one prism. He found an "almost countless number" of lines. He labeled the strongest dark lines A, B, C, D, etc. Frauenhofer between 1814 and 1823 discovered nearly 600 dark lines in the solar spectrum viewed at high resolution and designated the principal features with the letters A through K, and weaker lines with other letters (Table 1.4.1). Modern observations of sunlight can detect many thousands of lines. It is now understood that these lines are caused by absorption by the outer layers of the Sun.

Table 1.4.1 : Major Fraunhofer lines and the elements they are associated with.

Designation	Element	Wavelength (nm)
y	O_2	898.765
Z	O_2	822.696
A	O_2	759.370
B	O_2	686.719
C	H	656.281
a	O_2	627.661
D_1	Na	589.592
D_2	Na	588.995
D_3 or d	He	587.5618

The Fraunhofer lines are typical spectral absorption lines. These dark lines are produced whenever a cold gas is between a broad spectrum photon source and the detector. In this case, a decrease in the intensity of light in the frequency of the incident photon is seen as the photons are absorbed, then re-emitted in random directions, which are mostly in directions different from the original one. This results in an *absorption line*, since the narrow frequency band of light initially traveling toward the detector, has been turned into heat or re-emitted in other directions.

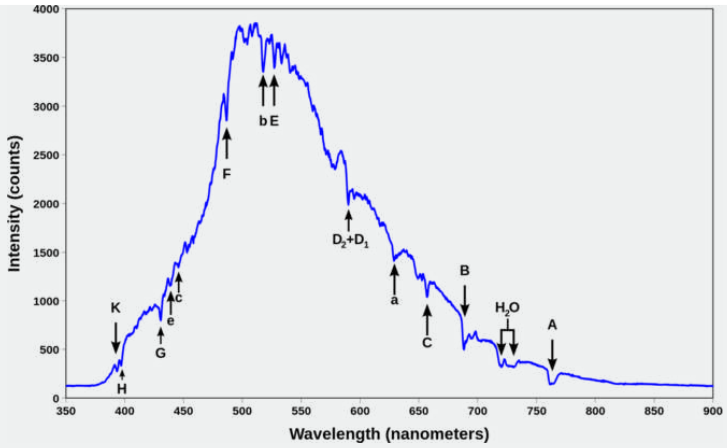


Figure 1.4.2 : Spectrum of blue sky. Dips are present at the Fraunhofer line wavelengths. (CC BY-SA 4.0; Eric Bajart via Wikipedia).

By contrast, if the detector sees photons emitted directly from a glowing gas, then the detector often sees photons emitted in a narrow frequency range by quantum emission processes in atoms in the hot gas, resulting in an *emission line*. In the Sun, Fraunhofer lines are seen from gas in the outer regions of the Sun, which are too cold to directly produce emission lines of the elements they represent.

Gases heated to incandescence were found by Bunsen, Kirkhoff and others to emit light with a series of sharp wavelengths. The emitted light analyzed by a spectrometer (or even a simple prism) appears as a multitude of narrow bands of color. These so called *line spectra* are characteristic of the atomic composition of the gas. The line spectra of several elements are shown in Figure 1.4.3 .

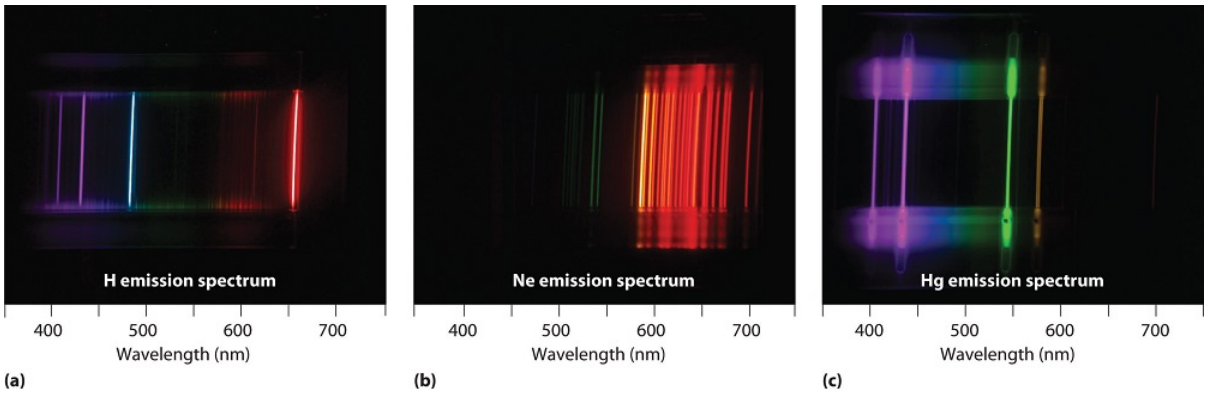


Figure 1.4.3 : The Emission Spectra of Elements Compared with Hydrogen. These images show (a) hydrogen gas, which is atomized to hydrogen atoms in the discharge tube; (b) neon; and (c) mercury. The strongest lines in the hydrogen spectrum are in the far UV Lyman series starting at 124 nm and below. The strongest lines in the mercury spectrum are at 181 and 254 nm, also in the UV; these are not shown. (CC BY-SA-NC; Anonymous by request).

7.3.2: The Balmer Series of Hydrogen

Obviously, if any pattern could be discerned in the spectral lines for a specific atom (in contract to the mixture that Fraunhofer lines represent), that might be a clue as to the internal structure of the atom. One might be able to build a model. A great deal of effort went into analyzing the spectral data from the 1860's on. The big breakthrough was made by Johann Balmer, a math and Latin teacher at a girls' school in Basel, Switzerland. Balmer had done no physics before and made his great discovery when he was almost sixty.

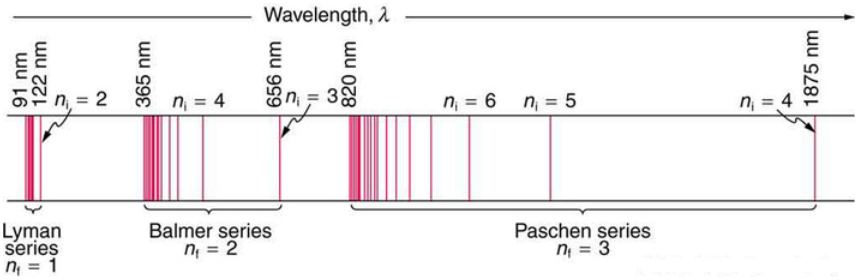


Figure 1.4.4 : A schematic of the hydrogen spectrum shows several series named for those who contributed most to their determination. Part of the Balmer series is in the visible spectrum, while the Lyman series is entirely in the UV, and the Paschen series and others are in the IR. Values of n_f and n_i are shown for some of the lines (CC BY-SA; OpenStax).

Balmer decided that the most likely atom to show simple spectral patterns was the lightest atom, hydrogen. Ångström had measured the four visible spectral lines to have wavelengths 656.21, 486.07, 434.01 and 410.12 nm (Figure 1.4.4). Balmer concentrated on just these four numbers, and found they were represented by the phenomenological formula:

$$\lambda = b\left(\frac{n_2^2}{n_2^2 - 4}\right) \tag{7.3.1}$$

where b = 364.56 nm and $n_2 = 3, 4, 5, 6$.

The first four wavelengths of Equation 7.3.1 (with n_2 = 3, 4, 5, 6) were in excellent agreement with the experimental lines from Ångström (Table 1.4.2). Balmer predicted that other lines exist in the ultraviolet that correspond to $n_2 \geq 7$ and in fact some of them had already been observed, unbeknown to Balmer.

Table 1.4.2 : The Balmer Series of Hydrogen Emission Lines

n_2	3	4	5	6	7	8	9	10
λ	*656*	*486*	*434*	*410*	397	389	383	380
color	*red*	*teal*	*blue*	*indigo*	violet	not visible	not visible	not visible

The n_2 integer in the Balmer series extends theoretically to infinity and the series represents a monotonically increasing energy (and frequency) of the absorption lines with increasing n_2 values. Moreover, the energy difference between successive lines decreased as n_2 increases (1.4.4). This behavior converges to a highest possible energy as Example 1.4.1 demonstrates. If the lines are plot according to their λ on a linear scale, you will get the appearance of the spectrum in Figure 1.4.4 ; these lines are called the **Balmer series**.

Balmer's general formula (Equation 7.3.1) can be rewritten in terms of the inverse wavelength typically called the *wavenumber* ($\tilde{\nu}$).

$$\tilde{\nu} = \frac{1}{\lambda} \tag{7.3.2}$$

$$= R_H\left(\frac{1}{4} - \frac{1}{n_2^2}\right) \tag{7.3.3}$$

where $n_2 = 3, 4, 5, 6$ and R_H is the Rydberg constant (discussed in the next section) equal to 109,737 cm^{-1}.

He further conjectured that the 4 could be replaced by 9, 16, 25, … and this also turned out to be true - but these lines, further into the infrared, were not detected until the early twentieth century, along with the ultraviolet lines.

The Wavenumber as a Unit of Frequency

The relation between wavelength and frequency for electromagnetic radiation is

$$\lambda\nu = c$$

In the SI system of units the wavelength, (λ) is measured in meters (m) and since wavelengths are usually very small one often uses the nanometer (nm) which is 10^{-9} m. The frequency (ν) in the SI system is measured in reciprocal seconds 1/s − which is

called a Hertz (after the discover of the photoelectron effect) and is represented by Hz.

It is common to use the reciprocal of the wavelength in centimeters as a measure of the frequency of radiation. This unit is called a wavenumber and is represented by ($\tilde{\nu}$) and is defined by

$$\begin{aligned}\tilde{\nu} &= \frac{1}{\lambda} \\ &= \frac{\nu}{c}\end{aligned}$$

Wavenumbers is a convenient unit in spectroscopy because it is directly proportional to energy.

$$\begin{aligned}E &= \frac{hc}{\lambda} \\ &= hc \times \frac{1}{\lambda} \\ &= hc\tilde{\nu} \\ &\propto \tilde{\nu}\end{aligned}$$

Example 1.4.1 : Balmer Series

Calculate the longest and shortest wavelengths (in nm) emitted in the Balmer series of the hydrogen atom emission spectrum.

Solution

From the behavior of the Balmer equation (Equation 7.3.1 and Table 1.4.2), the value of n_2 that gives the longest (i.e., greatest) wavelength (λ) is the smallest value possible of n_2, which is (n_2=3) for this series. This results in

$$\begin{aligned}\lambda_{longest} &= (364.56\ nm)\left(\frac{9}{9-4}\right) \\ &= (364.56\ nm)\,(1.8) \\ &= 656.2\ nm\end{aligned}$$

This is also known as the H_α line of atomic hydrogen and is bright red (Figure **7.3.3***a*).

For the shortest wavelength, it should be recognized that the shortest wavelength (greatest energy) is obtained at the limit of greatest (n_2):

$$\lambda_{shortest} = \lim_{n_2 \to \infty} (364.56\ nm)\left(\frac{n_2^2}{n_2^2-4}\right)$$

This can be solved via L'Hôpital's Rule, or alternatively the limit can be expressed via the equally useful energy expression (Equation 7.3.3) and simply solved:

$$\begin{aligned}\tilde{\nu}_{greatest} &= \lim_{n_2 \to \infty} R_H\left(\frac{1}{4} - \frac{1}{n_2^2}\right) \\ &= \lim_{n_2 \to \infty} R_H\left(\frac{1}{4}\right) \\ &= 27,434\ cm^{-1}\end{aligned}$$

Since $\frac{1}{\tilde{\nu}} = \lambda$ in units of cm, this converts to 364 nm as the shortest wavelength possible for the Balmer series.

The Balmer series is particularly useful in astronomy because the Balmer lines appear in numerous stellar objects due to the abundance of hydrogen in the universe, and therefore are commonly seen and relatively strong compared to lines from other elements.

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7.3.1: The Rydberg Formula and the Hydrogen Atomic Spectrum

Learning Objectives

- Describe Rydberg's theory for the hydrogen spectra.
- Interpret the hydrogen spectrum in terms of the energy states of electrons.

In an amazing demonstration of mathematical insight, in 1885 Balmer came up with a simple formula for predicting the wavelength of any of the lines in atomic hydrogen in what we now know as the Balmer series. Three years later, Rydberg generalized this so that it was possible to determine the wavelengths of any of the lines in the hydrogen emission spectrum. Rydberg suggested that all atomic spectra formed families with this pattern (he was unaware of Balmer's work). It turns out that there are families of spectra following Rydberg's pattern, notably in the alkali metals, sodium, potassium, etc., but not with the precision the hydrogen atom lines fit the Balmer formula, and low values of n_2 predicted wavelengths that deviate considerably.

Rydberg's phenomenological equation is as follows:

$$\tilde{\nu} = \frac{1}{\lambda} \tag{7.3.1.1}$$

$$= R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \tag{7.3.1.2}$$

where R_H is the **Rydberg constant** and is equal to 109,737 cm^{-1} ($2.18 \times 10^{-18}\ J$) and n_1 and n_2 are integers (whole numbers) with $n_2 > n_1$.

For the Balmer lines, $n_1 = 2$ and n_2 can be any whole number between 3 and infinity. The various combinations of numbers that can be substituted into this formula allow the calculation the wavelength of any of the lines in the hydrogen emission spectrum; there is close agreement between the wavelengths generated by this formula and those observed in a real spectrum.

7.3.1.1: Other Series

The results given by Balmer and Rydberg for the spectrum in the visible region of the electromagnetic radiation start with $n_2 = 3$, and $n_1 = 2$. Is there a different series with the following formula (e.g., $n_1 = 1$)?

$$\frac{1}{\lambda} = R_{\mathrm{H}} \left(\frac{1}{1^2} - \frac{1}{n^2} \right) \tag{7.3.1.3}$$

The values for n_2 and wavenumber $\tilde{\nu}$ for this series would be:

Table 1.5.1 : The Lyman Series of Hydrogen Emission Lines ($n_1 = 1$)

n_2	2	3	4	5	...
λ (nm)	121	102	97	94	...
$\tilde{\nu}$ (cm^{-1})	82,2291	97,530	102,864	105,332	...

Do you know in what region of the electromagnetic radiation these lines are? Of course, these lines are in the UV region, and they are not visible, but they are detected by instruments; these lines form a **Lyman series**. The existences of the Lyman series and Balmer's series suggest the existence of more series. For example, the series with $n_1 = 3$ and $n_2 = 4, 5, 6, 7, ...$ is called **Paschen series**.

Other Series

The spectral lines are grouped into series according to n_1 values. Lines are named sequentially starting from the longest wavelength/lowest frequency of the series, using Greek letters within each series. For example, the ($n_1 = 1/n_2 = 2$) line is called "Lyman-alpha" (Ly-α), while the ($n_1 = 3/n_2 = 7$) line is called "Paschen-delta" (Pa-δ). The first six series have specific names:

- Lyman series with $n_1 = 1$

- Lyman series with $n_1 = 1$
- Balmer series with $n_1 = 2$
- Paschen series (or Bohr series) with $n_1 = 3$
- Brackett series with $n_1 = 4$
- Pfund series with $n_1 = 5$
- Humphreys series with $n_1 = 6$

Example 1.5.1 : The Lyman Series

The so-called Lyman series of lines in the emission spectrum of hydrogen corresponds to transitions from various excited states to the *n* = 1 orbit. Calculate the wavelength of the lowest-energy line in the Lyman series to three significant figures. In what region of the electromagnetic spectrum does it occur?

Given: lowest-energy orbit in the Lyman series

Asked for: wavelength of the lowest-energy Lyman line and corresponding region of the spectrum

Strategy

A. Substitute the appropriate values into Equation 7.3.1.2 (the Rydberg equation) and solve for λ.
B. Locate the region of the electromagnetic spectrum corresponding to the calculated wavelength.

Solution

We can use the Rydberg equation (Equation 7.3.1.2) to calculate the wavelength:

$$\frac{1}{\lambda} = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

Solution A

For the Lyman series, $n_1 = 1$.

$$\begin{aligned} \frac{1}{\lambda} &= R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \\ &= 1.097 \times 10^7 \, m^{-1} \left(\frac{1}{1} - \frac{1}{4} \right) \\ &= 8.228 \times 10^6 \, m^{-1} \end{aligned}$$

Spectroscopists often talk about energy and frequency as equivalent. The cm^{-1} unit (wavenumbers) is particularly convenient. We can convert the answer in part A to cm^{-1}.

$$\begin{aligned} \tilde{\nu} &= \frac{1}{\lambda} \\ &= 8.228 \times 10^6 \, \cancel{m^{-1}} \left(\frac{\cancel{m}}{100 \, cm} \right) \\ &= 82,280 \, cm^{-1} \end{aligned}$$

and

$$\lambda = 1.215 \times 10^{-7} \, m = 122 \, nm$$

This emission line is called Lyman alpha and is the strongest atomic emission line from the sun and drives the chemistry of the upper atmosphere of all the planets producing ions by stripping electrons from atoms and molecules. It is completely absorbed by oxygen in the upper stratosphere, dissociating O_2 molecules to O atoms which react with other O_2 molecules to form stratospheric ozone

Solution B

his wavelength is in the ultraviolet region of the spectrum.

Exercise 1.5.1 : The Pfund Series

The Pfund series of lines in the emission spectrum of hydrogen corresponds to transitions from higher excited states to the $n_1 = 5$. Calculate the wavelength of the *second* line in the Pfund series to three significant figures. In which region of the spectrum does it lie?

Answer

$4.65 \times 10^3\ nm$; infrared

The above discussion presents only a phenomenological description of hydrogen emission lines and fails to provide a probe of the nature of the atom itself. Clearly a continuum model based on classical mechanics is not applicable, and as the next Section demonstrates, a simple connection between spectra and atomic structure can be formulated.

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7.3.2: The Bohr Theory of the Hydrogen Atom

Learning Objectives

- Introduce the fundamentals behind the Bohr Atom and demonstrate it can predict the Rydberg's equation for the atomic spectrum of hydrogen

7.3.2.1: Rutherford's Failed Planetary Atom

Ernest Rutherford had proposed a model of atoms based on the α-particle scattering experiments of Hans Geiger and Ernest Marsden. In these experiments helium nuclei (α-particles) were shot at thin gold metal foils. Most of the particles were not scattered; they passed unchanged through the thin metal foil. Some of the few that were scattered were scattered in the backward direction; i.e. they recoiled. This backward scattering requires that the foil contain heavy particles. When an α-particle hits one of these heavy particles it simply recoils backward, just like a ball thrown at a brick wall. Since most of the α-particles don't get scattered, the heavy particles (the nuclei of the atoms) must occupy only a very small region of the total space of the atom. Most of the space must be empty or occupied by very low-mass particles. These low-mass particles are the electrons that surround the nucleus.

There are some basic problems with the Rutherford model. The Coulomb force that exists between oppositely charge particles means that a positive nucleus and negative electrons should attract each other, and the atom should collapse. To prevent the collapse, the electron was postulated to be orbiting the positive nucleus. The Coulomb force (discussed below) is used to change the direction of the velocity, just as a string pulls a ball in a circular orbit around your head or the gravitational force holds the moon in orbit around the Earth. The origin for this hypothesis that suggests this perspective is plausible is the similarity of gravity and Coulombic interactions. The expression for the force of gravity between two masses (Newton's Law of gravity) is

$$F_{gravity} \propto \frac{m_1 m_2}{r^2} \tag{7.3.2.1}$$

with m_1 and m_2 representing the **mass** of object 1 and 2, respectively and r representing the distance between the objects centers

The expression for the Coulomb force between two charged species is

$$F_{Coulomb} \propto \frac{Q_1 Q_2}{r^2} \tag{7.3.2.2}$$

with Q_1 and Q_2 representing the **charge** of object 1 and 2, respectively and r representing the distance between the objects centers.

However, this analogy has a problem too. An electron going around in a circle is constantly being accelerated because its velocity vector is changing. A charged particle that is being accelerated emits radiation. This property is essentially how a radio transmitter works. A power supply drives electrons up and down a wire and thus transmits energy (electromagnetic radiation) that your radio receiver picks up. The radio then plays the music for you that is encoded in the waveform of the radiated energy.

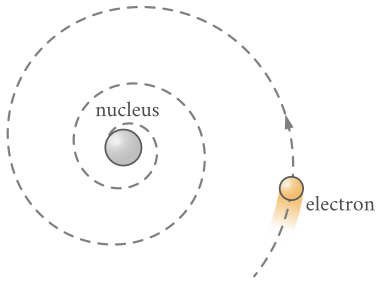


Figure 7.3.2.1 : The classical death spiral of an electron around a nucleus. (CC BY-NC; Ümit Kaya via LibreTexts)

If the orbiting electron is generating radiation, it is losing energy. If an orbiting particle loses energy, the radius of the orbit decreases. To conserve angular momentum, the frequency of the orbiting electron increases. The frequency increases continuously as the electron collapses toward the nucleus. Since the frequency of the rotating electron and the frequency of the radiation that is

emitted are the same, both change continuously to produce a continuous spectrum and not the observed discrete lines. Furthermore, if one calculates how long it takes for this collapse to occur, one finds that it takes about 10^{-11} seconds. This means that nothing in the world based on the structure of atoms could exist for longer than about 10^{-11} seconds. Clearly something is terribly wrong with this classical picture, which means that something was missing at that time from the known laws of physics.

Conservative Forces can be explained with Potentials

A conservative force is dependent only on the position of the object. If a force is conservative, it is possible to assign a numerical value for the potential at any point. When an object moves from one location to another, the force changes the potential energy of the object by an amount that does not depend on the path taken. The potential can be constructed as simple derivatives for 1-D forces:

$$F = -\frac{dV}{dx}$$

or as gradients in 3-D forces

$$F = -\nabla V$$

where ∇ is the vector of partial derivatives

$$\nabla = \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right)$$

The most familiar conservative forces are gravity and Coloumbic forces.

The Coulomb force law (Equation 7.3.2.2) comes from the corresponding Coulomb potential (sometimes call electrostatic potential)

$$V(r) = \frac{kQ_1Q_2}{r} \tag{7.3.2.3}$$

and it can be easily verified that the Coulombic force from this interaction ($F(r)$) is

$$F(r) = -\frac{dV}{dr} \tag{7.3.2.4}$$

As r is varied, the energy will change, so that we have an example of a potential energy curve $V(r)$ (Figure 7.3.2.2;). If Q_1 and Q_2 are the same sign, then the curve which is a purely **repulsive potential**, i.e., the energy increases monotonically as the charges are brought together and decreases monotonically as they are separated. From this, it is easy to see that like charges (charges of the same sign) repel each other.

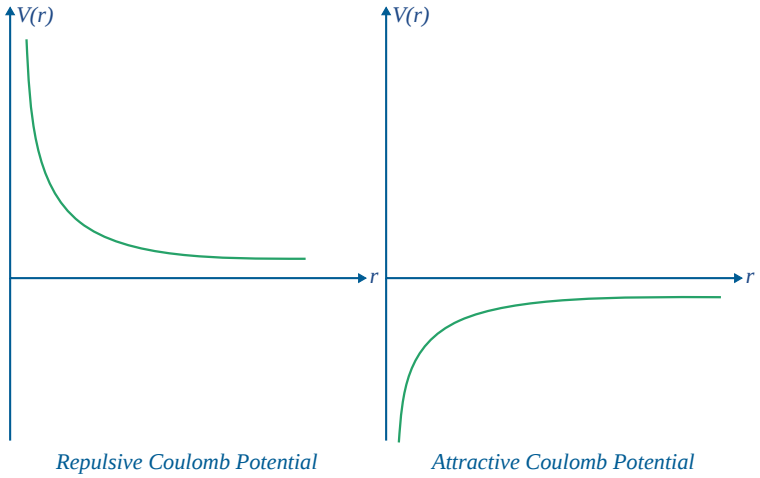


Figure 7.3.2.2 : Potential energy curve for the Coulomb interactions between two charges of same sign (left) and opposite signs (right). (CC BY-NC; Ümit Kaya via LibreTexts)

If the charges are of opposite sign, then the curve appears roughly Figure **7.3.2.2;** and this is a purely **attractive potential**. Thus, the energy decreases as the charges are brought together, implying that opposite charges attract

7.3.2.2: The Bohr Model

It is observed that line spectra discussed in the previous sections show that hydrogen atoms absorb and emit light at only discrete wavelengths. This observation is connected to the discrete nature of the allowed energies of a quantum mechanical system. Quantum mechanics postulates that, in contrast to classical mechanics, the energy of a system can only take on certain discrete values. This leaves us with the question: How do we determine what these allowed discrete energy values are? After all, it seems that Planck's formula for the allowed energies came out of nowhere.

The model we will describe here, due to Niels Bohr in 1913, is an early attempt to predict the allowed energies for single-electron atoms such as **H**, $\mathbf{He^{+}}$, $\mathbf{Li^{2+}}$, $\mathbf{Be^{3+}}$, etc. Although Bohr's reasoning relies on classical concepts and hence, is not a correct explanation, the reasoning is interesting, and so we examine this model for its historical significance.

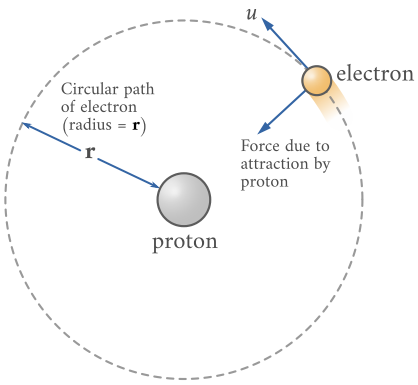


Figure 7.3.2.3 : Bohr atom with an electron revolving around a fixed nucleus. (CC BY-NC; Ümit Kaya via LibreTexts)

Consider a nucleus with charge $+Ze$ and one electron orbiting the nucleus. In this analysis, we will use another representation of the constant k in Coulomb's law (Equation 7.3.2.3), which is more commonly represented in the form:

$$k = \frac{1}{4\pi\epsilon_0} \tag{7.3.2.5}$$

where ϵ_0 is known as the **permittivity of free space** with the numerical value $\epsilon_0 = 8.8541878 \times 10^{-12}\ C^2 J^{-1} m^{-1}$.

The total energy of the electron (the nucleus is assumed to be fixed in space at the origin) is the sum of kinetic and potential energies:

$$E_{total} = \underbrace{\frac{p^2}{2m_e}}_{\text{kinetic energy}} - \underbrace{\frac{Ze^2}{4\pi\epsilon_0 r}}_{\text{potential energy}}$$

The force on the electron is

$$\vec{F} = -\frac{Ze^2}{4\pi\epsilon_0 r^3} r$$

and its magnitude is

$$F = \left|\vec{F}\right| = \frac{Ze^2}{4\pi\epsilon_0 r^3}|r| = \frac{Ze^2}{4\pi\epsilon_0 r^2}$$

since $\vec{F} = m_e\vec{a}$, the magnitude, it follows that $\left|\vec{F}\right| = m_e|\vec{a}|$. If we assume that the orbit is circular, then the acceleration is *purely centripetal*, so

$$|a| = \frac{v^2}{r}$$

where v is the velocity of the electron. Equating force $|F|$ to $m_e|a|$, we obtain

$$\frac{Ze^2}{4\pi\epsilon_0 r^2} = m_e\frac{v^2}{r}$$

or

$$\frac{Ze^2}{4\pi\epsilon_0} = m_e v^2 r$$

or

$$\frac{Ze^2 m_e r}{4\pi\epsilon_0} = (m_e v r)^2 \tag{7.3.2.6}$$

The reason for writing the equation this way is that the quantity $m_e vr$ is the classical orbital angular momentum of the electron. Bohr was familiar with Maxwell's theory of classical electromagnetism and knew that in a classical theory, the orbiting electron should radiate energy away and eventually collapse into the nucleus (Figure 7.3.2.1). He circumvented this problem by following Planck's idea underlying blackbody radiation and positing that the orbital angular momentum $m_e vr$ of the electron could only take on specific values

$$m_e vr = n\hbar \tag{7.3.2.7}$$

with $n = 1, 2, 3, ...$

> *Note that the electron must be in motion, so $n = 0$ is not allowed.*

Substituting Equation 7.3.2.7 into the Equation 7.3.2.6, we find

$$\frac{Ze^2 m_e r}{4\pi\epsilon_0} = n^2(\hbar)^2 \tag{7.3.2.8}$$

Equation 7.3.2.8 implies that orbits could only have certain allowed radii

$$r_n = \frac{4\pi\epsilon_0\hbar^2}{Ze^2 m_e}n^2 \tag{7.3.2.9}$$

$$= \frac{a_0}{Z}n^2 \tag{7.3.2.10}$$

with $n = 1, 2, 3, ...$ The collection of constants has been defined to be a_0

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{e^2 m_e} \tag{7.3.2.11}$$

a quantity that is known as the **Bohr radius**.

We can also calculate the allowed momenta since $m_e vr = n\hbar$, and $p = m_e v$. Thus,

$$p_n r_n = n\hbar \tag{7.3.2.12}$$

$$p_n = \frac{n\hbar}{r_n} \tag{7.3.2.13}$$

$$= \frac{\hbar Z}{a_0 n} \tag{7.3.2.14}$$

$$= \frac{Ze^2 m_e}{4\pi\epsilon_0\hbar n} \tag{7.3.2.15}$$

From p_n and r_n, we can calculate the allowed energies from

$$E_n = \frac{p_n^2}{2m_e} - \frac{Ze^2}{4\pi\epsilon_0 r_n} \tag{7.3.2.16}$$

Substituting in the expressions for p_n and r_n and simplifying gives

$$E_n = -\frac{Z^2 e^4 m_e}{32\pi^2 \epsilon_0^2 \hbar^2}\frac{1}{n^2} = -\frac{e^4 m_e}{8\epsilon_0^2 h^2}\frac{Z^2}{n^2} \tag{7.3.2.17}$$

We can redefine a new energy scale by defining the *Rydberg* as

$$1\ Ry = \frac{e^4 m_e}{8\epsilon_0^2 h^2} = 2.18 \times 10^{-18}\ J.$$

and this simplifies the allowed energies predicted by the Bohr model (Equation 7.3.2.17) as

$$E_n = -(2.18 \times 10^{-18})\frac{Z^2}{n^2}\ J = -\frac{Z^2}{n^2}\ R_y \tag{7.3.2.18}$$

Hence, the energy of the electron in an atom also is quantized. Equation 7.3.2.18 gives the energies of the electronic states of the hydrogen atom. It is very useful in analyzing spectra to represent these energies graphically in an energy-level diagram. An energy-level diagram has energy plotted on the vertical axis with a horizontal line drawn to locate each energy level (Figure 7.3.2.4).

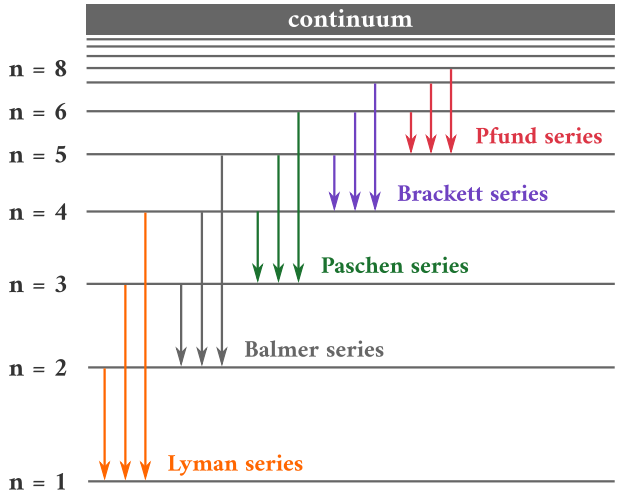


Figure 7.3.2.4 : Energy levels predicted by the Bohr model of hydrogen ($Z = 1$). (CC BY-NC; Ümit Kaya via LibreTexts)

These turn out to be the correct energy levels, apart from small corrections that cannot be accounted for in this pseudo-classical treatment. Despite the fact that the energies are essentially correct, the Bohr model masks the true quantum nature of the electron, which only emerges from a fully quantum mechanical analysis.

? Exercise 7.3.2.1

Calculate a value for the Bohr radius using Equation 7.3.2.8 to check that this equation is consistent with the value 52.9 pm. What would the radius be for $n = 1$ in the Li^{2+} ion?

Answer

Starting from Equation 7.3.2.8 and solving for r:

$$\frac{Ze^2 m_e r}{4\pi\epsilon_0} = n^2\hbar^2$$

$$r = \frac{4n^2\hbar^2\pi\epsilon_0}{Ze^2 m_e}$$

with

- e is the fundamental charge: $e = 1.60217662 \times 10^{-19} C^2$
- m_e is the mass of an electron: $m_e = 9.10938356 \times 10^{-31} kg$
- ϵ_o is the permittivity of free space: $\epsilon_o = 8.854 \times 10^{-12} C^2 N^{-1} m^{-2}$
- $\hbar$ is the reduced planks constant: $\hbar = 1.0546 \times 10^{-34} m^2 kg/s$

For the ground-state of the hydrogen atom: $Z = 1$ and $n = 1$.

$$\begin{aligned} r &= \frac{4\hbar^2 \pi \epsilon_0}{e^2 m_e} \\ &= \frac{4(1.0546 \times 10^{-34} m^2 kg/s)^2 \times \pi \times 8.854 \times 10^{-12} C^2 N^{-1} m^{-2}}{(1.60217662 \times 10^{-19} C)^2 (9.10938356 \times 10^{-31} kg)} \\ &= 5.29 \times 10^{-11} m = 52.9\, pm \end{aligned}$$

For the ground-state of the lithium +2 ion: $Z = 3$ and $n = 1$

$$\begin{aligned} r &= \frac{4\hbar^2 \pi \epsilon_0}{3e^2 m_e} \\ &= \frac{4(1.0546 \times 10^{-34} m^2 kg/s)^2 \times \pi \times 8.854 \times 10^{-12} C^2 N^{-1} m^{-2}}{3(1.60217662 \times 10^{-19} C)^2 (9.10938356 \times 10^{-31} kg)} \\ &= 1.76 \times 10^{-11} m = 17.6\, pm \end{aligned}$$

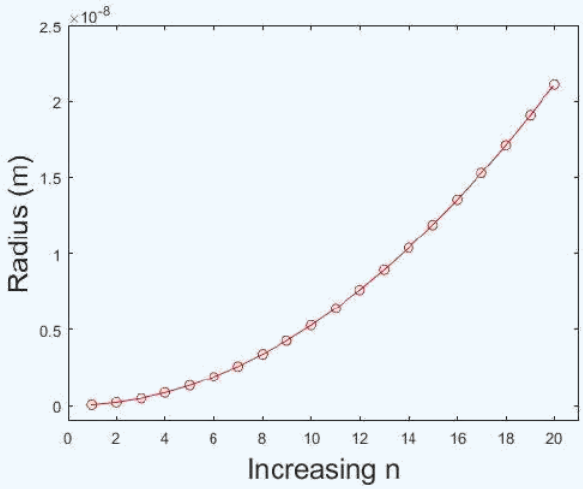
As expected, the $\mathbf{Li^{2+}}$ has a smaller radius than the $\mathbf{H}$ atoms because of the increased nuclear charge.

Exercise 7.3.2.2 : Rydberg states

How do the radii of the hydrogen orbits vary with n? Prepare a graph showing r as a function of n. States of hydrogen atoms with $n = 200$ have been prepared (called Rydberg states). What is the diameter of the atoms in these states?

Answer

This is a straightforward application of Equation of 7.3.2.10. The hydrogen atom has only certain allowable radii and these radii can be predicted from the equation that relates them with each n. Note that the electron must be in motion so $n = 0$ is not allowed.



This plot shows the relationship of radius as a function of n. Note that at $n = 1$ the radius is not zero. (CC BY-NC; Ümit Kaya via LibreTexts)

$4\pi\epsilon_0 = 1.113 \times 10^{-10} \mathrm{C^2 J^{-1} m^{-1}}$ and $\hbar = 1.054 \times 10^{-34} \mathrm{Js}$, also knowing

$$e = 1.602 \times 10^{-19} \mathrm{C\ with}$$
$$m_e = 9.109 \times 10^{-31} \mathrm{kg}$$

and Z is the nuclear charge, we use this equation directly. A simplification can be made by taking advantage of the fact that

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{e^2 m_e}$$

resulting in

$$r_n = \frac{a_0}{Z}n^2$$

where $a_0 = 5.292 \times 10^{-11}\text{m}$ which is the Bohr Radius.

Suppose we want to find the radius where $n = 200.n^2 = 40000$ so plugging in directly we have

$$r_n = \frac{(5.292 \times 10^{-11})}{(1)}(40000)$$
$$= 2.117 \times 10^{-6}m$$

for the radius of a hydrogen atom with an electron excited to the $\text{n} = 200$ state. The diameter is then $4.234 \times 10^{-6}\text{m}$.

7.3.2.3: Derivation of the Rydberg Equation from Bohr Model

Given a prediction of the allowed energies of a system, how could we go about verifying them? The general experimental technique known as *spectroscopy* permits us to probe the various differences between the allowed energies. Thus, if the prediction of the actual energies, themselves, is correct, we should also be able to predict these differences. Let us assume that we are able to place the electron in Bohr's hydrogen atom into an energy state E_n for $n > 1$, i.e. one of its so-called *excited states*. The electron will rapidly return to its lowest energy state, known as the *ground state* and, in doing so, emit light. The energy carried away by the light is determined by the condition that the total energy is conserved (Figure 7.3.2.6).

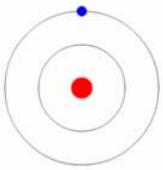


Figure 7.3.2.6 : A simple illustration of Bohr's model of the atom, with an electron making quantum leaps. (CC BY-SA 3.0 unported; Kurzon via Wikipedia)

Thus, if n_i is the integer that characterizes the initial (excited) state of the electron, and n_f is the final state (here we imagine that $n_f = 1$, but is applicable in cases that $n_f < n_i$, i.e., emission)

$$E_{nf} = E_{ni} - h\nu \tag{7.3.2.19}$$

or

$$\nu = \frac{E_{ni} - E_{nf}}{h} = \frac{Z^2 e^4 m_e}{8\epsilon_0^2 h^3}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \tag{7.3.2.20}$$

We can now identify the Rydberg constant R_H with the ratio of constants on the right hand side of Equation 7.3.2.20

$$R_H = \frac{m_e e^4}{8\epsilon_0^2 h^3} \tag{7.3.2.21}$$

Evaluating R_H from the fundamental constants in this formula gives a value within 0.5% of that obtained experimentally from the hydrogen atom spectrum.

Thus, by observing the emitted light, we can determine the energy difference between the initial and final energy levels, which results in the emission spectra discussed in Sections 1.4 and 1.5. Different values of n_f determine which emission spectrum is observed, and the examples shown in the figure are named after the individuals who first observed them. The figure below shows some of the transitions possible for different n_f and n_i values discussed previously.

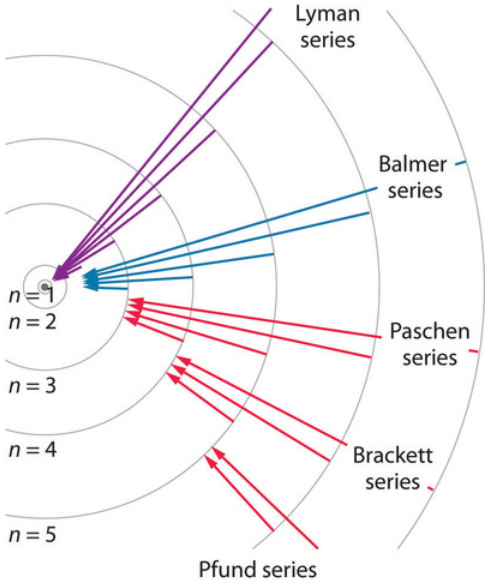


Figure 7.3.2.7 : Electron Transitions Responsible for the Various Series of Lines Observed in the Emission Spectrum of Hydrogen. The Lyman series of lines is due to transitions from higher-energy orbits to the lowest-energy orbit (n = 1); these transitions release a great deal of energy, corresponding to radiation in the ultraviolet portion of the electromagnetic spectrum. The Paschen, Brackett, and Pfund series of lines are due to transitions from higher-energy orbits to orbits with n = 3, 4, and 5, respectively; these transitions release substantially less energy, corresponding to infrared radiation. Orbits are not drawn to scale. (CC BY-NC-SA 3.0; anonymous)

If the atom absorbs light it ends up in an excited state as a result of the absorption. The absorption is only possible for light of certain frequencies, and again, conservation of energy determines what these frequencies are. If light is absorbed, then the final energy E_{nf} will be related to the initial energy E_{ni} with $n_f > n_i$ by

$$E_{nf} = E_{ni} + h\nu \tag{7.3.2.22}$$

or

$$\nu = \frac{E_{nf} - E_{ni}}{h} = \frac{Z^2 e^4 m_e}{8\epsilon_0^2 h^3}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right) \tag{7.3.2.23}$$

Exercise 7.3.2.3

a. Calculate the energy of a photon that is produced when an electron in a hydrogen atom goes from an orbit with $n = 4$ to an orbit with $n = 1$.

b. What happens to the energy of the photon as the initial value of n approaches infinity?

Answer

a:

$$\begin{aligned} E_{nf} &= E_{ni} - h\nu \\ E_{photon} = h\nu &= E_{nf} - E_{ni} \\ &= \frac{Z^2 e^4 m_e}{8\epsilon_o^2 h^2}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \\ &= \frac{e^4 m_e}{8\epsilon_o^2 h^2}\left(\frac{1}{1^2} - \frac{1}{4^2}\right) \\ &= 2.18 \times 10^{-18}\left(1 - \frac{1}{16}\right) \\ &= 2.04 \times 10^{-18} J \end{aligned}$$

b:

As $n_i \to \infty$

$$E_{photon} = \frac{e^4 m_e}{8\epsilon_o^2 h^2}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

$$\frac{1}{n_i^2} \to 0$$

$$E_{photon} \to \frac{e^4 m_e}{8\epsilon_o^2 h^2}\left(\frac{1}{n_f^2}\right)$$

Bohr's proposal explained the hydrogen atom spectrum, the origin of the Rydberg formula, and the value of the Rydberg constant. Specifically it demonstrated that the integers in the Rydberg formula are a manifestation of quantization. The energy, the angular momentum, and the radius of the orbiting electron all are quantized. This quantization also parallels the concept of stable orbits in the Bohr model. Only certain values of E, M, and r are possible, and therefore the electron cannot collapse onto the nucleus by continuously radiating energy because it can only have certain energies, and it cannot be in certain regions of space. The electron can only jump from one orbit (quantum state) to another. The quantization means that the orbits are stable, and the electron cannot spiral into the nucleus in spite of the attractive Coulomb force.

Although Bohr's ideas successfully explained the hydrogen spectrum, they failed when applied to the spectra of other atoms. In addition a profound question remained. Why is angular momentum quantized in units of $\hbar$? As we shall see, de Broglie had an answer to this question, and this answer led Schrödinger to a general postulate that produces the quantization of angular momentum as a consequence. This quantization is not quite as simple as proposed by Bohr, and we will see that it is not possible to determine the distance of the electron from the nucleus as precisely as Bohr thought. In fact, since the position of the electron in the hydrogen atom is not at all as well defined as a classical orbit (such as the moon orbiting the earth) it is called an orbital. An electron orbital represents or describes the position of the electron around the nucleus in terms of a mathematical function called a wavefunction that yields the **probability** of positions of the electron.

Contributors and Attributions

- Mark Tuckerman (New York University)
- David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski ("Quantum States of Atoms and Molecules")
- Template:Contriboundless

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7.4: Matter Has Wavelike Properties

Learning Objectives

- To introduce the wave-particle duality of light extends to matter
- To describe how matter (e.g., electrons and protons) can exhibit wavelike properties, e.g., interference and diffraction patterns
- To use algebra to find the de Broglie wavelength or momentum of a particle when either one of these quantities is given

The next real advance in understanding the atom came from an unlikely quarter - a student prince in Paris. Prince Louis de Broglie was a member of an illustrious family, prominent in politics and the military since the 1600's. Louis began his university studies with history, but his elder brother Maurice studied x-rays in his own laboratory, and Louis became interested in physics. After World War I, de Broglie focused his attention on Einstein's two major achievements, the theory of special relativity and the quantization of light waves. He wondered if there could be some connection between them. Perhaps the quantum of radiation really should be thought of as a particle. De Broglie suggested that if waves (photons) could behave as particles, as demonstrated by the photoelectric effect, then the converse, namely that particles could behave as waves, should be true. He associated a wavelength λ to a particle with momentum p using Planck's constant as the constant of proportionality:

$$\lambda = \frac{h}{p} \tag{7.4.1}$$

which is called the **de Broglie wavelength**. The fact that particles can behave as waves but also as particles, depending on which experiment you perform on them, is known as the **wave-particle duality**.

Deriving the de Broglie Wavelength

From the discussion of the photoelectric effect, we have the first part of the particle-wave duality, namely, that electromagnetic waves can behave like particles. These particles are known as *photons*, and they move at the speed of light. Any particle that moves at or near the speed of light has kinetic energy given by Einstein's special theory of relatively. In general, a particle of mass m and momentum p has an energy

$$E = \sqrt{p^2c^2 + m^2c^4} \tag{7.4.2}$$

Note that if $p = 0$, this reduces to the famous rest-energy expression $E = mc^2$. However, photons are massless particles (technically rest-massless) that always have a finite momentum p. In this case, Equation 7.4.2 becomes

$$E = pc.$$

From Planck's hypothesis, one quantum of electromagnetic radiation has energy $E = h\nu$. Thus, equating these two expressions for the kinetic energy of a photon, we have

$$h\nu = \frac{hc}{\lambda} = pc \tag{7.4.3}$$

Solving for the wavelength λ gives Equation 7.4.1:

$$\lambda = \frac{h}{p} = \frac{h}{mv}$$

where v is the velocity of the particle. Hence, de Broglie argued that if particles can behave as waves, then a relationship like this, which pertains particularly to waves, should also apply to particles.

Equation 7.4.1 allows us to associate a wavelength λ to a particle with momentum p. As the momentum increases, the wavelength decreases. In both cases, this means the energy becomes larger. i.e., short wavelengths *and* high momenta correspond to high energies.

> *It is a common feature of quantum mechanics that particles and waves with short wavelengths correspond to high energies and vice versa.*

Having decided that the photon might well be a particle with a rest mass, even if very small, it dawned on de Broglie that in other respects it might not be too different from other particles, especially the very light electron. In particular, maybe the electron also had an associated wave. The obvious objection was that if the electron was wavelike, why had no diffraction or interference effects been observed? But there was an answer. If de Broglie's relation between momentum and wavelength also held for electrons, the wavelength was sufficiently short that these effects would be easy to miss. As de Broglie himself pointed out, the wave nature of light is not very evident in everyday life. As the next section will demonstrate, the validity of de Broglie's proposal was confirmed by electron diffraction experiments of G.P. Thomson in 1926 and of C. Davisson and L. H. Germer in 1927. In these experiments it was found that electrons were scattered from atoms in a crystal and that these scattered electrons produced an interference pattern. These diffraction patterns are characteristic of wave-like behavior and are exhibited by both electrons (i.e., matter) and electromagnetic radiation (i.e., light).

Example 1.6.1 : Electron Waves

Calculate the de Broglie wavelength for an electron with a kinetic energy of 1000 eV.

Solution

To calculate the de Broglie wavelength (Equation 7.4.1), the momentum of the particle must be established and requires knowledge of both the mass and velocity of the particle. The mass of an electron is $9.109383 \times 10^{-28}\ g$ and the velocity is obtained from the given kinetic energy of 1000 eV:

$$\begin{aligned} KE &= \frac{mv^2}{2} \\ &= \frac{p^2}{2m} = 1000\ eV \end{aligned}$$

Solve for momentum

$$p = \sqrt{2mKE}$$

convert to SI units

$$p = \sqrt{(1000\ \cancel{eV})\left(\frac{1.6 \times 10^{-19}\ J}{1\ \cancel{eV}}\right)(2)(9.109383 \times 10^{-31}\ kg)}$$

expanding definition of joule into base SI units and cancel

$$\begin{aligned} p &= \sqrt{(3.1 \times 10^{-16}\ kg \cdot m^2/s^2)(9.109383 \times 10^{-31}\ kg)} \\ &= \sqrt{2.9 \times 10^{-40}\ kg^2\ m^2/s^2} \\ &= 1.7 \times 10^{-23} kg \cdot m/s \end{aligned}$$

Now substitute the momentum into the equation for de Broglie's wavelength (Equation 7.4.1) with Planck's constant ($h = 6.626069 \times 10^{-34}\ J \cdot s$). After expanding units in Plank's constant

$$\begin{aligned} \lambda &= \frac{h}{p} \\ &= \frac{6.626069 \times 10^{-34}\ kg \cdot m^2/s}{1.7 \times 10^{-23} kg \cdot m/s} \\ &= 3.87 \times 10^{-11}\ m \\ &= 38.9\ pm \end{aligned}$$

Exercise 1.6.1 : Baseball Waves

Calculate the de Broglie wavelength for a fast ball thrown at 100 miles per hour and weighing 4 ounces. Comment on whether the wave properties of baseballs could be experimentally observed.

Answer

Following the unit conversions below, a 4 oz baseball has a mass of 0.11 kg. The velocity of a fast ball thrown at 100 miles per hour in m/s is 44.7 m/s.

$$m = (4\ \cancel{oz})\left(\frac{0.0283\ kg}{1\ \cancel{oz}}\right) = 0.11 kg$$

$$v = \left(\frac{100\ \cancel{mi}}{\cancel{hr}}\right)\left(\frac{1609.34\ m}{\cancel{mi}}\right)\left(\frac{1\ \cancel{hr}}{3600\ s}\right) = 44.7\ m/s$$

The de Broglie wavelength of this fast ball is:

$$\lambda = \frac{h}{mv} = \frac{6.626069 \times 10^{-34}\ kg \cdot m^2/s}{(0.11\ kg)(44.7\ m/s)} = 1.3 \times 10^{-34} m$$

Exercise 1.6.2 : Electrons vs. Protons

If an electron and a proton have the same velocity, which would have the longer de Broglie wavelength?

a. The electron
b. The proton
c. They would have the same wavelength

Answer

Equation 7.4.1 shows that the de Broglie wavelength of a particle's matter wave is inversely proportional to its momentum (mass times velocity). Therefore the smaller mass particle will have a smaller momentum and longer wavelength. The electron is the lightest and will have the longest wavelength.

This was the prince's Ph.D. thesis, presented in 1924. His thesis advisor was somewhat taken aback, and was not sure if this was sound work. He asked de Broglie for an extra copy of the thesis, which he sent to Einstein. Einstein wrote shortly afterwards: *"I believe it is a first feeble ray of light on this worst of our physics enigmas*" and the prince got his Ph.D.

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7.5: The Heisenberg Uncertainty Principle

Learning Objectives

- To understand that sometime you cannot know everything about a quantum system as demonstrated by the Heisenberg uncertainly principle.

In classical physics, studying the behavior of a physical system is often a simple task due to the fact that several physical qualities can be measured simultaneously. However, this possibility is absent in the quantum world. In 1927 the German physicist Werner Heisenberg described such limitations as the Heisenberg Uncertainty Principle, or simply the Uncertainty Principle, stating that it is not possible to measure both the momentum and position of a particle simultaneously.

The Heisenberg Uncertainty Principle is a fundamental theory in quantum mechanics that defines why a scientist cannot measure multiple quantum variables simultaneously. Until the dawn of quantum mechanics, it was held as a fact that all variables of an object could be known to exact precision simultaneously for a given moment. Newtonian physics placed no limits on how better procedures and techniques could reduce measurement uncertainty so that it was conceivable that with proper care and accuracy all information could be defined. Heisenberg made the bold proposition that there is a lower limit to this precision making our knowledge of a particle inherently uncertain.

7.5.1: Probability

Matter and photons are waves, implying they are spread out over some distance. What is the position of a particle, such as an electron? Is it at the center of the wave? The answer lies in how you measure the position of an electron. Experiments show that you will find the electron at some definite location, unlike a wave. But if you set up exactly the same situation and measure it again, you will find the electron in a different location, often far outside any experimental uncertainty in your measurement. Repeated measurements will display a statistical distribution of locations that appears wavelike (Figure 1.9.1).

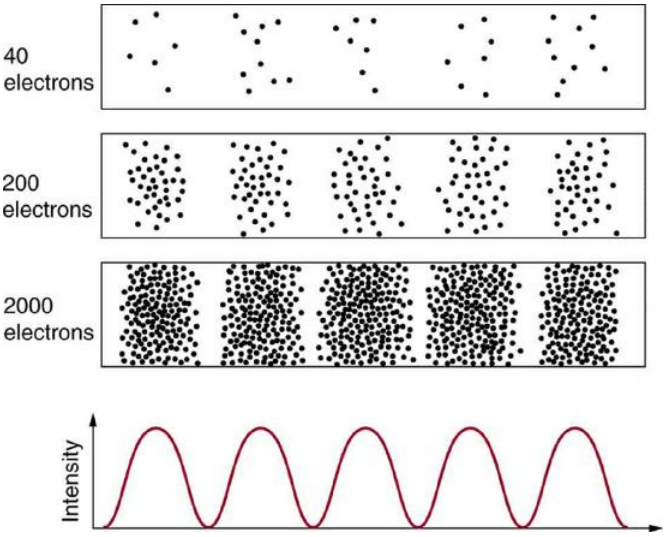


Figure 1.9.1 : The building up of the diffraction pattern of electrons scattered from a crystal surface. Each electron arrives at a definite location, which cannot be precisely predicted. The overall distribution shown at the bottom can be predicted as the diffraction of waves having the de Broglie wavelength of the electrons (CC BY 4.0; OpenStax).

After de Broglie proposed the wave nature of matter, many physicists, including Schrödinger and Heisenberg, explored the consequences. The idea quickly emerged that, *because of its wave character, a particle's trajectory and destination cannot be precisely predicted for each particle individually*. However, each particle goes to a definite place (Figure 1.9.1). After compiling enough data, you get a distribution related to the particle's wavelength and diffraction pattern. There is a certain *probability* of finding the particle at a given location, and the overall pattern is called a **probability distribution**. Those who developed quantum mechanics devised equations that predicted the probability distribution in various circumstances.

It is somewhat disquieting to think that you cannot predict exactly where an individual particle will go, or even follow it to its destination. Let us explore what happens if we try to follow a particle. Consider the double-slit patterns obtained for electrons and photons in Figure 1.9.2 . The interferrence patterns build up statistically as individual particles fall on the detector. This can be observed for photons or electrons—for now, let us concentrate on electrons. You might imagine that the electrons are interfering with one another as any waves do. To test this, you can lower the intensity until there is never more than one electron between the slits and the screen. The same interference pattern builds up!

This implies that a particle's probability distribution spans both slits, and the particles actually interfere with themselves. Does this also mean that the electron goes through both slits? An electron is a basic unit of matter that is not divisible. But it is a fair question, and so we should look to see if the electron traverses one slit or the other, or both. One possibility is to have coils around the slits that detect charges moving through them. What is observed is that an electron always goes through one slit or the other; it does not split to go through both.

But there is a catch. If you determine that the electron went through one of the slits, you no longer get a double slit pattern—instead, you get single slit interference. There is no escape by using another method of determining which slit the electron went through. Knowing the particle went through one slit forces a single-slit pattern. If you do not observe which slit the electron goes through, you obtain a double-slit pattern. How does knowing which slit the electron passed through change the pattern? The answer is fundamentally important—*measurement affects the system being observed*. Information can be lost, and in some cases it is impossible to measure two physical quantities simultaneously to exact precision. For example, you can measure the position of a moving electron by scattering light or other electrons from it. Those probes have momentum themselves, and by scattering from the electron, they change its momentum *in a manner that loses information*. There is a limit to absolute knowledge, even in principle.

7.5.2: Heisenberg's Uncertainty Principle

It is mathematically possible to express the uncertainty that, Heisenberg concluded, always exists if one attempts to measure the momentum and position of particles. First, we must define the variable "x" as the position of the particle, and define "p" as the momentum of the particle. The momentum of a photon of light is known to simply be its frequency, expressed by the ratio h/λ, where h represents Planck's constant and λ represents the wavelength of the photon. The position of a photon of light is simply its wavelength (λ). To represent finite change in quantities, the Greek uppercase letter delta, or Δ, is placed in front of the quantity. Therefore,

$$\Delta p = \frac{h}{\lambda} \tag{7.5.1}$$

$$\Delta x = \lambda \tag{7.5.2}$$

By substituting Δx for λ into Equation 7.5.1, we derive

$$\Delta p = \frac{h}{\Delta x} \tag{7.5.3}$$

or,

$$\Delta p \Delta x = h \tag{7.5.4}$$

early form of uncertainty principle

A Common Trend in Quantum Systems

Equation 7.5.4 can be derived by assuming the particle of interest is behaving as a particle, and not as a wave. Simply let $\Delta p = mv$, and $\Delta x = h/(mv)$ (from De Broglie's expression for the wavelength of a particle). Substituting in Δp for mv in the second equation leads to Equation 7.5.4.

Equation 7.5.4 was further refined by Heisenberg and his colleague Niels Bohr, and was eventually rewritten as

$$\Delta p_x \Delta x \geq \frac{h}{4\pi} = \frac{\hbar}{2} \tag{7.5.5}$$

with $\hbar = \frac{h}{2\pi} = 1.0545718 \times 10^{-34}\, m^2 \cdot kg/s$.

Equation 7.5.5 reveals that the more accurately a particle's position is known (the smaller Δx is), the less accurately the momentum of the particle in the x direction (Δp_x) is known. Mathematically, this occurs because the smaller Δx becomes, the larger Δp_x must become in order to satisfy the inequality. However, the more accurately momentum is known the less accurately position is known (Figure 1.9.2).

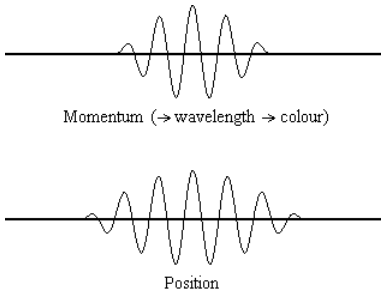


Figure 1.9.2 : The animation shows the relevant spreads in the uncertainty for position and momentum of light/photons (light wave's corresponding photon particle). From the result of de Broglie, we know that for a particle with known momentum, p will have a precise value for its de Broglie wavelength can be determined (and hence a specific color of the light).

What is the Proper Definition of Uncertainty?

Equation 7.5.5 relates the uncertainty of momentum and position. An immediate questions that arise is if Δx represents the full range of possible x values or if it is half (e.g., $\langle x \rangle \pm \Delta x$). Δx is the standard deviation and is a statistic measure of the spread of x values. The use of half the possible range is more accurate estimate of Δx. As we will demonstrated later, once we construct a wavefunction to describe the system, then both x and Δx can be explicitly derived. However for now, Equation 7.5.5 will work.

For example: If a problem argues a particle is trapped in a box of length, L, then the uncertainly of it position is $\pm L/2$. So the value of Δx used in Equation 7.5.5 should be $L/2$, not L.

Example 1.9.1

An electron is confined to the size of a magnesium atom with a 150 pm radius. What is the **minimum** uncertainty in its velocity?

Solution

The uncertainty principle (Equation 7.5.5):

$$\Delta p \Delta x \geq \frac{\hbar}{2}$$

can be written

$$\Delta p \geq \frac{\hbar}{2 \Delta x}$$

and substituting $\Delta p = m \Delta v$ since the mass is not uncertain.

$$\Delta v \geq \frac{\hbar}{2\, m\, \Delta x}$$

the relevant parameters are

- mass of electron $m = m_e = 9.109383 \times 10^{-31}\ kg$
- uncertainty in position: $\Delta x = 150 \times 10^{-12} m$

$$\Delta v \geq \frac{1.0545718 \times 10^{-34}\ \cancel{kg}\, m^2/s}{(2)\ (9.109383 \times 10^{-31}\ \cancel{kg})\ (150 \times 10^{-12}\ \cancel{m})}$$

$$= 3.9 \times 10^5\ m/s$$

Exercise 1.9.1

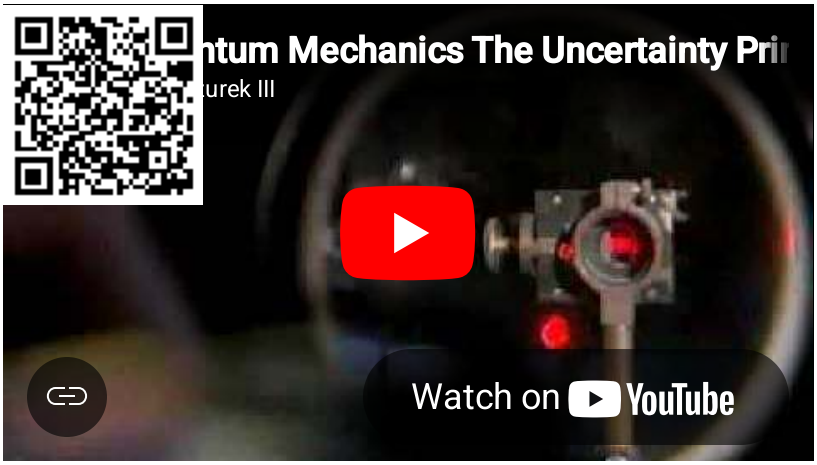
What is the maximum uncertainty of velocity the electron described in Example 1.9.1 ?

Answer

Infinity. There is no limit in the maximum uncertainty, just the minimum uncertainty.

7.5.3: Understanding the Uncertainty Principle through Wave Packets and the Slit Experiment

It is hard for most people to accept the uncertainty principle, because in classical physics the velocity and position of an object can be calculated with certainty and accuracy. However, in quantum mechanics, the wave-particle duality of electrons does not allow us to accurately calculate both the momentum and position because the wave is not in one exact location but is spread out over space. A "wave packet" can be used to demonstrate how either the momentum or position of a particle can be precisely calculated, but not both of them simultaneously. An accumulation of waves of varying wavelengths can be combined to create an average wavelength through an interference pattern: this average wavelength is called the "wave packet". The more waves that are combined in the "wave packet", the more precise the position of the particle becomes and the more uncertain the momentum becomes because more wavelengths of varying momenta are added. Conversely, if we want a more precise momentum, we would add less wavelengths to the "wave packet" and then the position would become more uncertain. Therefore, there is no way to find both the position and momentum of a particle simultaneously.



Several scientists have debated the Uncertainty Principle, including Einstein. Einstein created a slit experiment to try and disprove the Uncertainty Principle. He had light passing through a slit, which causes an uncertainty of momentum because the light behaves like a particle and a wave as it passes through the slit. Therefore, the momentum is unknown, but the initial position of the particle is known. Here is a video that demonstrates particles of light passing through a slit and as the slit becomes smaller, the final possible array of directions of the particles becomes wider. As the position of the particle becomes more precise when the slit is narrowed, the direction, or therefore the momentum, of the particle becomes less known as seen by a wider horizontal distribution of the light.

Example 1.9.2

The speed of a 1.0 g projectile is known to within $10^{-6}\ m/s$.

a. Calculate the *minimum* uncertainty in its position.
b. What is the *maximum* uncertainty of its position?

Solution a

From Equation 7.5.5, the $\Delta p_x = m\Delta v_x$ with $m = 1.0\ g$. Solving for Δx to get

$$\begin{aligned}\Delta x &= \frac{\hbar}{2m\Delta v} \\ &= \frac{1.0545718 \times 10^{-34}\ m^2 \cdot kg/s}{(2)(0.001\ kg)(10^{-6}\ m/s)} \\ &= 5.3 \times 10^{-26}\ m\end{aligned}$$

This negligible for all intents and purpose as expected for any macroscopic object.

Solution b

Unlimited (or the size of the universe). The Heisenberg uncertainty principles does not quantify the maximum uncertainty.

Exercise 1.9.2

Estimate the minimum uncertainty in the speed of an electron confined to a hydrogen atom within a diameter of $1 \times 10^{-10} m$?

Answer

We need to quantify the uncertainty of the electron in position. We can estimate that as $\pm 5 \times 10^{-10} m$. Hence, substituting the relavant numbers into Equation 7.5.5 and solving for Δv we get

$$\Delta v = 1.15 \times 10^{6}\ km/s$$

Notice that the uncertainty is significantly greater for the electron in a hydrogen atom than in the magnesium atom (Example 1.9.1) as expected since the magnesium atom is appreciably bigger.

Heisenberg's Uncertainty Principle not only helped shape the new school of thought known today as quantum mechanics, but it also helped discredit older theories. Most importantly, the Heisenberg Uncertainty Principle made it obvious that there was a fundamental error in the Bohr model of the atom. Since the position and momentum of a particle cannot be known simultaneously, Bohr's theory that the electron traveled in a circular path of a fixed radius orbiting the nucleus was obsolete. Furthermore, Heisenberg's uncertainty principle, when combined with other revolutionary theories in quantum mechanics, helped shape wave mechanics and the current scientific understanding of the atom.

Humor: Heisenberg and the Police

- Heisenberg get pulled over for speeding by the police. The officer asks him "Do you know how fast you were going?"
- Heisenberg replies, "No, but we know exactly where we are!"
- The officer looks at him confused and says "you were going 108 miles per hour!"
- Heisenberg throws his arms up and cries, "Great! Now we're lost!"

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CHAPTER OVERVIEW

8: The Postulates of Quantum Mechanics

8.1: The Classical Wave Equation
8.2: The Schrödinger Equation
8.3: Operators in Quantum Mechanics
8.4: Quantum Math
8.4.1: Wavefunctions Have a Probabilistic Interpretation
8.5: Postulate 1 of Quantum Mechanics
8.6: Postulate 2 of Quantum Mechanics
8.6.1: Hermitian Operators
8.6.2: Commuting Operators Allow Infinite Precision
8.7: Postulates 3 and 4 of Quantum Mechanics
8.7.1: Eigenfunctions of Operators are Orthogonal
8.8: Postulate 5 of Quantum Mechanics
8.9: Postulates and Principles of Quantum Mechanics (Exercises)

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8.1: The Classical Wave Equation

Learning Objectives

- To introduce the wave equation including time and position dependence

In the most general sense, waves are particles or other media with wavelike properties and structure (presence of crests and troughs).

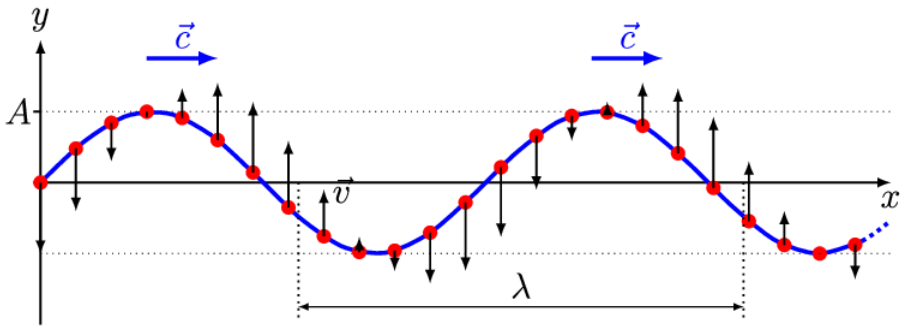


Figure 2.1.1 : A simple translational (transverse) wave. (CC BY-SA 4.0 International; And1mu via Wikimedia Commons)

The simplest wave is the (spatially) one-dimensional sine wave (Figure 2.1.1) with an varing amplitude A described by the equation:

$$A(x,t) = A_o \sin(kx - \omega t + \phi)$$

where

- A_o is the maximum amplitude of the wave, maximum distance from the highest point of the disturbance in the medium (the crest) to the equilibrium point during one wave cycle. In Figure 2.1.1 , this is the maximum vertical distance between the baseline and the wave.
- x is the space coordinate
- t is the time coordinate
- k is the wavenumber
- ω is the angular frequency
- ϕ is the phase constant.

One can categorize “waves” into two different groups: *traveling waves* and *stationary waves*.

8.1.1: Traveling Waves

Traveling waves, such as ocean waves or electromagnetic radiation, are waves that “move,” meaning that they have a frequency and are propagated through time and space. Another way of describing this property of “wave movement” is in terms of energy transmission – a wave travels, or transmits energy, over a set distance. The most important kinds of traveling waves in everyday life are electromagnetic waves, sound waves, and perhaps water waves, depending on where you live. It is difficult to analyze waves spreading out in three dimensions, reflecting off objects, etc., so we begin with the simplest interesting examples of waves, those restricted to move along a line. Let’s start with a rope, like a clothesline, stretched between two hooks. You take one end off the hook, holding the rope, and, keeping it stretched fairly tight, wave your hand up and back once. If you do it fast enough, you’ll see a single bump travel along the rope:

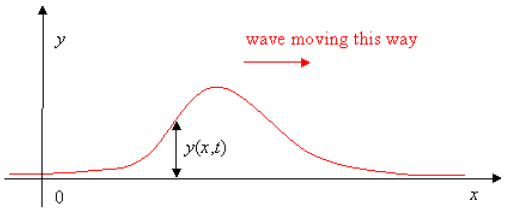


Figure 2.1.2 : A one-dimensional traveling wave at one instance of time t.

This is the simplest example of a *traveling wave*. You can make waves of different shapes by moving your hand up and down in different patterns, for example an upward bump followed by a dip, or two bumps. You'll find that the traveling wave *keeps the same shape* as it moves down the rope. Taking the rope to be stretched tightly enough that we can take it to be horizontal, we'll use its rest position as our *x*-axis (Figure 2.1.1). The y-axis is taken vertically upwards, and we only wave the rope in an up-and-down way, so actually $y(x,t)$ will be how far the rope is from its rest position at x at time t: that is, Figure 2.1.2 shows where the rope is at a single time t.

We can now express the observation that the wave "keeps the same shape" more precisely. Taking for convenience time $t = 0$ to be the moment when the peak of the wave passes $x = 0$, we graph here the rope's position at t = 0 and some later times t as a movie (Figure 2.1.3). Denoting the first function by $y(x,0) = f(x)$, then the second $y(x,t) = f(x - vt)$: it is the same function with the "same shape," but just moved over by vt, where v is the velocity of the wave.

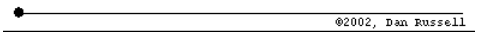


Figure 2.1.3 : A one-dimensional traveling wave at as a function of time. Traveling waves propagate energy from one spot to another with a fixed velocity v. (CC BY-NC-ND; Daniel A. Russell).

To summarize: on sending a traveling wave down a rope by jerking the end up and down, from observation the wave travels at constant speed and keeps its shape, so the displacement *y* of the rope at any horizontal position at x at time t has the form

$$y(x,t) = f(x - vt) \tag{8.1.1}$$

We are neglecting frictional effects—in a real rope, the bump gradually gets smaller as it moves along.

8.1.2: Standing Waves

In contrast to traveling waves, *standing waves*, or stationary waves, remain in a constant position with crests and troughs in fixed intervals. One way of producing a variety of standing waves is by plucking a melody on a set of guitar or violin strings. When placing one's finger on a part of the string and then plucking it with another, one has created a standing wave. The solutions to this problem involve the string oscillating in a sine-wave pattern (Figure 2.1.4) with no vibration at the ends. There is also no vibration at a series of equally-spaced points between the ends; these "quiet" places are *nodes*. The places of maximum oscillation are *antinodes*.

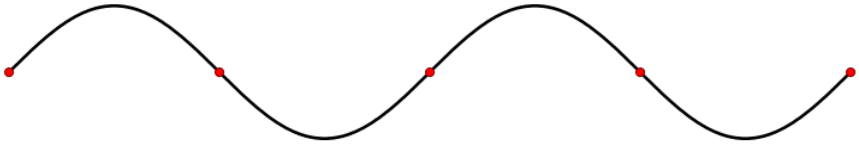


Figure 2.1.4 : Animation of standing wave in the stationary medium with marked wave nodes (red circles). (public domain; LucasVB).

Bound vs. Free particles and Traveling vs. Stationary Waves

Traveling waves exhibit movement and propagate through time and space and stationary wave have crests and troughs at fixed intervals separated by nodes. "Free" particles like the photoelectron discussed in the photoelectron effect, exhibit traveling

wave like properties. In contrast, electrons that are "bound" waves will exhibit stationary wave like properties. The latter was invoked for the Bohr atom for quantizing angular moment of an electron bound within a hydrogen atom.

8.1.3: The Wave Equation

The mathematical description of the one-dimensional waves (both traveling and standing) can be expressed as

$$\frac{\partial^2 u(x,t)}{\partial x^2} = \frac{1}{v^2}\frac{\partial^2 u(x,t)}{\partial t^2} \tag{8.1.2}$$

with u is the amplitude of the wave at position x and time t, and v is the velocity of the wave (Figure 2.1.2).

Equation 8.1.2 is called the classical wave equation in one dimension and is a *linear partial differential equation*. It tells us how the displacement u can change as a function of position and time and the function. The solutions to the wave equation ($u(x,t)$) are obtained by appropriate integration techniques. It may not be surprising that not all possible waves will satisfy Equation 8.1.2 and the waves that do must satisfy both **the initial conditions** and the **boundary conditions**, i.e. on how the wave is produced and what is happening on the ends of the string.

For example, for a standing wave of string with length L held taut at two ends (Figure 2.1.3), the boundary conditions are

$$u(0,t) = 0 \tag{8.1.3}$$

and

$$u(L,t) = 0 \tag{8.1.4}$$

for all values of t. As expected, different system will have different boundary conditions and hence different solutions.

Mathematical Origin of Quantization

The initial conditions and the boundary conditions used to solve the wave equation will result in restrictions of "allowed" waves to exist in a similar fashion that only certain solutions exist for the electrons in the Bohr atom.

The first six wave solutions $u(x,t)$ to Equation 8.1.2 subject to the boundary conditions in Equations 8.1.3 and 8.1.4 (discussed in detail later) results in the wave in Figure 2.1.5 . These are standing waves that exist with frequencies based on the number of *nodes* (0, 1, 2, 3,...) they exhibit (more discussed in the following Section).

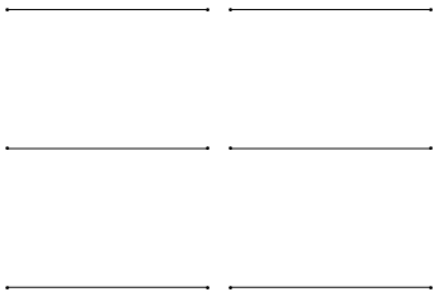


Figure 2.1.5 : Standing waves in a string (both spatially and temporally). The first six solutions ($u(x,t)$. from Wikipedia.

Curvature of Wave Solutions

Since the acceleration of the wave amplitude (right side of Equation 8.1.2) is proportional to $\frac{\partial^2}{\partial x^2}$, the greater curvature in the material produces a greater acceleration, i.e., greater changing velocity of the wave (Figure 2.1.4) and greater frequency of oscillation. As discussed later, the higher frequency waves (i..e, more nodes) are higher energy solutions; this as expected from the experiments discussed in Chapter 1 including Plank's equation $E = h\nu$.

8.1.4: Summary

Waves which exhibit movement and are propagated through time and space. The two basic types of waves are traveling and stationary. Both exhibit wavelike properties and structure (presence of crests and troughs) which can be mathematically described by a wavefunction or amplitude function. Both wave types display movement (up and down displacement), but in different ways.Traveling waves have crests and troughs which are constantly moving from one point to another as they travel over a length or distance. In this way, energy is transmitted along the length of a traveling wave. In contrast, standing waves have nodes at fixed positions; this means that the wave's crests and troughs are also located at fixed intervals. Therefore, standing waves only experience vibrational movement (up and down displacement) on these set intervals - no movement or energy travels along the length of a standing wave.

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8.3: Operators in Quantum Mechanics

3.02: Linear Operators in Quantum Mechanics

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3.03: The Schrödinger Equation is an Eigenvalue Problem

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8.4.1: Wavefunctions Have a Probabilistic Interpretation

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8.5: Postulate 1 of Quantum Mechanics

Learning Objectives

- Introduce the first postulate of quantum mechanics
- Recognize invalid wavefunction categories

In classical mechanics, the configuration or state of a system is given by a point (x,p) in the space of coordinates and momenta. This specifies everything else in the system in a fully deterministic way, in that any observable Q that can be expressed as $Q(x,p)$ can be found, and any that cannot is irrelevant. Yet, as we have seen with the diffraction of electrons, it is **impossible** to know both the position and momentum of the electron exactly at every point along the trajectory. This is mathematically expressed as the famous position-momentum uncertainty principle. Hence, specifying a state by (x,p) in classical mechanics clearly will not work in quantum mechanics. So what specifies the state of a quantum system? This is where the **first Postulate of quantum mechanics** comes in.

Postulate I

The state of the system is **completely** specified by ψ. All possible information about the system can be found in the wavefunction ψ.

The properties of a quantum mechanical system are determined by a wavefunction $\psi(r,t)$ that depends upon the spatial coordinates of the system and time, r and t. For a single particle system, r is the set of coordinates of that particle $r=(x_1,y_1,z_1)$. For more than one particle, r is used to represent the complete set of coordinates $r=(x_1,y_1,z_1,x_2,y_2,z_2,\ldots x_n,y_n,z_n)$. Since the state of a system is defined by its properties, ψ specifies or identifies the state and sometimes is called the state function rather than the wavefunction.

What does ψ mean? This is best answered in terms of the probability density $P(x)$ that determines the probability (density) that an object in the state $\psi(x)$ will be found at position x (the Born interpretation).

$$P(x)=\psi^*(x)\psi(x) \tag{8.5.1}$$

$$=|\psi(x)|^2 \tag{8.5.2}$$

Hence, for valid (e.g., well-behaved) wavefunctions, the normalized probability in Equation 8.5.2 holds true, such that the integral over all space is equal to 1.

$$\int_{-\infty}^{\infty}\psi^*(x)\psi(x)\,dx=1 \tag{8.5.3}$$

Equation 8.5.3 means that the chance to find a particle is 100% somewhere within all space (e.g. somewhere between $-\infty$ and $+\infty$). A wavefunction is said to be **square-integrable** if Equation 8.5.3 can be satisfied (so that the Born Interpretation to be applicable).

Definition: Square-Integrable Functions

A complex-valued function, $f(x)$, is a *square-integrable* function if the integral of the square of the absolute value is finite.

$$\int_{-\infty}^{\infty}f^*(x)f(x)\,dx<\infty$$

For this to be true, the integrals of the positive and negative portions of the real and imaginary parts of $f(x)$ must both be finite.

Let us examine this set of examples in further detail in Figure 4.1.1 . The first wavefunction ψ_1 is sharply peaked at a particular value of x, and the probability density, being its square, is likewise peaked there as well. This is the wavefunction for a particle well localized at a position given by the center of the peak, as the probability density is high there, and the width of the peak is small, so the uncertainty in the position is very small.

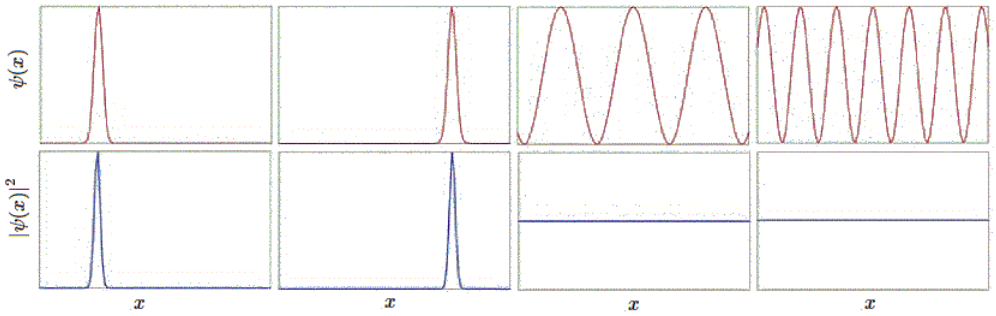


Figure 4.1.1 : Examples of good wavefunctions, $\psi(x)$, (red, top) and corresponding probability densities, $P(x)$, (blue, bottom).

The second wavefunction ψ_2 has the same peak profile, but shifted to a different position center. All of the properties of the first wavefunction hold here too, so this simply describes a particle that is well-localized at that different position. The third and fourth wavefunctions ψ_3 and ψ_4 respectively look like sinusoids of different spatial periods. The wavefunctions are actually complex of the form

$$\psi(x) = Ne^{ikx}$$

so only the real part is being plotted in Figure 4.1.1 . Note that even though the periods, k, of the oscillating wavefunctions are different,

$$\begin{aligned} P(x) &= \psi^*(x)\psi(x) \\ &= |e^{ikx}|^2 \\ &= N^2 \left(e^{-ikx}\right)\left(e^{ikx}\right) \\ &= N^2 \end{aligned}$$

for all k, so the corresponding probability densities, $P(x)$, are the same except for the normalization constant (Equation 8.5.2). We saw before that it does not make a whole lot of sense to think of a sinusoidal wave as being localized in some place. Indeed, the positions for these two wavefunctions are ill-defined, so they are not well-localized, and the uncertainty in the position is large in each case. This is Heisenberg Uncertainty Principle in action.

8.5.1: Ill-behaved (invalid) Wavefunctions

The Born interpretation in Equation 8.5.2 means that many wavefunctions which would be acceptable mathematical solutions of the Schrödinger equation are **not acceptable** because of their implications for the physical properties of the system. To satisfy this interpretation, wavefunctions must be:

- single valued,
- continuous, and
- finite.

These aspects mean that the valid wavefunction must be one-to-one, it cannot have an undefined slope, and cannot go to $-\infty$ or $+\infty$. For example, the wavefunction must not be infinite over any finite region. If it is, then the integral in Equation 8.5.3 is equal to infinity. This implies that the particle described by such a wavefunction has a zero probability of being anywhere where the wavefunction is not infinite, but is certain to be found at all points where the wavefunction is infinite.

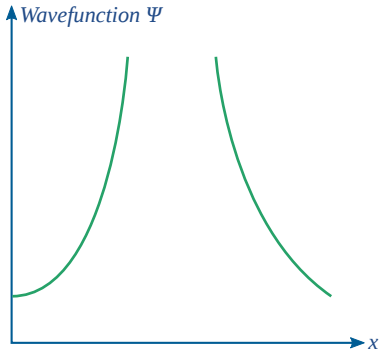


Figure 4.1.2 : This function is an invalid wavefunction since the amplitude is going to infinity over a region (the middle in this case). (CC BY-NC; Ümit Kaya via LibreTexts)

The Born interpretation also renders unacceptable solutions of the Schrödinger equation for which $|\psi(x)|^2$ has more than one value at any point. This would suggest that there were multiple different probabilities of finding the particle at that point, which is clearly absurd. The requirement that the square modulus of the wavefunction must be single-valued usually implies that the wavefunction itself must be single valued. The function in Figure 4.1.3 violates this requirement. The grey lines indicate the region where the wavefunction is multivalued.

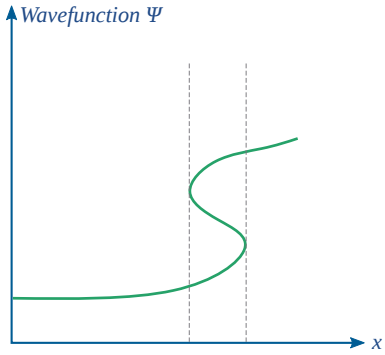


Figure 4.1.3 : This function is an invalid wavefunction since it is not a proper function (i. e., not one-to-one). (CC BY-NC; Ümit Kaya via LibreTexts)

Further restrictions arise because the wavefunction must satisfy the Schrödinger equation, which is a second-order differential equation. This implies that the second derivative of the function must exist, which implies that the first derivative of the wavefunction to exist (otherwise the second derivative is also undefined and the wavefunction cannot be a solution of the Schrödinger equation). The functions in Figure 4.1.4 are also not acceptable for these reasons.

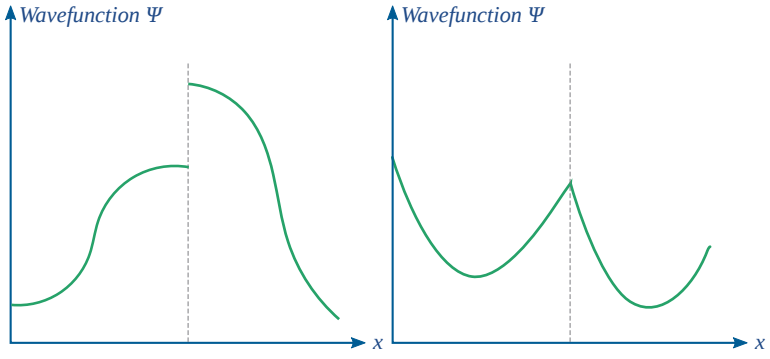


Figure 4.1.4 : These functions are invalid wavefunctions. (left) The first derivative of a function gives its gradient at a given point, and it thus exists as long as the function is continuous - only if there is a break in the function is there a point at which its first derivative does not exist. (right) The second derivative of this wavefunction is discontinuous at the point indicated, where the gradient of the line changes by more than 180º. In practice, this requirement may be somewhat flexible, particularly if the potential energy of the system shows rapid changes with distance. (CC BY-NC; Ümit Kaya via LibreTexts)

Exercise 4.1.1

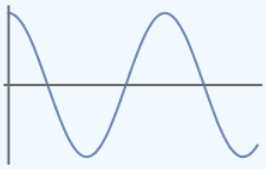
Determine if each of the following functions is acceptable as a wavefunction over the indicated regions:

a. $\cos x$ over $(0, \infty)$
b. e^{x} over $(-\infty, \infty)$
c. e^{-x} over $[0, \infty)$
d. $\tan \theta$ over $[0, 2\theta]$

Solution a

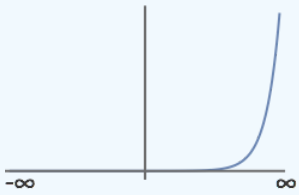
This is not an acceptable wavefunction. It is **single-valued** across the entire range. There is a single value for each value of x. It is **continuous** over the defined limits of integration, as we can see from a plot given below. However, it is not square-integrable.

$$\int_0^{\infty} |\cos(x)|^2 dx \not< \infty$$



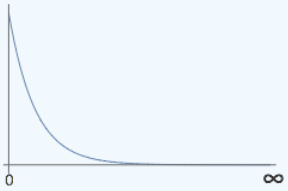
Solution b

This is not an acceptable wavefunction. Over the limits of integration from $-\infty$ to ∞, this function is not square-integrable. Note in the plot below, how the function is indefinite approaching the limits of ∞.



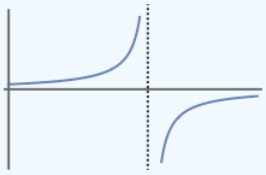
Solution c

This is an acceptable wavefunction over the given limits. It is **finite** over the given limits. It is **continuous** within given limits. It is **single-valued.** It is square-integrable with $\int_0^{\infty} |\Psi(x)|^2 dx = \frac{1}{2}$.



Solution d

This is not an acceptable wavefunction. It is discontinuous over the limits of integration.



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8.6: Postulate 2 of Quantum Mechanics

Learning Objectives

- Understand how the correspondence principle argues that a unique quantum operator exist for every classical observable.
- Recognize several of the commonly used quantum operators

An observable is a dynamic variable of a system that can be experimentally measured (e.g., position, momentum and kinetic energy). In systems governed by classical mechanics, it is a real-valued function (never complex), however, in quantum physics, every observable in quantum mechanics is represented by an independent operator that is used to obtain physical information about the observable from the wavefunction. It is a general principle of quantum mechanics that there is an operator for every physical observable. For an observable that is represented in classical physics by a function $Q(x,p)$, the corresponding operator is $Q(\hat{x},\hat{p})$.

Postulate II: The Correspondence Principle

For every observable property of a system there is a corresponding quantum mechanical operator. This is often referred to as the **Correspondence Principle**.

Classical dynamical variables, such as x and p, are represented in quantum mechanics by *linear operators* which act on the wavefunction. The operator for position of a particle in three dimensions is just the set of coordinates x, y, and z, which is written as a vector, r:

$$\vec{r} = (x,y,z) \tag{8.6.1}$$

$$= x\vec{i} + y\vec{j} + z\vec{k} \tag{8.6.2}$$

The operator for a component of linear momentum is

$$\hat{p}_x = -i\hbar\frac{\partial}{\partial x} \tag{8.6.3}$$

and the operator for kinetic energy in one dimension is

$$\hat{T}_x = \left(-\frac{\hbar^2}{2m}\right)\frac{\partial^2}{\partial x^2} \tag{8.6.4}$$

and in three dimensions

$$\hat{p} = -i\hbar\nabla \tag{8.6.5}$$

and

$$\hat{T} = \left(-\frac{\hbar^2}{2m}\right)\nabla^2 \tag{8.6.6}$$

The total energy operator is called the Hamiltonian operator, $\hat{H}$ and consists of the kinetic energy operator plus the potential energy operator.

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + \hat{V}(x,y,z) \tag{8.6.7}$$

The Hamiltonian Operator

The Hamiltonian operator is named after the Irish mathematician William Hamilton and comes from the his formulation of Classical Mechanics that is based on the total energy:

$$\hat{H} = \hat{T} + \hat{V}$$

rather than Newton's second law,

$$\vec{F} = m\vec{a}$$

In many cases only the kinetic energy of the particles and the electrostatic or Coulomb potential energy due to their charges are considered, but in general all terms that contribute to the energy appear in the Hamiltonian. These additional terms account for such things as external electric and magnetic fields and magnetic interactions due to magnetic moments of the particles and their motion.

Table 4.2.1 : Some common Operators in Quantum Mechanics

Name	Observable Symbol	Operator Symbol	Operation
Position (in 1D)	x	$\hat{X}$	Multiply by x
Position (in 3D)	$\vec{r}$	$\hat{R}$	Multiply by $\vec{r}$
Momentum (in 1D)	p_x	$\hat{P}_x$	$-i\hbar\frac{d}{dx}$
Momentum (in 3D)	$\vec{p}$	$\hat{P}$	$-i\hbar\left[\hat{i}\,\frac{d}{dx}+\hat{j}\frac{d}{dy}+\hat{k}\frac{d}{dz}\right]$
Kinetic Energy (in 1D)	T_x	$\hat{T_x}$	$\frac{-\hbar^2}{2m}\frac{d^2}{dx^2}$
Kinetic Energy (in 3D)	T	$\hat{T}$	$\frac{-\hbar^2}{2m}\left[\frac{d^2}{dx^2}+\frac{d^2}{dy^2}+\frac{d^2}{dz^2}\right]$ Which can be simplified to $\frac{-\hbar^2}{2m}\nabla^2$
Potential Energy (in 1D)	$V(x)$	$\hat{V}(x)$	Multiply by $V(x)$
Potential Energy (in 3D)	$V(x,y,z)$	$\hat{V}(x,y,z)$	Multiply by $V(x,y,z)$
Total Energy	E	$\hat{E}$	$\frac{-\hbar^2}{2m}\nabla^2+V(x,y,z)$
Angular Momentum (x axis component)	L_x	$\hat{L_x}$	$-i\hbar\left[y\frac{d}{dz}-z\frac{d}{dy}\right]$
Angular Momentum (y axis component)	L_y	$\hat{L_y}$	$-i\hbar\left[z\frac{d}{dx}-x\frac{d}{dz}\right]$
Angular Momentum (z axis component)	L_z	$\hat{L_z}$	$-i\hbar\left[x\frac{d}{dy}-y\frac{d}{dx}\right]$

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8.6.1: Hermitian Operators

Learning Objectives

- Understand the properties of a Hermitian operator and their associated eigenstates
- Recognize that all experimental obervables are obtained by Hermitian operators

Consideration of the quantum mechanical description of the particle-in-a-box exposed two important properties of quantum mechanical systems. We saw that the eigenfunctions of the Hamiltonian operator are orthogonal, and we also saw that the position and momentum of the particle could not be determined exactly. We now examine the generality of these insights by stating and proving some fundamental theorems. These theorems use the Hermitian property of quantum mechanical operators that correspond to observables, which is discuss first.

8.6.1.1: Hermitian Operators

Since the eigenvalues of a quantum mechanical operator correspond to measurable quantities, the eigenvalues must be real, and consequently a quantum mechanical operator must be Hermitian. To prove this, we start with the premises that ψ and φ are functions, $\int d\tau$ represents integration over all coordinates, and the operator $\hat{A}$ is **Hermitian** by definition if

$$\int \psi^* \hat{A} \psi \, d\tau = \int (\hat{A}^* \psi^*) \psi \, d\tau \tag{8.6.1.1}$$

This equation means that the complex conjugate of $\hat{A}$ can operate on ψ^* to produce the same result after integration as $\hat{A}$ operating on φ, followed by integration. To prove that a quantum mechanical operator $\hat{A}$ is Hermitian, consider the eigenvalue equation and its complex conjugate.

$$\hat{A}\psi = a\psi \tag{8.6.1.2}$$

$$\hat{A}^* \psi^* = a^* \psi^* = a\psi^* \tag{8.6.1.3}$$

Note that $a^* = a$ because the eigenvalue is real. Multiply Equation 8.6.1.2 and 8.6.1.3 from the left by ψ^* and ψ, respectively, and integrate over the full range of all the coordinates. Note that ψ is normalized. The results are

$$\int \psi^* \hat{A} \psi \, d\tau = a \int \psi^* \psi \, d\tau = a \tag{8.6.1.4}$$

$$\int \psi \hat{A}^* \psi^* \, d\tau = a \int \psi \psi^* \, d\tau = a \tag{8.6.1.5}$$

Since both integrals equal a, they must be equivalent.

$$\int \psi^* \hat{A} \psi \, d\tau = \int \psi \hat{A}^* \psi^* \, d\tau \tag{8.6.1.6}$$

The operator acting on the function,

$$\hat{A}^* \int \psi^* \hat{A} \psi \, d\tau = \int \psi \hat{A}^* \psi^* \, d\tau_*$$

produces a new function. Since functions commute, Equation 8.6.1.6 can be rewritten as

$$\int \psi^* \hat{A} \psi d\tau = \int (\hat{A}^* \psi^*) \psi d\tau \tag{8.6.1.7}$$

This equality means that $\hat{A}$ is Hermitian.

Contributors and Attributions

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8.6.2: Commuting Operators Allow Infinite Precision

Learning Objectives

- To connect the Heisenberg Uncertainty principle to the commutation relations.
- Develop proficiency in calculating the commutator of two operators.

If two operators commute then both quantities can be measured at the same time with infinite precision, if not then there is a tradeoff in the accuracy in the measurement for one quantity vs. the other. This is the mathematical representation of the Heisenberg Uncertainty principle.

8.6.2.1: Commuting Operators

One important property of operators is that the order of operation matters. Thus in general

$$\hat{A}\hat{E}f(x) \neq \hat{E}\hat{A}f(x)$$

unless the two operators **commute**. Two operators commute if the following equation is true:

$$\left[\hat{A},\hat{E}\right] = \hat{A}\hat{E} - \hat{E}\hat{A} = 0$$

To determine whether two operators commute first operate $\hat{A}\hat{E}$ on a function $f(x)$. Then operate$\hat{E}\hat{A}$ the same function $f(x)$. If the same answer is obtained subtracting the two functions will equal zero and the two operators will commute.on

If two operators commute, then they can have the same set of eigenfunctions. By definition, two operators $\hat{A}$ and $\hat{B}$ commute if the effect of applying $\hat{A}$ then $\hat{B}$ is the same as applying $\hat{B}$ then $\hat{A}$, i.e.

$$\hat{A}\hat{B} = \hat{B}\hat{A}.$$

For example, the operations brushing-your-teeth and combing-your-hair commute, while the operations getting-dressed and taking-a-shower do not. This theorem is very important. If two operators commute and consequently have the same set of eigenfunctions, then the corresponding physical quantities can be evaluated or measured exactly simultaneously with no limit on the uncertainty. As mentioned previously, the eigenvalues of the operators correspond to the measured values.

If $\hat{A}$ and $\hat{B}$ commute and ψ is an eigenfunction of $\hat{A}$ with eigenvalue b, then

$$\hat{B}\hat{A}\psi = \hat{A}\hat{B}\psi = \hat{A}b\psi = b\hat{A}\psi \tag{8.6.2.1}$$

Equation 8.6.2.1 says that $\hat{A}\psi$ is an eigenfunction of $\hat{B}$ with eigenvalue b, which means that when $\hat{A}$ operates on ψ, it cannot change ψ. At most, $\hat{A}$ operating on ψ can produce a constant times ψ.

$$\hat{A}\psi = a\psi \tag{8.6.2.2}$$

$$\hat{B}(\hat{A}\psi) = \hat{B}(a\psi) = a\hat{B}\psi = ab\psi = b(a\psi) \tag{8.6.2.3}$$

Equation 8.6.2.3 shows that Equation 8.6.2.2 is consistent with Equation 8.6.2.1. Consequently ψ also is an eigenfunction of $\hat{A}$ with eigenvalue a.

Example 4.6.1

Do the following pairs of operators commute?

a. $\hat{A} = \dfrac{d}{dx}$ and $\hat{E} = x^2$
b. $\hat{B} = \dfrac{h}{x}$ and $\hat{C}\{f(x)\} = f(x) + 3$
c. $\hat{J} = 3x$ and $\hat{O} = x^{-1}$

Solution a

This requires evaluating $\left[\hat{A},\hat{E}\right]$, which requires solving for $\hat{A}\{\hat{E}f(x)\}$ and $\hat{E}\{\hat{A}f(x)\}$ for arbitrary wavefunction $f(x)$ and asking if they are equal.

$$\hat{A}\{\hat{E}f(x)\} = \hat{A}\{x^2 f(x)\} = \frac{d}{dx}\{x^2 f(x)\} = 2xf(x) + x^2 f'(x)$$

From the product rule of differentiation.

$$\hat{E}\{\hat{A}f(x)\} = \hat{E}\{f'(x)\} = x^2 f'(x)$$

Now ask if they are equal

$$\left[\hat{A},\hat{E}\right] = 2xf(x) + x^2 f'(x) - x^2 f'(x) = 2xf(x) \neq 0$$

Therefore the two operators do not commute.

Solution b

This requires evaluating $\left[\hat{B},\hat{C}\right]$ like in Example 4.6.1 .

$$\hat{B}\{\hat{C}f(x)\} = \hat{B}\{f(x)+3\} = \frac{h}{x}(f(x)+3) = \frac{hf(x)}{x} + \frac{3h}{x}$$

$$\hat{C}\{\hat{B}f(x)\} = \hat{C}\{\frac{h}{x}f(x)\} = \frac{hf(x)}{x} + 3$$

Now ask if they are equal

$$\left[\hat{B},\hat{C}\right] = \frac{hf(x)}{x} + \frac{3h}{x} - \frac{hf(x)}{x} - 3 \neq 0$$

The two operators do **not** commute.

Solution c

This requires evaluating $\left[\hat{J},\hat{O}\right]$

$$\hat{J}\{\hat{O}f(x)\} = \hat{J}\{f(x)3x\} = f(x)3x/x = 3f(x)$$

$$\hat{O}\{\hat{J}f(x)\} = \hat{O}\{\frac{f(x)}{x}\} = \frac{f(x)3x}{x} = 3f(x)$$

$$\left[\hat{J},\hat{O}\right] = 3f(x) - 3f(x) = 0$$

Because the difference is zero, the two operators commute.

8.6.2.2: General Heisenberg Uncertainty Principle

Although it will not be proven here, there is a general statement of the uncertainty principle in terms of the commutation property of operators. If two operators $\hat{A}$ and $\hat{B}$ do not commute, then the uncertainties (standard deviations σ) in the physical quantities associated with these operators must satisfy

$$\sigma_A \sigma_B \geq \left| \int \psi^* [\hat{A}\hat{B} - \hat{B}\hat{A}] \psi \, d\tau \right| \tag{8.6.2.4}$$

where the integral inside the square brackets is called the **commutator**, and $\left|\ \right|$ signifies the modulus or absolute value. If $\hat{A}$ and $\hat{B}$ commute, then the right-hand-side of Equation 8.6.2.4 is zero, so either or both σ_A and σ_B could be zero, and there is no restriction on the uncertainties in the measurements of the eigenvalues a and b. If $\hat{A}$ and $\hat{B}$ do not commute, then the right-hand-side of Equation 8.6.2.4 will not be zero, and neither σ_A nor σ_B can be zero unless the other is infinite. Consequently, both a and b cannot be eigenvalues of the same wavefunctions and cannot be measured simultaneously to arbitrary precision.

? Exercise4.6.1

Show that the commutator for position and momentum in one dimension equals $-i\hbar$ and that the right-hand-side of Equation 8.6.2.4 therefore equals $\hbar/2$ giving $\sigma_x\sigma_{px} \geq \frac{\hbar}{2}$.

8.6.2.3: Applications

Operators are very common with a variety of purposes. They are used to figure out the energy of a wavefunction using the Schrödinger Equation.

$$\hat{H}\psi = E\psi$$

They also help to explain observations made in the experimentally. An example of this is the relationship between the magnitude of the angular momentum and the components.

$$\left[\hat{L}^2, \hat{L}_x^2\right] = \left[\hat{L}^2, \hat{L}_y^2\right] = \left[\hat{L}^2, \hat{L}_z^2\right] = 0$$

However the components do not commute themselves. An additional property of commuters that commute is that both quantities can be measured simultaneously. Thus, the magnitude of the angular momentum and ONE of the components (usually z) can be known at the same time however, NOTHING is known about the other components.

> *The physical quantities corresponding to operators that commute can be measured simultaneously to any precision.*

8.6.2.2A Example

Determine whether the following two operators commute:

$$\hat{K} = \alpha \int [1]^{[\infty]} d[x]$$

and

$$\hat{H} = d/dx$$

Solution

Evaluate

$$\left[\hat{K}, \hat{H}\right]$$

8.6.2.2B Example

Determine whether the following two operators commute:

$$\hat{I} = 5$$

and

$$\hat{L} = \int_{[1]}^{[\infty]} d[x]$$

Solution

The identity operator, $\hat{I}$ is a real number and commutes with everything. Thus, these two operators commute. We can also directly evaluate the commutator:

$$\left[\hat{I}, \hat{L}\right]$$

$$\left[\hat{I}, \hat{L}\right] f(x) = 5\int_1^\infty f(x)d(x) - \int_1^\infty 5f(x)d(x) = 0$$

8.6.2.2 Exercise

Show that the components of the angular momentum do not commute.

$$\hat{L}_x = -i\hbar\left[-\sin\left(\phi\frac{\delta}{\delta\theta}\right) - \cot(\Theta)\cos\left(\phi\frac{\delta}{\delta\phi}\right)\right]$$

$$\hat{L}_y = -i\hbar\left[\cos\left(\phi\frac{\delta}{\delta\theta}\right) - \cot(\Theta)\cos\left(\phi\frac{\delta}{\delta\phi}\right)\right]$$

$$\hat{L}_z = -i\hbar\frac{\delta}{\delta\theta}$$

Solution

This requires evaluating the following commucators:

$$\left[\hat{L}_z, \hat{L}_x\right] = i\hbar\hat{L}_y$$

$$\left[\hat{L}_x, \hat{L}_y\right] = i\hbar\hat{L}_z$$

$$\left[\hat{L}_y, \hat{L}_z\right] = i\hbar\hat{L}_x$$

8.6.2.4: References

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2. McQuarrie, D.A. Quantum Chemistry, 2nd Edition; University Science Books:Sausalito, 2008
3. Schechter, M. Operator Methods in Quantum Mechanics; Dover Publications, 2003

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8.7: Postulates 3 and 4 of Quantum Mechanics

Learning Objectives

- To be introduced to the role of eigenvalue equations in obtaining observables from a system
- Understand how expectation values are calculated if the wavefunctions is not an eigenstate of the operator for the observable.

Recall, that we can identify the total energy operator, which is called the Hamiltonian operator, $\hat{H}$, as consisting of the kinetic energy operator plus the potential energy operator.

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + \hat{V}(x,y,z) \tag{8.7.1}$$

Using this notation, we write the Schrödinger Equation as

$$\hat{H}\,|\psi(x,y,z)\rangle = E|\,\psi(x,y,z)\rangle \tag{8.7.2}$$

Equation 8.7.2 says that the Hamiltonian operator operates on the wavefunction to produce the energy, which is a number, (a quantity of Joules), times the wavefunction. Such an equation, where the operator, operating on a function, produces a constant times the function, is called an **eigenvalue equation**. The function is called an **eigenfunction**, and the resulting numerical value is called the **eigenvalue**. Eigen here is the German word meaning self or own.

It is a general principle of Quantum Mechanics that there is an operator for every physical observable. A physical observable is anything that can be measured. If the wavefunction that describes a system is an eigenfunction of an operator, then the value of the associated observable is extracted from the eigenfunction by operating on the eigenfunction with the appropriate operator. The value of the observable for the system is the eigenvalue, and the system is said to be in an eigenstate. Equation 8.7.2 states this principle mathematically for the case of energy as the observable.

Postulate III: Obtaining Observables Requires Solving Eigenvalue Problems

If a system is described by the eigenfunction Ψ of an operator $\hat{A}$ then the value measured for the observable property corresponding to $\hat{A}$ will always be the eigenvalue a, which can be calculated from the eigenvalue equation.

$$\hat{A}\,|\Psi\rangle = a|\,\Psi\rangle \tag{8.7.3}$$

Consider a general real-space operator $A(x)$. When this operator acts on a general wavefunction $\psi(x)$ the result is usually a wavefunction with a completely different shape. However, there are certain special wavefunctions which are such that when A acts on them the result is just a multiple of the original wavefunction. These special wavefunctions are called *eigenstates*, and the multiples are called *eigenvalues*. Thus, if

$$A\,|\psi_a(x)\rangle = a|\,\psi_a(x)\rangle \tag{8.7.4}$$

where a is a complex number, then ψ_a is called an **eigenstate** of A corresponding to the eigenvalue a.

Suppose that A is an operator corresponding to some physical dynamical variable. Consider a particle whose wavefunction is ψ_a. The expectation of value A in this state is simply

$$\begin{aligned}\langle A\rangle &= \int_{-\infty}^{\infty} \psi_a^* A \psi_a dx \\ &= a\int_{-\infty}^{\infty} \psi_a^* \psi_a dx \\ &= a.\end{aligned}$$

where use has been made of Equation 8.7.4 and the normalization condition. Moreover,

$$\begin{aligned}\langle A^2\rangle &= \int_{-\infty}^{\infty} \psi_a^* A^2 \psi_a dx \\ &= a\int_{-\infty}^{\infty} \psi_a^* A \psi_a dx \\ &= a^2 \int_{-\infty}^{\infty} \psi_a^* \psi_a dx \\ &= a^2.\end{aligned}$$

So the variance of A is

$$\begin{aligned}\sigma_A^2 &= \langle A^2\rangle - \langle A\rangle^2 = a^2 - a^2 \\ &= 0.\end{aligned}$$

The fact that the variance is *zero* implies that every measurement of A is bound to yield the same result: namely, a. Thus, the eigenstate ψ_a is a state which is associated with a *unique* value of the dynamical variable corresponding to A. This unique value is simply the associated eigenvalue determined by Equation 8.7.4.

8.7.1: Expectation Values

We have seen that $|\psi(x,t)|^2$ is the probability density of a measurement of a particle's displacement yielding the value x at time t. Suppose that we made a large number of independent measurements of the displacement on an equally large number of identical quantum systems. In general, measurements made on different systems will yield different results. However, from the definition of probability, the mean of all these results is simply

$$\langle x\rangle = \int_{-\infty}^{\infty} x|\psi|^2 dx \tag{8.7.5}$$

Here, $\langle x\rangle$ is called the *expectation value* of x. Similarly the expectation value of any function of x is

$$\langle f(x)\rangle = \int_{-\infty}^{\infty} f(x)|\psi|^2 dx. \tag{8.7.6}$$

Postulate IV

The average value of an observable measurement of a state in (*normalized*) wavefunction ψ with operator $\hat{A}$ is given by the expectation value $\langle a\rangle$:

$$\langle a\rangle = \langle \psi\,|a|\,\psi\rangle \tag{8.7.7}$$

$$= \int_{-\infty}^{\infty} \psi^* \hat{A}\psi dx \tag{8.7.8}$$

If an unnormalized wavefunction where used, then Equation 8.7.8 changes to

$$\langle a\rangle = \frac{\langle \psi\,|a|\,\psi\rangle}{\langle\psi|\psi\rangle} \tag{8.7.9}$$

$$= \frac{\int_{-\infty}^{\infty} \psi^* \hat{A}\psi dx}{\int_{-\infty}^{\infty} \psi^*\psi dx} \tag{8.7.10}$$

The denominator is just the normalization requirement discussed earlier. In general, the results of the various different measurements of x will be scattered around the expectation value $\langle x\rangle$. The degree of scatter is parameterized by the quantity

$$\sigma_x^2 = \int_{-\infty}^{\infty} (x - \langle x\rangle)^2 |\psi|^2 dx \tag{8.7.11}$$

$$\equiv \langle x^2\rangle - \langle x\rangle^2, \tag{8.7.12}$$

which is known as the *variance* of x. The square-root of this quantity, σ_x, is called the *standard deviation* of x. We generally expect the results of measurements of x to lie within a few standard deviations of the expectation value (Figure 4.3.1).

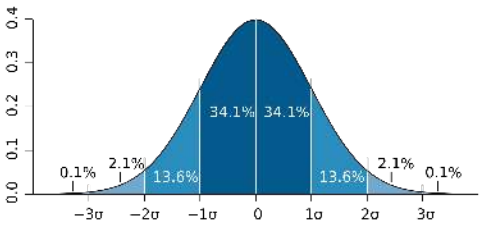


Figure 4.3.1 : A plot of a normal distribution (or bell-shaped curve) where each band has a width of 1 standard deviation. image usd with permission from Wikipedia.

Example 4.3.1

For a particle in a box in its ground state, calculate the expectation value of the

a. *position*,
b. the *linear momentum*,
c. the *kinetic energy*, and
d. the total energy

Solution

First the wavefunction needs to be defined. From the particle in the box solutions, the ground state wavefunction ($n = 1$) is

$$\psi = \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right)$$

We can confirm that the wavefunction is normalized.

$$\int \psi^* \psi \, d\tau = \int_0^L \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right) \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right) dx = 1$$

Hence, the Equation 8.7.8 is the relevant equation to use.

Solution a

The expectation value of the **position** is:

$$\begin{aligned} \langle x \rangle &= \int \psi^* x \psi \, d\tau = \int_0^L \sqrt{\frac{2}{L}} x \sin\left(\frac{\pi x}{L}\right) \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right) dx \\ &= \frac{2}{L} \int_0^L x \sin^2\left(\frac{\pi x}{L}\right) dx \\ &= \frac{L}{2} \end{aligned}$$

Solution b

The expectation value of the **momentum** is:

$$\begin{aligned} \langle p \rangle &= \int \psi^* \hat{p} \psi \, d\tau = \int_0^L \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right) \left(-i\hbar \frac{d}{dx}\right) \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right) dx \\ &= \frac{2i\hbar\pi}{L^2} \int_0^L \sin\left(\frac{\pi x}{L}\right) \cos\left(\frac{\pi x}{L}\right) dx \\ &= 0 \end{aligned}$$

Solution c

The expectation value of the **kinetic energy** is:

$$\langle T \rangle = \int \psi^* \hat{K} \psi \, d\tau = \frac{2}{L} \int_0^L \sin\left(\frac{\pi x}{L}\right) \left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}\right) \sin\left(\frac{\pi x}{L}\right) dx$$
$$= \frac{\hbar^2 \pi^2}{2mL^2} \frac{2}{L} \int_0^L \sin^2\left(\frac{\pi x}{L}\right) dx$$
$$= \frac{\hbar^2 \pi^2}{2mL^2}$$

A position "on average" is in the middle of the box ($L/2$). It has equal probability of traveling towards the left or right, so the average momentum and velocity must be zero.

Solution d

The average kinetic energy must be equal to the total energy of the ground state of the particle in the box, as there is no other energy component (i.e, $V = 0$).

8.7.2: Expanding the Wavefunction

It is also possible to demonstrate that the eigenstates of an operator attributed to a observable form a **complete set** (*i.e.*, that any general wavefunction can be written as a linear combination of these eigenstates). However, the proof is quite difficult, and we shall not attempt it here.

In summary, given an operator $\hat{A}$, any general wavefunction, $\psi(x)$, can be written

$$\psi = \sum_i c_i \phi_i$$

where the c_i are complex weights, and the $\phi(x)$ are the properly normalized (and mutually orthogonal) eigenstates of $\hat{A}$: i.e.,

$$A\phi_i = a_i \phi_i$$

where a_i is the eigenvalue corresponding to the eigenstate ϕ_i, and

$$\int_{-\infty}^{\infty} \phi_i^* \phi_j dx = \delta_{ij}. \tag{8.7.13}$$

Here, δ_{ij} is called the **Kronecker delta-function**, and takes the value unity when its two indices are equal, and zero otherwise. It follows from Equations 8.7.10 and 8.7.13 that

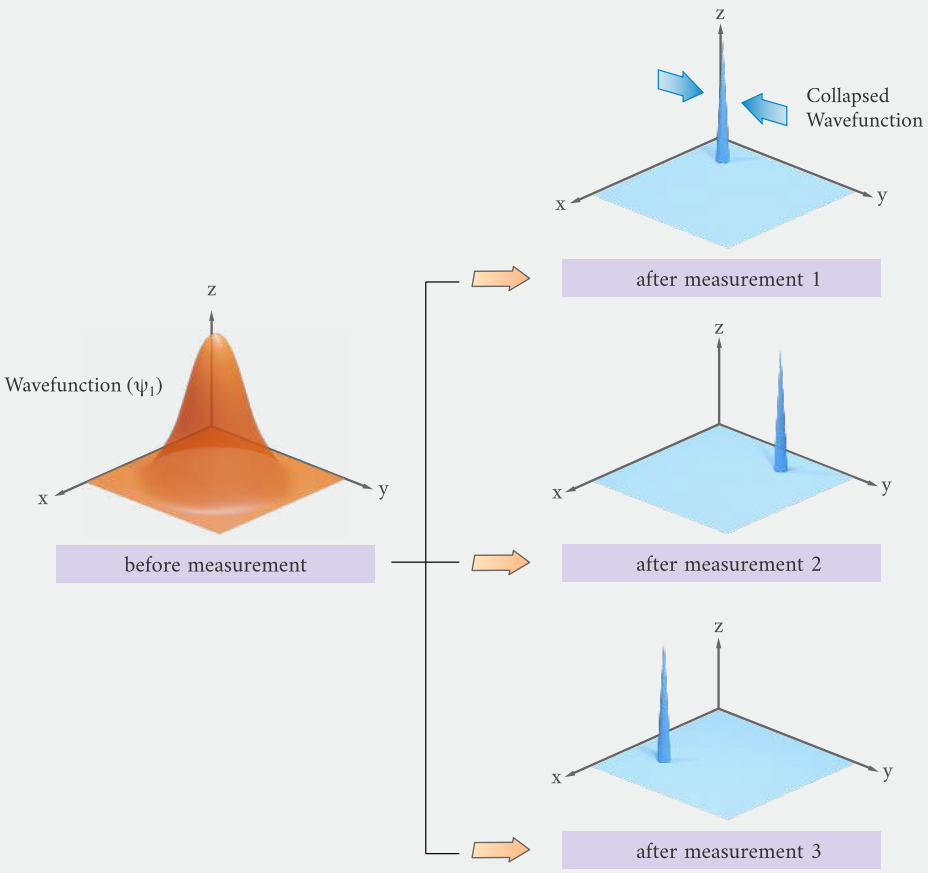
$$c_i = \int_{-\infty}^{\infty} \phi_i^* \psi dx. \tag{8.7.14}$$

Thus, the expansion coefficients in Equation 8.7.14 are easily determined, given the wavefunction ψ and the eigenstates ϕ_i. Moreover, if ψ is a properly normalized wavefunction then Equations 8.7.10 and 8.7.13 yield

$$\sum_i |c_i|^2 = 1.$$

Collapsing the Wavefunction

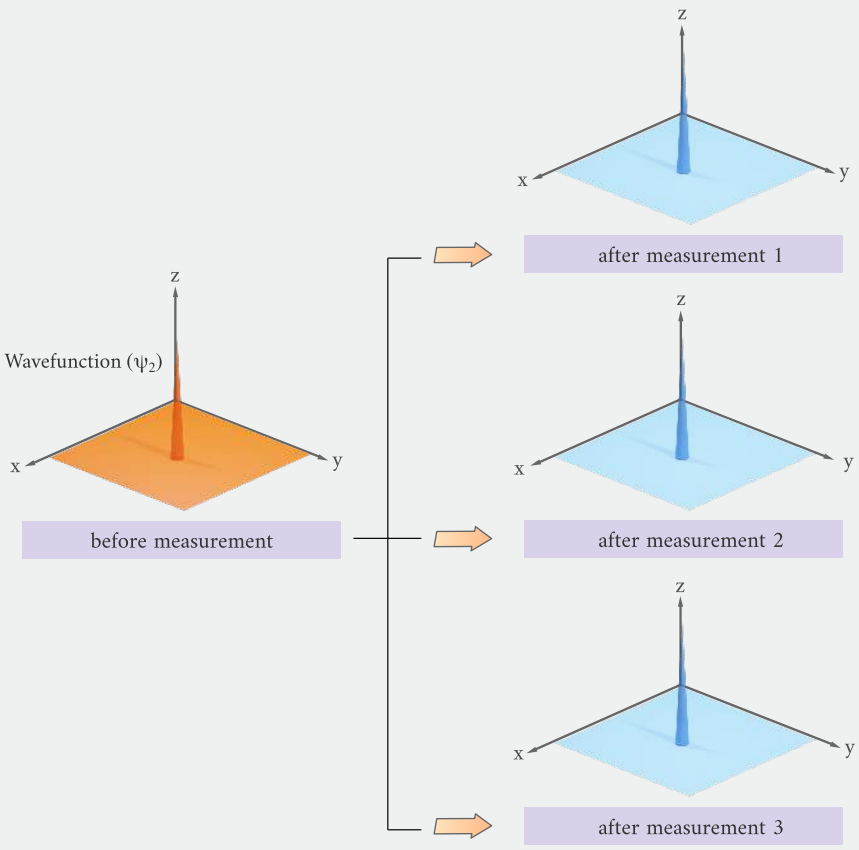
Wavefunction collapse is said to occur when a wavefunction—initially in a superposition of several eigenstates—appears to reduce to a single eigenstate (by "observation"). A particle (or a system in general) can be found in a given state $\psi(x,t)$. Suppose now a measurement is performed on the wavefuction to characterize a specific property of the system.



The measurement of position (with the position operator) effectively collapses this wavefunction that is a superposition of position eigenstates, which are delta-functions and are continuous - i.e. not quantized. Using a different measurement operation may in quantized values (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

Mathematically, an operator $\hat{A}$ is associated with this measurement process, which you suppose has a *complete orthonormal set* of eigenvalues: $\{\phi_i\}$ that is typically an infinite set of functionals that depend on quantum number n. The wavefunction Ψ can be expand and a set of basis functions can be selected to specifies the wavefunction is the coefficients $\{c_n\}$ of the expansion. Therefore, if the system is perturbed, then your wavefunction will have another set of coefficients $\{c'_n\}$.

https://chem.libretexts.org/@go/page/456217



The measurement of position (with the position operator) does not collapse this wavefunction since it is in a position eigenstate in contrast to the wavefunction above. Using a different measurement operation (e.g., kinetic energy) may "collapse" the wavefunction into a different eigenstate (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

If you wavefunction is in the eigenstate of the operator, then each measurement via that operator will give the same result.

Contributors and Attributions

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8.7.1: Eigenfunctions of Operators are Orthogonal

Learning Objectives

- Understand the properties of a Hermitian operator and their associated eigenstates

Eigenfunctions of a Hermitian operator are orthogonal if they have different eigenvalues.

Because of this theorem, we can identify orthogonal functions easily without having to integrate or conduct an analysis based on symmetry or other considerations.

Proof

ψ and φ are two eigenfunctions of the operator Â with real eigenvalues a_1 and a_2, respectively. Since the eigenvalues are real, $a_1^* = a_1$ and $a_2^* = a_2$.

$$\hat{A}\psi = a_1\psi$$

$$\hat{A}^*\psi^* = a_2\psi^*$$

Multiply the first equation by φ^* and the second by ψ and integrate.

$$\int \psi^* \hat{A}\psi \, d\tau = a_1 \int \psi^*\psi \, d\tau$$

$$\int \psi \hat{A}^*\psi^* \, d\tau = a_2 \int \psi\psi^* \, d\tau \tag{8.7.1.1}$$

Subtract the two equations in Equation 8.7.1.1 to obtain

$$\int \psi^* \hat{A}\psi \, d\tau - \int \psi \hat{A}^*\psi^* \, d\tau = (a_1 - a_2) \int \psi^*\psi \, d\tau \tag{8.7.1.2}$$

The left-hand side of Equation 8.7.1.2 is zero because $\hat{A}$ is Hermitian yielding

$$0 = (a_1 - a_2) \int \psi^*\psi \, d\tau \tag{8.7.1.3}$$

If a_1 and a_2 in Equation 8.7.1.3 are not equal, then the integral **must** be zero. This result proves that **nondegenerate eigenfunctions** of the same operator are orthogonal.

□

Two wavefunctions, $\psi_1(x)$ and $\psi_2(x)$, are said to be *orthogonal* if

$$\int_{-\infty}^{\infty} \psi_1^* \psi_2 \, dx = 0. \tag{8.7.1.4}$$

Consider two eigenstates of $\hat{A}$, $\psi_a(x)$ and $\psi_{a'}(x)$, which correspond to the two *different* eigenvalues a and a', respectively. Thus,

$$A\psi_a = a\psi_a \tag{8.7.1.5}$$

$$A\psi_a' = a'\psi_a' \tag{8.7.1.6}$$

Multiplying the complex conjugate of the first equation by $\psi_{a'}(x)$, and the second equation by $\psi_{a'}^*(x)$, and then integrating over all x, we obtain

$$\int_{-\infty}^{\infty} (A\psi_a)^* \psi_{a'} dx = a \int_{-\infty}^{\infty} \psi_a^* \psi_{a'} dx, \tag{8.7.1.7}$$

$$\int_{-\infty}^{\infty} \psi_a^* (A\psi_{a'}) dx = a' \int_{-\infty}^{\infty} \psi_a^* \psi_{a'} dx. \tag{8.7.1.8}$$

However, from Equation 8.7.1.2, the left-hand sides of the above two equations are equal. Hence, we can write

$$(a - a') \int_{-\infty}^{\infty} \psi_a^* \psi_{a'} dx = 0.$$

By assumption, $a \neq a'$, yielding

$$\int_{-\infty}^{\infty} \psi_a^* \psi_{a'} dx = 0.$$

In other words, eigenstates of an Hermitian operator corresponding to *different* eigenvalues are automatically *orthogonal*.

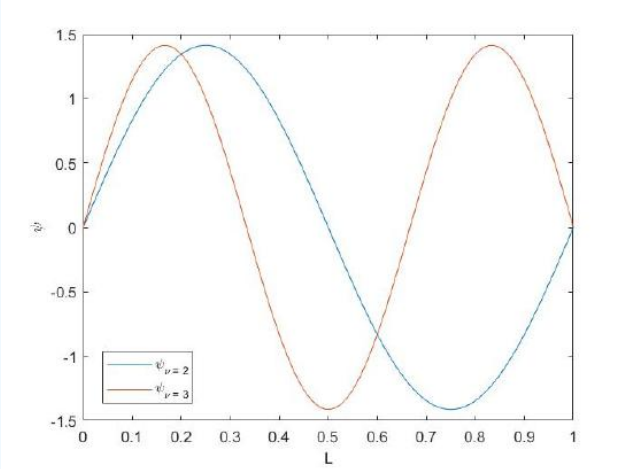
> The eigenvalues of operators associated with experimental measurements are all *real*.

Example8.7.1.1

Draw graphs and use them to show that the particle-in-a-box wavefunctions for $\psi(n = 2)$ and $\psi(n = 3)$ are orthogonal to each other.

Solution

The two PIB wavefunctions are qualitatively similar when plotted



These wavefunctions are orthogonal when

$$\int_{-\infty}^{\infty} \psi(n = 2)\psi(n = 3)dx = 0$$

and when the PIB wavefunctions are substituted this integral becomes

$$\int_0^L \sqrt{\frac{2}{L}} \sin\left(\frac{2n}{L}x\right) \sqrt{\frac{2}{L}} \sin\left(\frac{2n}{L}x\right) dx = ?$$

$$\frac{2}{L} \int_0^L \sin\left(\frac{2}{L}x\right) \sin\left(\frac{3}{L}x\right) = ?$$

We can expand the integrand using trigonometric identities to help solve the integral, but it is easier to take advantage of the symmetry of the integrand, specifically, the $\psi(n = 2)$ wavefunction is even (blue curves in above figure) and the $\psi(n = 3)$ is odd (purple curve). Their product (even times odd) is an odd function and the integral over an odd function is zero. Therefore $\psi(n = 2)$ and $\psi(n = 3)$ wavefunctions are orthogonal.

This can be repeated an infinite number of times to confirm the entire set of PIB wavefunctions are mutually orthogonal as the Orthogonality Theorem guarantees.

8.7.1.1: Orthogonality of Degenerate Eigenstates

Consider two eigenstates of $\hat{A}$, ψ_a and ψ'_a, which correspond to the *same* eigenvalue, a. Such eigenstates are termed **degenerate**. The above proof of the orthogonality of different eigenstates fails for degenerate eigenstates. Note, however, that *any* linear combination of ψ_a and ψ'_a is also an eigenstate of $\hat{A}$ corresponding to the eigenvalue a. Thus, even if ψ_a and ψ'_a are not orthogonal, we can always choose two linear combinations of these eigenstates which are orthogonal. For instance, if ψ_a and ψ'_a are properly normalized, we can define the **overlap integral**

$$S = \int_{-\infty}^{\infty} \psi_a^* \psi'_a dx, \tag{8.7.1.9}$$

It is easily demonstrated (but not here) that

$$\psi''_a = \frac{|S|}{\sqrt{1-|S|^2}} \left(\psi_a - S^{-1}\psi'_a\right) \tag{8.7.1.10}$$

is a properly normalized eigenstate of $\hat{A}$, corresponding to the eigenvalue a, which is orthogonal to ψ_a. It is straightforward to generalize the above argument to three or more degenerate eigenstates. Hence, we conclude that the eigenstates of a Hermitian operator are, or can be chosen to be, **mutually orthogonal.**

Theorem: Gram-Schmidt Orthogonalization

Degenerate eigenfunctions are **not** automatically orthogonal, but can be made so mathematically via the Gram-Schmidt Orthogonalization.

The above theorem argues that if the eigenvalues of two eigenfunctions are the same then the functions are said to be degenerate and linear combinations of the degenerate functions can be formed that will be orthogonal to each other. Since the two eigenfunctions have the same eigenvalues, the linear combination also will be an eigenfunction with the same eigenvalue. The proof of this theorem shows us one way to produce orthogonal degenerate functions.

Proof

If ψ_a and ψ'_a are degenerate, but not orthogonal, we can define a new composite wavefunction $\psi''_a = \psi'_a - S\psi_a$ where S is the overlap integral:

$$S = \langle \psi_a | \psi'_a \rangle$$

then ψ_a and ψ''_a will be orthogonal.

$$\begin{aligned} \langle \psi_a | \psi''_a \rangle &= \langle \psi_a | \psi'_a - S\psi_a \rangle \\ &= \cancel{\langle \psi_a | \psi'_a \rangle}^{S} - S \cancel{\langle \psi_a | \psi_a \rangle}^{1} \\ &= S - S = 0 \end{aligned}$$

Oct 19, 2019, 9:08 AM

Double exponent: use braces to clarify

then ψ_a and Φ will be orthogonal.

$$\begin{aligned} \int \psi_A^* \Phi d\tau &= \int \psi_a^* (\psi'_a - S\psi_a) d\tau \\ &= \int \psi_a^* \psi'_a d\tau - S \int \psi_a^* \psi_a d\tau \\ &= S - S = 0 \end{aligned}$$

□

Exercise 8.7.1.2

Find N that normalizes ψ if $\psi = N(\varphi_1 - S\varphi_2)$ where φ_1 and φ_2 are normalized wavefunctions and S is their overlap integral.

$$S = \langle \varphi_1 | \varphi_2 \rangle$$

Answer

Remember that to normalize an arbitrary wavefunction, we find a constant N such that $\langle \psi | \psi \rangle = 1$. This equates to the following procedure:

$$\begin{aligned}
\langle \psi | \psi \rangle &= \langle N(\varphi_1 - S\varphi_2) | N(\varphi_1 - S\varphi_2) \rangle = 1 \\
N^2 \langle (\varphi_1 - S\varphi_2) | (\varphi_1 - S\varphi_2) \rangle &= 1 \\
N^2 \left[\cancelto{1}{\langle \varphi_1 | \varphi_1 \rangle} - S \cancelto{S}{\langle \varphi_2 | \varphi_1 \rangle} - S \cancelto{S}{\langle \varphi_1 | \varphi_2 \rangle} + S^2 \cancelto{1}{\langle \varphi_2 | \varphi_2 \rangle} \right] &= 1 \\
N^2 (1 - S^2 \cancel{- S^2 + S^2}) &= 1 \\
N^2 (1 - S^2) &= 1
\end{aligned}$$

therefore

$$N = \frac{1}{\sqrt{1 - S^2}}$$

We conclude that the eigenstates of operators are, or can be chosen to be, **mutually orthogonal**.

Contributors and Attributions

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8.8: Postulate 5 of Quantum Mechanics

4.04: The Time-Dependent Schrödinger Equation

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8.9: Postulates and Principles of Quantum Mechanics (Exercises)

Solutions to select questions can be found online.

4.3

The function $\psi^*\psi$ has to be real, nonnegative, finite, and of definite value everywhere. Why?

Solution

If we follow the Born interpretation of wavefuntions, then $\psi^*\psi$ is a probability density and hence must follow standard probability properties including being non-negative, finite and of a definite value at any relevant point in the space of the wavefunction. Moreover, the integral of $\psi^*\psi$ over all this space must be equal to 1.

4.5

Why are the following functions not acceptable wave functions for a 1D particle in a box with length a ? N is a normalization constant.

a. $\psi = N\cos\frac{n\pi x}{L}$

b. $\psi = \frac{N}{\sin\frac{n\pi x}{a}}$

c. $\psi = N\tan\frac{a_{\pi x}}{a}$

Solution

The boundary conditions that need to be met are $\psi(0) = \psi(a) = 0$. This does not meet them. The proposed wavefunction blows up to infinity at $x = 0$ and $x = a$ Tan is not defined for $x = \frac{a}{2}$

4.12

Show that the sets of functions: $\sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right)$ where n = 1,2,3... is orthonormal.

Solution

Let

$$\psi = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right)$$

Because $\psi^* = \psi$ and is real, then

$$\int_0^L \psi^*\psi dx = \int_0^L \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right)\sqrt{\frac{2}{L}}\sin\left(\frac{m\pi x}{L}\right)dx$$

Letting $n = m$

$$\int_0^L \psi^*\psi dx = \frac{2}{L}\int_0^L \sin\left(\frac{n\pi x}{L}\right)\sin\left(\frac{n\pi x}{L}\right)dx$$
$$= \frac{2}{L}\int_0^L \sin^2\left(\frac{n\pi x}{L}\right)dx$$
$$\frac{2}{L}\int_0^L \sin^2\left(\frac{n\pi x}{L}\right)dx = 1$$

Letting $n \neq m$

$$\int_0^L \psi^*\psi dx = \frac{2}{L}\int_0^L \sin\left(\frac{n\pi x}{L}\right)\sin\left(\frac{m\pi x}{L}\right)dx$$
$$= \frac{2}{L}\frac{1}{2}\int_0^L \left[\cos\left(\frac{(n-m)\pi x}{L}\right) - \cos\left(\frac{(n+m)\pi x}{L}\right)\right]dx$$
$$= \frac{1}{L}\left[\frac{L}{(n-m)\pi}\left[\sin\left(\frac{(n-m)\pi L}{L}\right) - \sin\left(\frac{(n-m)\pi 0}{L}\right)\right] - \frac{L}{(n+m)\pi}\left[\sin\left(\frac{(n+m)\pi L}{L}\right) - \sin\left(\frac{(n+m)\pi 0}{L}\right)\right]\right] = 0$$

and thus $\sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right)$ (n=1, 2, 3, ...) are orthonormal.

4.13

Show that $a \cdot b \cdot c = \sum_{ik} a_i b_i c_k e_k$

$$\sum_i a_i e_i \cdot \sum_j b_j e_j \cdot \sum_k c_k e_k = \sum_{ik} a_i b_i c_k e_k$$

$$\sum_i \sum_j a_i b_j (e_i \cdot e_j) \cdot \sum_k c_k e_k = \sum_{ik} a_i b_i c_k e_k$$

$$e_i \cdot e_j = \delta_{ij} = 1$$

when $i = j$

$$\sum_i a_i b_i \cdot \sum_k c_k e_k = \sum_{ik} a_i b_i c_k e_k$$

$$\sum_{ik} a_i b_i c_k e_k = \sum_{ik} a_i b_i c_k e_k$$

4.14

Determine if the following operators commute

$$\hat{B} = \frac{d}{dx}$$

and

$$\hat{C} = x^5$$

Solution

We must solve $\left[\hat{B}, \hat{C}\right]$, by solving for $\hat{B}\{\hat{C}f(x)\}$ and $\hat{C}\{\hat{B}f(x)\}$ for a wavefunction $f(x)$ and see if they are equal.

$$\hat{B}\{\hat{C}f(x)\} = \hat{B}\{x^5 f(x)\} = \frac{d}{dx}\{x^5 f(x)\} = 5xf(x) + x^5 f'(x)$$

$$\hat{C}\{\hat{B}f(x)\} = \hat{C}\{f'(x)\} = x^5 f'(x)$$

since

$$\left[\hat{B}, \hat{C}\right] = 5xf(x) + x^5 f'(x) - x^2 f'(x) = 5xf(x) \neq 0$$

The two operators do not commute.

4.15

Do the following combinations of angular momentum operators commute? Show work to the justify the answer (do not just write "yes" or no").

a. $\mathbf{L}_x$ and $\mathbf{L}_y$
b. $\mathbf{L}_y$ and $\mathbf{L}_z$
c. $\mathbf{L}_z$ and $\mathbf{L}_x$

with

$$\mathbf{L}_x = -\mathrm{i}\,\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$$

$$\mathbf{L}_y = -\mathrm{i}\,\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)$$

$$\mathbf{L}_z = -\mathrm{i}\,\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$$

Estimate the answer to Part C based on the pattern gathered from parts A and B; no work necessary for Part C.

Solution

a.

$$[\mathbf{L}_x, \mathbf{L}_y] = (yp_z - zp_y)(zp_x - xp_z)\Psi - (zp_x - xp_z)(yp_z - zp_y)\Psi,$$

$$= (zp_xyp_z - z^2p_xp_y - xyp_zp_z - xzp_yp_z)\Psi - (yp_zzp_x - yxp_zp_z + z^2p_yp_x + zxp_zp_y)\Psi$$

$$[\mathbf{L}_x, \mathbf{L}_y] = i\hbar\mathbf{L}_z,$$

Does **not** commute, i.e., is not zero.

b.

$$[\mathbf{L}_y, \mathbf{L}_z] = (zp_x - xp_z)(xp_y - yp_x)\Psi - (xp_y - yp_x)(zp_x - xp_z)\Psi$$

$$= (xp_yzp_x - x^2p_yp_z - yzp_xp_x - yxp_zp_x)\Psi - (zp_xxp_y - zyp_xp_x + x^2p_zp_y + xyp_xp_z)\Psi$$

$$[\mathbf{L}_y, \mathbf{L}_z] = i\hbar\mathbf{L}_x,$$

Does **not** commute, i.e., is not zero.

c. This part only requires that we notice the rotation of variables and consistency of format/equations. In doing so, we better understand the relation between the parts of the angular momentum operator. The work below does not need to be shown for credit, but it may clarify things or make the solution clearer if you are still having trouble assessing and using the pattern.

$$[\mathbf{L}_z, \mathbf{L}_x] = (xp_y - yp_x)(yp_z - zp_y)\Psi - (yp_z - zp_y)(xp_y - yp_x)\Psi$$

$$= (yp_zxp_y - y^2p_zp_x - zxp_yp_y - zyp_xp_y)\Psi - (xp_yyp_z - xzp_yp_y + y^2p_xp_z + yzp_yp_x)\Psi$$

$$[\mathbf{L}_z, \mathbf{L}_x] = i\hbar\mathbf{L}_y,$$

Does not commute, i.e., is not zero.

These calculations show that you can have only one well-defined component of the angular momentum because of the uncertainty principle says the others will not be known (since they do not commute).

4.17

For two operators to commute, what property must hold? Use the operators $\hat{L}^2$ and $\hat{L}_z$ as an example to show that this property holds.

Solution

The commuters when applied to a wavefunction must equal the 0 eigenfunction.

$$\hat{L}^2\hat{L}_z\psi(x) - \hat{L}_z\hat{L}^2\psi(x) = 0$$

$$\hat{L}^2\hat{L}_z - \hat{L}_z\hat{L}^2\psi(x) = \hat{0}\psi(x)$$

$$\hat{L}^2\hat{L}_z - \hat{L}_z\hat{L}^2 = 0$$

4.21

Show that the angular momentum and kinetic energy operators commute and therefore can be measured simultaneously to arbitrary precision.

Solution

Show that

$$[\hat{K}, \hat{L}] = 0$$

where the operators can be broken up into 3 components

$$L_x = -\mathrm{i}\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$$

$$L_y = -\mathrm{i}\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)$$

$$L_z = -\mathrm{i}\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$$

and $\hat{K}_x = \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$. The same can be written for $\hat{K}$ in the y and z directions.

$$[\hat{K}, \hat{L}] = [\hat{K}_x, \hat{L}_x] + [\hat{K}_y, \hat{L}_y] + [\hat{K}_z, \hat{L}_z]$$

For the x-direction

$$[\hat{K}_x, \hat{L}_x] = \left[\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}, -i\hbar\left(y\frac{d}{dz} - z\frac{d}{dy}\right)\right]$$

$$\frac{-\hbar^2}{2m}\frac{d^2}{dx^2}\left(-i\hbar\left(y\frac{d}{dz} - z\frac{d}{dy}\right)\right) - -i\hbar\left(y\frac{d}{dz} - z\frac{d}{dy}\right)\frac{-\hbar^2}{2m}\frac{d^2}{dx^2}$$

$$\frac{i\hbar^3}{2m}\left(y\frac{d^3}{dx^2dz} - z\frac{d^3}{dx^2dy}\right) - \frac{i\hbar^3}{2m}\left(y\frac{d^3}{dx^2dz} - z\frac{d^3}{dx^2dy}\right) = 0$$

The process can be repeated for the y and z directions and following the same steps the commutations turn out to be 0. Therefore, kinetic energy and angular momentum commute.

4.22

Show that the position and angular momentum operator commutes. Can the position and angular momentum be measured simultaneously to a arbitrary precision?

Solution

First, we must prove that the position operator, $\hat{\mathbf{R}} = \mathbf{i}\hat{x} + \mathbf{j}\hat{y} + \mathbf{k}\hat{z}$, and the angular momentum operator $\hat{\mathbf{L}} = \mathbf{i}\hat{L_x} + \mathbf{j}\hat{L_y} + \mathbf{k}\hat{L_z}$, commute.

In order to prove the commutation,

$$[\hat{\mathbf{R}}, \hat{\mathbf{L}}] = [\mathbf{i}\hat{x} + \mathbf{j}\hat{y} + \mathbf{k}\hat{z}, \mathbf{i}\hat{L_x} + \mathbf{j}\hat{L_y} + \mathbf{k}\hat{L_z}]$$

$$= [\hat{x}, \hat{L_x}] + [\hat{y}, \hat{L_y}] + [\hat{z}, \hat{L_z}]$$

$$= 0$$

where we have used the fact that

$$\mathbf{i}\cdot\mathbf{i} = \mathbf{j}\cdot\mathbf{j} = \mathbf{k}\cdot\mathbf{k} = 1$$

and

$$\mathbf{i}\cdot\mathbf{j} = \mathbf{j}\cdot\mathbf{k} = \mathbf{k}\cdot\mathbf{i} = 0$$

Now that we have proved that the two operators commute, the relationship of commutation means that the position and total angular momentum of any electrons can be measured simultaneously to arbitrary precision.

4.25

If both $|\Psi_n\rangle$ and $|\Psi_m\rangle$ satisfy the **time-independent** Schrödinger Equation (these are called *stationary states*)

$$|\Psi_n(x,t)\rangle = \Psi_n(x)e^{-iE_nt/\hbar}$$

and

$$|\Psi_m(x,t)\rangle = \Psi_m(x)e^{-iE_mt/\hbar}$$

show that any linear superposition of the two wavefunctions

$$|\Psi(x,t)\rangle = c_n|\Psi_n(x,t)\rangle + c_m|\Psi_m(x,t)\rangle$$

also satisfies the **time-dependent** Schrödinger Equation.

Solution

The time-dependent Schrödinger Equation is

$$\hat{H}\Psi(x,t) = i\hbar\,\partial\Psi(x,y)/\partial t$$

Plug Ψ(x,t) into the time-dependent equation.

$$\hat{H}c_n\Psi_n(x)e^{-iE_nt/\hbar} + c_m\Psi_m(x)e^{-iE_mt/\hbar} = i\hbar\,\partial/\partial t c_n\Psi_n(x)e^{-iE_nt/\hbar} + c_m\Psi_m(x)e^{-iE_mt/\hbar}$$

$$\hat{H}c_n\Psi_n(x)e^{-iE_nt/\hbar} + c_m\Psi_m(x)e^{-iE_mt/\hbar} = E_nc_n\Psi_n(x)e^{-iE_nt/\hbar} + E_mc_m\Psi_m(x)e^{-iE_mt/\hbar}$$

$$\partial/\partial t c_n\Psi_n(x)e^{-iE_nt/\hbar} + c_m\Psi_m(x)e^{-iE_mt/\hbar} = -[(iE_mc_me^{-iE_mt/\hbar}\Psi_m(x))/\hbar] - [(iE_nc_ne^{-iE_nt/\hbar}\Psi_n(x))/\hbar]$$

combine all the constants (except for E) into c_n and c_m

$$i\hbar\,[-[(ic_me^{-iE_mt/\hbar}\Psi_m(x))/\hbar] - [(ic_ne^{-iE_nt/\hbar}\Psi_n(x))/\hbar]] = E_nc_n\Psi_n(x)e^{-iE_nt/\hbar} + E_mc_m\Psi_m(x)e^{-iE_mt/\hbar}$$

Since $\hat{H}\Psi(x,t)$ and $i\hbar\,\partial\Psi(x,y)/\partial t$ are equal, they satisfy the time-dependent equation.

4.26

Starting with

$$\langle x\rangle = \int \psi^*(x,t)x\psi(x,t)dx$$

and the time-independent Schrödinger equation, demonstrate that

$$\frac{d\langle x\rangle}{dt} = \int \psi^* \frac{i}{\hbar}(\hat{H}x - x\hat{H})\psi dx$$

Given that

$$\hat{H} = \frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)$$

show that

$$\hat{H}x - x\hat{H} = -2\frac{\hbar^2}{2m}\frac{d}{dx}$$
$$= -\frac{\hbar^2}{m}\frac{i}{\hbar}\hat{P}_x = -\frac{ih}{m}\hat{P}_x$$

4.28

Derive the condition on operators that arises from forcing eigenvalues to be real with complex conjugates.

Solution

Starting with an eigenvalue problem with a $\hat{G}$ as our operator we recognize

$$\hat{G}\psi = \lambda\psi$$

Solving for our eigenvalue we must multiply by our complex conjugate wavefunction and integrate both sides to see

$$\int \psi^* \hat{G}\psi d\tau = \int \psi^* \lambda\psi d\tau = \lambda \int \psi^*\psi d\tau = \lambda$$

We can repeat this calculation but with a complex conjugate of our initial eigenvalue problem

$$\hat{G}^*\psi^* = \lambda^*\psi^*$$

Solving for our eigenvalue we multiply ψ and integrate both sides to find that

$$\int \psi\hat{G}^*\psi^* d\tau = \int \psi\lambda^*\psi^* d\tau = \lambda^* \int \psi\psi^* d\tau = \lambda$$

Since we restricted λ to be real both eigenvalue problems return the same eigenvalue. We can then relate the operator side of both equations to know that

$$\boxed{\int \psi^* \hat{G}\psi d\tau = \int \psi\hat{G}^*\psi^* d\tau}$$

4.31

Prove that the position operator is Hermitian.

Solution

We must see if the operator satisfies the following requirement to be in Hermitian:

$$\int_{-\infty}^{\infty} (\hat{A}\psi^*)\psi \, dx = \int_{-\infty}^{\infty} \psi^* \hat{A}\psi \, dx$$

Substitute $\hat{X}$ for $\hat{A}$ into the above equation:

$$\int_{-\infty}^{\infty} (\hat{A}\psi^*)\psi \, dx = \int_{-\infty}^{\infty} \psi^* \hat{A}\psi \, dx$$

$$\int_{-\infty}^{\infty} (\hat{X}\psi^*)\psi \, dx = \int_{-\infty}^{\infty} \psi^* \hat{X}\psi \, dx$$

$$\int_{-\infty}^{\infty} (\hat{X}\psi)^*\psi \, dx = \int_{-\infty}^{\infty} \psi^* \hat{X}\psi \, dx$$

$$\int_{-\infty}^{\infty} \psi^* \hat{X}^*\psi \, dx = \int_{-\infty}^{\infty} \psi^* \hat{X}\psi \, dx$$

Since $\hat{X}^* \equiv \hat{X}$:

$$\int_{-\infty}^{\infty} \psi^* \hat{X}\psi \, dx = \int_{-\infty}^{\infty} \psi^* \hat{X}\psi \, dx$$

Therefore the Position Operator is Hermitian.

4.31

Prove that the momentum operator is a Hermitian

Solution

Hermitian: $\int \psi_j^* \hat{H} \psi_i dx$

Momentum Operator: $\hat{P} = -i\hbar \frac{d}{dx}$

We will first start by showing you

$$\int_{-\infty}^{\infty} \psi_j (-i\hbar \frac{d}{dx}) psi_i dx$$

$\frac{d\psi_i}{dx} dx = d\psi_i$

$\int_{-\infty}^{\infty} \psi_j (-i\hbar \frac{d}{dx}) psi_i dx$ = iħ $\int_{-\infty}^{\infty} psi_j d\psi_i$

Using integration by parts with u = \psi_{j}*\ and dv = d\psi_{i}

We can notice now that for a confined particle the product \psi_{j}^{*}\psi_{i} will go to zero at each of the endpoints

We get in the end $-i\hbar \frac{d}{dx}$ = $-i\hbar \frac{d}{dx}$ → momentum operator

4.32

Which of the following operators are Hermitian:

a. x,
b. d/dx
c. hd^2/dx^2
d. id^2/dx^2

Solution

A Hermitian Operator $\hat{A}$ satisfies

$$< \Psi^* |A| \Psi >=< \Psi |A^*| \Psi* >$$

x

$$\int \Psi * x \Psi dx = \int \Psi x \Psi * dx$$

where $x^* = x$.

Operator x is Hermitian

d/dx

$$\int \Psi * d/dx \Psi dx$$

$$= \int \Psi * d\Psi$$

Here we can use Integration by Parts \int vdu = uv + \int udv with v=Ψ* and dv = dΨ

$$= [\Psi * \Psi] - \int \Psi d\Psi *$$

[Ψ*Ψ] evaluated at infinity and negative infinity is 0, because of the assumption that this wavefunction approaches 0 as one extends to infinity in both directions

$$= - \int \Psi d/dx \Psi * dx$$

Here we inserted dx/dx into the integral

$$= \int \Psi (-d/dx) \Psi * dx$$

d/dx* = d/dx, not -d/dx,so this operator is **not Hermitian.**

hd^2/dx^2

$$\int \Psi * h(d^2/dx^2) \Psi dx$$

$$= h \int \Psi * (d^2/dx) \Psi$$

Here we can use Integration by Parts \int vdu = uv + \int udv with u=Ψ* and dv=d(dΨ/dx)

$$= h[\Psi * d\Psi/dx] - \int (d\Psi/dx) d\Psi *$$

$$= h[\Psi * d\Psi/dx] - \int (d\Psi * /dx) d\Psi$$

[Ψ*dΨ/dx] evaluated at infinity and negative infinity is 0, because of the assumption that this wavefunction approaches 0 as one extends to infinity in both directions. This implies that that dΨ/dx, for example, also approach 0.

$$= -h \int (d\Psi * /dx) d\Psi$$

Here we can use Integration by Parts \int vdu = uv + \int udv with u=dΨ*/dx and dv=dΨ

$$= -h([\Psi d\Psi*/dx] - \int \Psi d^2\Psi*/dx$$

[Ψ*dΨ/dx] evaluated at infinity and negative infinity is 0, because of the assumption that this wavefunction approaches 0 as one extends to infinity in both directions. This implies that that dΨ*/dx, for example, also approaches 0.

$$= h \int \Psi(d^2\Psi*/dx)$$

$$= h \int \Psi(d^2\Psi*/dx^2)dx$$

$$= \int \Psi h(d^2/dx^2)\Psi* dx$$

$h(d^2/dx^2)^* = h(d^2/dx^2)$, so this operator is Hermitian

id^2/dx^2

$$\int \Psi* i(d^2/dx^2)\Psi dx$$

$$= i \int \Psi*(d^2/dx)\Psi$$

Here we can use Integration by Parts

$$\int vdu = uv + \int udv$$

with u=Ψ* and dv=d(dΨ/dx)

$$= i[\Psi* d\Psi/dx] - \int (d\Psi/dx)d\Psi*$$

$$= i[\Psi* d\Psi/dx] - \int (d\Psi*/dx)d\Psi$$

[Ψ*dΨ/dx] evaluated at infinity and negative infinity is 0, because of the assumption that this wavefunction approaches 0 as one extends to infinity in both directions. This implies that that dΨ/dx, for example, also approach 0.

$$= -i \int (d\Psi*/dx)d\Psi$$

Here we can use Integration by Parts *int vdu = uv + *int udv* with u=dΨ*/dx and dv=dΨ

$$= -i([\Psi d\Psi*/dx] - \int \Psi d^2\Psi*/dx$$

[Ψ*dΨ/dx] evaluated at infinity and negative infinity is 0, because of the assumption that this wavefunction approaches 0 as one extends to infinity in both directions. This implies that that dΨ*/dx, for example, also approach 0.

$$= i \int \Psi(d^2\Psi*/dx)$$

$$= i \int \Psi(d^2\Psi*/dx^2)dx$$

$$= \int \Psi i(d^2/dx^2)\Psi* dx$$

$$i(d^2/dx^2)* = -i(d^2/dx^2)$$

so this operator is NOT Hermitian

4.32

Determine whether the following operators are Hermitian and whether they commute:

$$\hat{A} = i\frac{d}{dx}$$

and

$$\hat{B} = i\frac{d^2}{dx^2}$$

Given that -∞<x<∞ and the operators functions are well behaved.

Solution

If the operator satisfies this condition it is *Hermitian*

$$\int_{-\infty}^{\infty} f^*(x)\,\hat{A}f(x)\,dx = \int_{-\infty}^{\infty} f(x)\,\hat{A}f^*(x)\,dx$$

A)

$$\int_{-\infty}^{\infty} f^*\left(i\frac{df}{dx}\right)dx = i\int_{-\infty}^{\infty} f^*\frac{df}{dx}dx = i\left([_{-\infty}^{\infty} f^*f] - \int_{-\infty}^{\infty} f\frac{df^*}{dx}dx\right)$$

$$= -i\int_{-\infty}^{\infty} f\frac{df^*}{dx}dx = \int_{-\infty}^{\infty} f\left(-i\frac{d}{dx}\right)f^*dx$$

$$\int_{-\infty}^{\infty} f\left(i\frac{d}{dx}\right)^* f^*dx$$

This operator is Hermitian

B)

$$\int_{-\infty}^{\infty} f^*\left(i\frac{d^2f}{dx^2}\right)dx = [_{-\infty}^{\infty} f^*i\frac{df}{dx}] - \int_{-\infty}^{\infty}\frac{df^*}{dx}\frac{df}{dx}dx$$

$$= -i[_{-\infty}^{\infty} f\frac{df^*}{dx}] + i\int_{-\infty}^{\infty} f\frac{d^2f^*}{dx^2}dx$$

$$= -\int_{-\infty}^{\infty} f\frac{id^2}{dx^2}^* f^*dx$$

This operator is **not** Hermitian

If the operators commute they have to satisfy this condition

$$\hat{A}\hat{B}f = \hat{B}\hat{A}f$$

$$\hat{A}\hat{B}f = \frac{id}{dx}\left(\frac{d^2f}{dx^2}\right) = \frac{id^3f}{dx^3}$$

$$\hat{B}\hat{A}f = \frac{id^2}{dx^2}\left(\frac{df}{dx}\right) = \frac{id^3f}{dx^3}$$

This pair of operators commutes.

4.34

Consider two wavefunctions

$$\psi_1(x) = A\sin(k_1x) + B\cos(k_1x) \tag{8.9.1}$$

and

$$\psi_2(x) = C\sin(k_2x) + D\cos(k_2x)$$

Given the boundary conditions are:

$$\psi(0) = 0$$

and

$$\frac{d\psi_1}{dx} = \frac{d\psi_2}{dx} \quad atx = 0$$

$$A + B = C, k_1(A - B) = k_2C$$

and given a expression of

$$R = \frac{B^2}{A^2} \tag{8.9.2}$$

Derive the simplest expression of R based on the terms from the boundary conditions provided above.

Solution

Since

$$A + B = C, k_1(A - B) = k_2C \tag{8.9.3}$$

,

$$k_1(A - B) = k_2(A + B) \tag{8.9.4}$$

$$k_1A - k_1B = k_2A + k_2B \tag{8.9.5}$$

$$(k_1 - k_2)A = (k_1 + k_2)B \tag{8.9.6}$$

Thus,

$$\frac{B}{A} = \frac{k_1 - k_2}{k_1 + k_2} \tag{8.9.7}$$

$$R = \frac{B^2}{A^2} = \left(\frac{B}{A}\right)^2 = \left(\frac{k_1 - k2}{k_1 + k_2}\right)^2 \tag{8.9.8}$$

4.34

A particle is moving in a field. Half-way through the field, there is a line that represents potential energy. To the left of the line, the potential energy is

$$x < 0$$

and to the right of the line the potential energy is

$$x > 0$$

. If the particle's energy is less than the potential energy line will the particle reflect when the its energy is greater than the Potential energy barrier height?

Solution

When

$$x < 0$$

the Schrödinger equation is as followed:

$$\frac{-\hbar^2}{2m}\frac{d^2\psi_1}{dx^2} = E\psi_1$$

and the solution to this equation is:

$$\psi_1(x) = Ae^{ik_1x} + Be^{-ik_1x}$$

where

$$k_1 = (\frac{2mE}{\hbar^2})^{1/2}$$

Region Two where $x > 0$:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi_2}{dx^2} + V_0\psi_2 = E\psi_2$$

and the solution to the equation is:

$$\psi_2(x) = Ce^{ik_2x} + De^{-ik_2x}$$

and

$$k_2 = [\frac{2m(E - V_0)}{\hbar^2}]^{1/2}$$

Notice the difference between the two Schrödinger equations. Equation one does not have a potential energy component because it is before the potential energy field hence have zero potential energy. After the potential energy field, the Schrödinger equation has a potential energy component because the particle has potential energy at this moment.

When you solve the differential solutions to the Schrödinger equations you find that the amount that is reflected back of a particle by the line is equal to the amount that is transmitted after the line. This is all we can find out for the information given. However, if we solve this solution for when the Energy of the particle is greater than the potential energy line and compare the differential solutions to all four wave functions then we find that all particles will be reflected by the barrier.

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9.2: Applying the Postulates to the Particle in a 1D Box

9.2.1: The Average Momentum of a Particle in a Box is Zero

9.3: Particle in a Box and the Uncertainty Principle

9.4: Particle in a Three-Dimensional Box

9.E: The Schrödinger Equation and a Particle in a Box (Exercises)

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9.1: The Particle in a One-Dimensional Box

3.05: The Energy of a Particle in a Box is Quantized

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9.2: Applying the Postulates to the Particle in a 1D Box

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9.2.1: The Average Momentum of a Particle in a Box is Zero

3.07: The Average Momentum of a Particle in a Box is Zero

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9.3: Particle in a Box and the Uncertainty Principle

3.08: The Uncertainty Principle - Estimating Uncertainties from Wavefunctions

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9.4: Particle in a Three-Dimensional Box

3.09: A Particle in a Three-Dimensional Box

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9.E: The Schrödinger Equation and a Particle in a Box (Exercises)

3.E: The Schrödinger Equation and a Particle in a Box (Exercises)

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10.1.1: Things to review

This course requires that you are comfortable with same basic mathematical operations and basic calculus. It is imperative that you go over this chapter carefully and identify the topics you may need to review before starting the semester. You will be too busy learning new concepts soon, so this is the right time for you to seek help if you need it.

Notice: This chapter does not contain a review of topics you should already know. Instead, it gives you a list of topics that you should be comfortable with so you can review them independently if needed. Also, remember that you can use the formula sheet at all times, so locate the information you have and use it whenever needed!

1.1.1 The Equation of a straight line

- given two points calculate the slope, the x-intercept and the y-intercept of the straight line through the points.
- given a graph of a straight line write its corresponding equation.
- given the equation of a straight line sketch the corresponding graph.

1.1.2 Trigonometric Functions

- definition of sin, cos,tan of an angle.
- values of the above trigonometric functions evaluated at 0, π/2, π, 3/2π, 2π.
- derivatives and primitives of sin and cos.

1.1.3 Logarithms

- the natural logarithm ($\ln x$) and its relationship with the exponential function.
- the decimal logarithm ($\log x$) and its relationship with the function 10^x.
- properties of logarithms (natural and decimal)
  - $\ln(1) = ?$
  - $\ln(ab) = ?$
  - $\ln(a/b) = ?$
  - $\ln(a^b) = ?$
  - $\ln(1/a) = ?$

1.1.4 The exponential function

- properties
  - $e^0 = ?$
  - $e^{-x} = 1/... ?$
  - $e^{-\infty} = ?$
  - $e^a e^b = ?$
  - $e^a / e^b = ?$
  - $(e^a)^b = ?$

1.1.5 Derivatives

- concept of the derivative of a function in terms of the slope of the tangent line.
- derivative of a constant, e^x, x^n, $\ln x$, $\sin x$ and $\cos x$.
- derivative of the sum of two functions.
- derivative of the product of two functions.
- the chain rule.
- higher derivatives (second, third, etc).
- locating maxima, minima and inflection points.

1.1.6 Indefinite Integrals (Primitives)

- primitive of a constant, x^n, x^{-1}, e^x, $\sin x$ and $\cos x$.

1.1.7 Definite Integrals

- using limits of integration.
- properties of definite integrals (see recommended exercises below).

Test yourself!

Identify what you need to review by taking this non-graded quiz. http://tinyurl.com/laq5aza

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10.1.2: Odd and Even Functions

Many of you probably heard about odd and even functions in previous courses, but for those who did not, here is a brief introduction.

- An odd function obeys the relation $f(x) = -f(-x)$. For example, $\sin x$ is odd because $\sin x = -\sin(-x)$.
- An even function obeys the relation $f(x) = f(-x)$. For example, $\cos x$ is even because $\cos x = \cos(-x)$.

Even functions are symmetric with respect to the y−axis. In other words, if you were to put a mirror perpendicular to the screen at $x = 0$, the right side of the plot would produce a reflection that would overlap with the left side of the plot. Check Figure 10.1.2.1 to be sure you understand what this means.

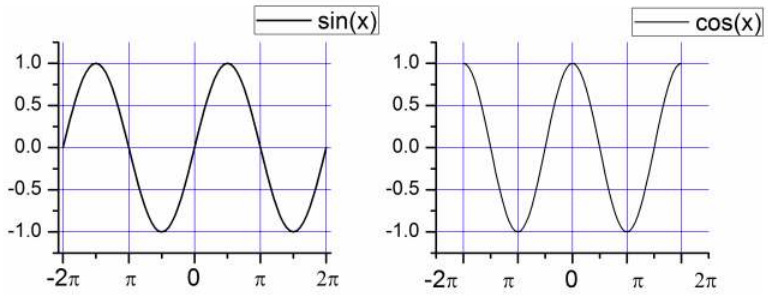


Figure 10.1.2.1: Odd and even functions. (CC BY-NC-SA; Marcia Levitus)

Odd functions are symmetric in a different way. Imagine that you have an axis perpendicular to the screen that contains the point (0,0). Now rotate every point of your graph 180 degrees. If the plot you create after rotation overlaps with the plot before the rotation, the function is odd. Check Figure 10.1.2.1 to be sure you understand what this means.

Note that functions do not necessarily need to be even or odd. The function e^x, for instance, is clearly neither, as $e^x \neq e^{-x}$ (condition for even) and $e^x \neq -e^{-x}$ (condition for odd). You can also sketch the function e^x and verify that it does not have the symmetry of an odd or even function. For any function,

$$\int_{-a}^{a} f(x)dx = \int_{-a}^{0} f(x)dx + \int_{0}^{a} f(x)dx$$

For an odd function, this integral equals zero:

$$\int_{-a}^{a} f(x)dx = \int_{-a}^{0} f(x)dx + \int_{0}^{a} f(x)dx = 0 \tag{10.1.2.1}$$

This should be obvious just by looking at the plot of $\sin x$. The area under the curve between 0 and a cancels out with the area under the curve between $-a$ and 0. This is great news because it means that we do not have to bother integrating odd functions as long as the limits of integration span from $-a$ to a, where a can be any number, including infinity. As it turns out this happens often in quantum mechanics, so it is something worth keeping in mind!

For an even function,

$$\int_{-a}^{a} f(x)dx = 2\int_{0}^{a} f(x)dx$$

because the area under the curve between 0 and a equals the area under the curve between $-a$ and 0. This not as helpful as Equation 10.1.2.1, but still might help in some cases. For example, let's say that you need to evaluate $\int_{-\infty}^{\infty} x^2 e^{-x^2} dx$ and the only material that you have available is the formula sheet. You find an expression for

$$\int_{0}^{\infty} x^{2n} e^{-ax^2} dx$$

which you can use with $n = 1$ to obtain

$$\int_{0}^{\infty} x^2 e^{-x^2} dx = \frac{\sqrt{\pi}}{4}$$

(be sure you can get this result on your own).

How do you get $\int_{-\infty}^{\infty} x^2 e^{-x^2} dx$? If the integrand is even, you just need to multiply by 2. This is in fact an even function, because $x^2 = (-x)^2$, and therefore it is clear that $x^2 e^{-x^2} = (-x)^2 e^{-(-x)^2}$. Therefore,

$$\int_{-\infty}^{\infty} x^2 e^{-x^2} dx = \frac{\sqrt{\pi}}{2}$$

It is useful to know that the product of two even functions or two odd functions is an even function, and the product of an odd function and an even function is odd. For example,

- $\sin^2 x$ is the product of two odd functions, and is therefore even.
- $\cos^2 x$ is the product of two even functions, and is therefore even.
- $\sin x \cos x$ is the product of an odd function and an even function, and is therefore odd.

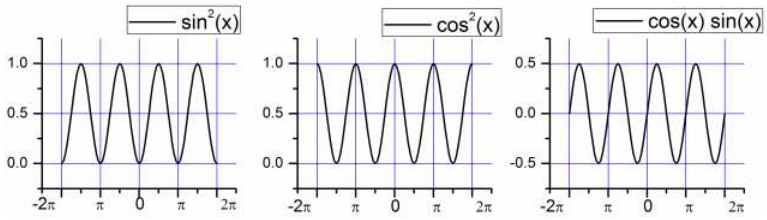


Figure 10.1.2.2: Products of odd and even functions. (CC BY-NC-SA; Marcia Levitus)

Need help understanding how to identify odd and even functions? External links:

http://www.youtube.com/watch?v=8VgmBe3ulb8

http://www.youtube.com/watch?v=68enNRhFORc

Odd, even or neither?

See if you can classify the functions shown in this short quiz.

http://tinyurl.com/l4pehb8

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10.1.3: The Exponential Function

In Section 1.1 you were asked to review some properties of the exponential function. Here, we will learn (or review) how to sketch exponential functions with negative exponents quickly. These types of functions appear very often in chemistry, so it is important that you know how to visualize them without the help of a computer or calculator.

Suppose we want to sketch the function $y = ae^{-kx}$, where a and k are positive real numbers (e.g. $y = 3e^{-2x}$). We could consider negative values of the variable x, but often x represents a time or another variable for which only positive values make sense, so we will consider values of $x \geq 0$.

First, let's find out the value of $y(0)$, where the function crosses the y–axis. Because $e^0 = 1$, $y(0) = a$. The number a is often called "the pre-exponential factor" (i.e. the factor before the exponential), or the "amplitude" of the function. This is the amplitude because it will be the highest point in our plot.

Now, let's see what happens as $x \to \infty$. From Section 1.1, it is expected that you know that $e^{-\infty} = 0$, and therefore, you should be able to conclude that $y(x)$ decreases from an initial value $y(0) = a$ to zero. Whether the function will decay to zero slowly or rapidly will depend on the value of k.

Let's now consider two points in the curve $y = ae^{-kx}$

$$y_1 = ae^{-kx_1}$$
$$y_2 = ae^{-kx_2}$$

and let's further assume that $y_1/y_2 = 2$ (see Figure 10.1.3.1, left). What is the separation between x_2 and x_1 ($\Delta x = x_2 - x_1$)?

We know that $y_1/y_2 = 2$, so

$$2 = \frac{e^{-kx_1}}{e^{-kx_2}}$$

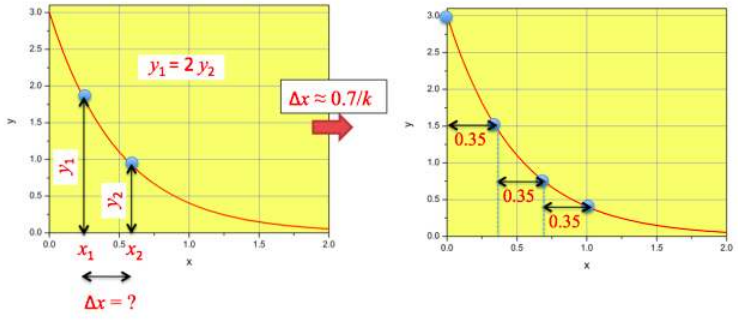


Figure 10.1.3.1: Sketching the function $y = 3e^{2x}$ (CC BY-NC-SA; Marcia Levitus)

Using the properties of the exponential function:

$$2 = e^{-k(x_1 - x_2)} = e^{-k(-\Delta x)} = e^{k(\Delta x)}$$

and solving for Δx:

$$\ln(2) = k(\Delta x)$$
$$\Delta x = \ln(2)/k$$

This means that the function decays to 50% of its former value every time we move $\ln 2/k$ units to the right in the x–axis.

To sketch the function, we just need to remember that $\ln(2) \approx 0.7$. Therefore, to sketch $y = 3e^{-2x}$, we place the first point at $y = 3$ and $x = 0$, and the second point at $y = 3/2$ and $x \approx 0.7/2 = 0.35$. We can continue adding points following the same logic: every time we drop the value of y by half, we move $\ln(2)/k$ units to the right in the x–axis (see Figure 10.1.3.1, right).

> Sketching an exponential function with negative exponent. http://tinyurl.com/n6pdvyh

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10.1.4: The Period of a Periodic Function

A function $f(x)$ is said to be periodic with period P if $f(x) = f(x + P)$. In plain English, the function repeats itself in regular intervals of length P. The period of the function of Figure 10.1.4.1 is 2π.

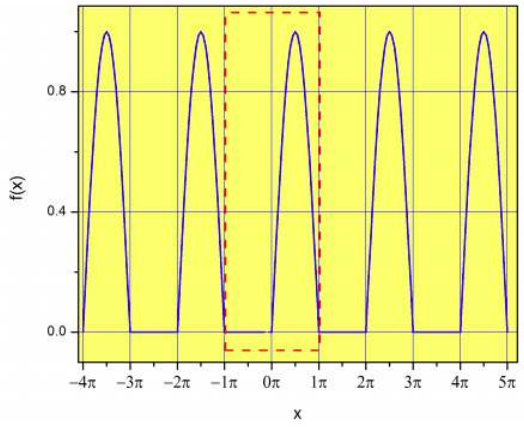


Figure 10.1.4.4: A periodic function with period $P = 2\pi$ (CC BY-NC-SA; Marcia Levitus)

We know that the period of $\sin(x)$ is 2π, but what is the period of the function $\sin(nx)$?

The period of $\sin(x)$ is 2π, so:

$$\sin(nx) = \sin(nx + 2\pi)$$

By definition, for a periodic function of period P, the function repeats itself if we add P to x:

$$sin(nx) = \sin(n(x + P)) = \sin(nx + nP))$$

Comparing the two equations: $2\pi = nP$, and therefore $P = 2\pi/n$.

For example, the period of $\sin(2x)$ is π, and the period of $\sin(3x)$ is $2\pi/3$ (see Figure 10.1.4.2).

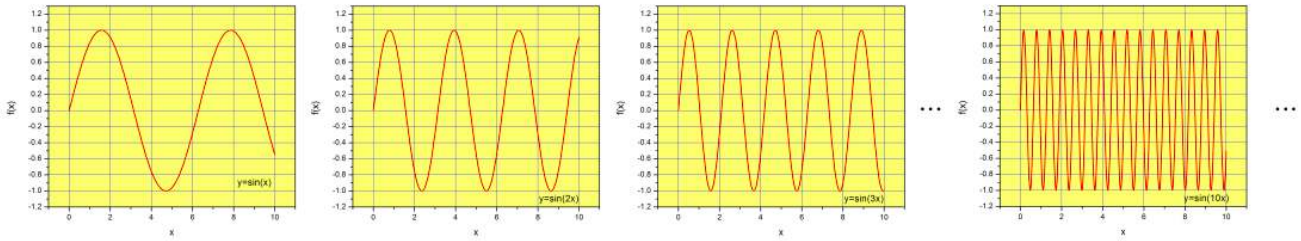


Figure 10.1.4.2: Some examples of the family of functions $\sin(nx)$. From left to right: $\sin(x)$, $\sin(2x)$, $\sin(3x)$ and $\sin(10x)$ (CC BY-NC-SA; Marcia Levitus)

You can follow the same logic to prove that the period of $\cos(nx)$ is $2\pi/n$. These are important results that we will use later in the semester, so keep them in mind!

> Test yourself with this short quiz! http://tinyurl.com/k4wop6l

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10.1.5: Exercises

To see if you are on track, solve the following exercises using only the formula sheet (no calculators, computers, books, etc!).

1. Draw the straight line that has a y-intercept of 3/2 and a slope of 1/2.
2. Express $\frac{3}{4} - \frac{2}{3} + 1$ as a single fraction.
3. Simplify $(a - 4a^3)/a^{-2}$.
4. Express $\ln 8 - 5 \ln 2$ as the logarithm of a single number.
5. Given $\ln P = -\frac{a}{RT} + b \ln T + c$, where a, b, c and R are constants, obtain $\frac{d(\ln P)}{dT}$
6. Obtain $\frac{dy}{dx}$
    1. $y = \sin x e^{mx}$ (m is a constant).
    2. $y = \frac{1}{\sqrt{1-x^2}}$
7. Obtain the first, second and third derivatives of
    1. $y = e^{-2x}$
    2. $y = \cos(2x)$
    3. $y = 3 + 2x - 4x^2$
8. Evaluate $\int_0^{\pi} \cos 3\theta d\theta$.
9. Use the properties of integrals and your previous result to evaluate $\int_{\pi}^{0} \cos 3\theta d\theta$. What about $\int_0^{\pi/4} \cos 3\theta d\theta + \int_{\pi/4}^{\pi} \cos 3\theta d\theta$?
10. Given $f(x) = \begin{cases} 0 & \text{if } x < 0 \\ 3 + 2x & \text{if } 0 < x < 1 \\ 0 & \text{if } x > 1 \end{cases}$ Sketch $f(x)$ and calculate $\int_{-\infty}^{\infty} f(x) dx$
11. What is the value of this integral? $\int_{-\infty}^{\infty} x e^{-x^2} dx$
12. Sketch $\sin(x/2)$. What is the period of the function?
13. The plots below (Figure 10.1.5.1) represent the following functions: $y = 3e^{-x/2}$, $y = 3e^{-x}$, $y = 3e^{-2x}$ and $y = 2e^{-2x}$. Which one is which?

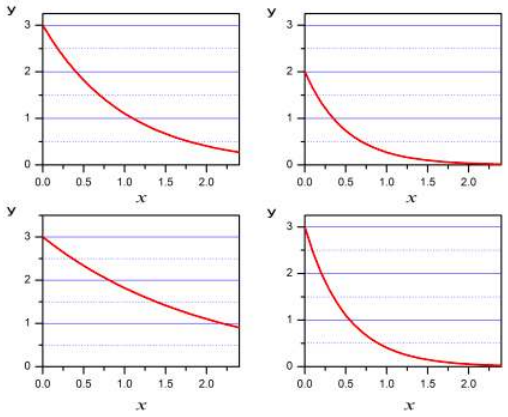


Figure for problem 13. (CC BY-NC-SA; Marcia Levitus)

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SECTION OVERVIEW

10.2: Series

Chapter Objectives

- Learn how to obtain Maclaurin and Taylor expansions of different functions.
- Learn how to express infinite sums using the summation operator (**Σ**)
- Understand how a series expansion can be used in the physical sciences to obtain an approximation that is valid in a particular regime (e.g. low concentration of solute, low pressure of a gas, small oscillations of a pendulum, etc).
- Understand how a series expansion can be used to prove a mathematical relationship.

10.2.1: Maclaurin Series

10.2.2: Linear Approximations

10.2.3: Taylor Series

10.2.4: Other Applications of Mclaurin and Taylor series

10.2.5: Problems

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10.2.1: Maclaurin Series

A function $f(x)$ can be expressed as a series in powers of x as long as $f(x)$ and all its derivatives are finite at $x = 0$. For example, we will prove shortly that the function $f(x) = \frac{1}{1-x}$ can be expressed as the following infinite sum:

$$\frac{1}{1-x} = 1 + x + x^2 + x^3 + x^4 + ... \tag{10.2.1.1}$$

We can write this statement in this more elegant way:

$$\frac{1}{1-x} = \sum_{n=0}^{\infty} x^n \tag{10.2.1.2}$$

If you are not familiar with this notation, the right side of the equation reads "sum from $n = 0$ to $n = \infty$ of x^n." When $n = 0$, $x^n = 1$, when $n = 1$, $x^n = x$, when $n = 2$, $x^n = x^2$, etc (compare with Equation 10.2.1.1). The term "series in powers of x" means a sum in which each summand is a power of the variable x. Note that the number 1 is a power of x as well ($x^0 = 1$). Also, note that both Equations 10.2.1.1 and 10.2.1.2 are exact, they are not approximations.

Similarly, we will see shortly that the function e^x can be expressed as another infinite sum in powers of x (i.e. a Maclaurin series) as:

$$e^x = 1 + x + \frac{1}{2}x^2 + \frac{1}{6}x^3 + \frac{1}{24}x^4 + ... \tag{10.2.1.3}$$

Or, more elegantly:

$$e^x = \sum_{n=0}^{\infty} \frac{1}{n!}x^n \tag{10.2.1.4}$$

where $n!$ is read "n factorial" and represents the product $1 \times 2 \times 3... \times n$. If you are not familiar with factorials, be sure you understand why $4! = 24$. Also, remember that by definition $0! = 1$, not zero.

At this point you should have two questions: 1) how do I construct the Maclaurin series of a given function, and 2) why on earth would I want to do this if $\frac{1}{1-x}$ and e^x are fine-looking functions as they are. The answer to the first question is easy, and although you should know this from your calculus classes we will review it again in a moment. The answer to the second question is trickier, and it is what most students find confusing about this topic. We will discuss different examples that aim to show a variety of situations in which expressing functions in this way is helpful.

How to obtain the Maclaurin Series of a Function

In general, a well-behaved function ($f(x)$ and all its derivatives are finite at $x = 0$) will be expressed as an infinite sum of powers of x like this:

$$f(x) = \sum_{n=0}^{\infty} a_n x^n = a_0 + a_1 x + a_2 x^2 + ... + a_n x^n \tag{10.2.1.5}$$

Be sure you understand why the two expressions in Equation 10.2.1.5 are identical ways of expressing an infinite sum. The terms a_n are called the **coefficients**, and are constants (that is, they are NOT functions of x). If you end up with the variable x in one of your coefficients go back and check what you did wrong! For example, in the case of e^x (Equation 10.2.1.3), $a_0 = 1, a_1 = 1, a_2 = 1/2, a_3 = 1/6, etc.$ In the example of Equation 10.2.1.1, all the coefficients equal 1. We just saw that two very different functions can be expressed using the same set of functions (the powers of x). What makes $\frac{1}{1-x}$ different from e^x are the coefficients a_n. As we will see shortly, the coefficients can be negative, positive, or zero.

How do we calculate the coefficients? Each coefficient is calculated as:

$$a_n = \frac{1}{n!}\left(\frac{d^n f(x)}{dx^n}\right)_0 \tag{10.2.1.6}$$

That is, the n-th coefficient equals one over the factorial of n multiplied by the n-th derivative of the function $f(x)$ evaluated at zero. For example, if we want to calculate a_2 for the function $f(x) = \frac{1}{1-x}$, we need to get the second derivative of $f(x)$, evaluate it at $x = 0$, and divide the result by $2!$. Do it yourself and verify that $a_2 = 1$. In the case of a_0 we need the zeroth-order derivative, which equals the function itself (that is, $a_0 = f(0)$, because $\frac{1}{0!} = 1$). It is important to stress that although the derivatives are usually functions of x, the coefficients are constants because they are expressed in terms of the derivatives evaluated at $x = 0$.

Note that in order to obtain a Maclaurin series we evaluate the function and its derivatives at $x = 0$. This procedure is also called the expansion of the function around (or about) zero. We can expand functions around other numbers, and these series are called Taylor series (see Section 3).

Example 10.2.1.1

Obtain the Maclaurin series of $sin(x)$.

Solution

We need to obtain all the coefficients $(a_0, a_1 ... etc)$. Because there are infinitely many coefficients, we will calculate a few and we will find a general pattern to express the rest. We will need several derivatives of $sin(x)$, so let's make a table:

n	$\frac{d^n f(x)}{dx^n}$	$\left(\frac{d^n f(x)}{dx^n}\right)_0$
0	$\sin(x)$	0
1	$\cos(x)$	1
2	$-\sin(x)$	0
3	$-\cos(x)$	-1
4	$\sin(x)$	0
5	$\cos(x)$	1

Remember that each coefficient equals $\left(\frac{d^n f(x)}{dx^n}\right)_0$ divided by $n!$, therefore:

n	$n!$	a_n
0	1	0
1	1	1
2	2	0
3	6	$-\frac{1}{6}$
4	24	0
5	120	$\frac{1}{120}$

This is enough information to see the pattern (you can go to higher values of n if you don't see it yet):

1. the coefficients for even values of n equal zero.
2. the coefficients for $n = 1, 5, 9, 13, ...$ equal $1/n!$
3. the coefficients for $n = 3, 7, 11, 15, ...$ equal $-1/n!$.

Recall that the general expression for a Maclaurin series is $a_0 + a_1x + a_2x^2 ... a_nx^n$, and replace $a_0 ... a_n$ by the coefficients we just found:

$$\sin(x) = x - \frac{1}{3!}x^3 + \frac{1}{5!}x^5 - \frac{1}{7!}x^7 ...$$

This is a correct way of writing the series, but in the next example we will see how to write it more elegantly as a sum.

Example 10.2.1.2

Express the Maclaurin series of $\sin(x)$ as a sum.

Solution

In the previous example we found that:

$$\sin(x) = x - \frac{1}{3!}x^3 + \frac{1}{5!}x^5 - \frac{1}{7!}x^7 ... \tag{10.2.1.7}$$

We want to express this as a sum:

$$\sum_{n=0}^{\infty} a_n x^n$$

The key here is to express the coefficients a_n in terms of n. We just concluded that 1) the coefficients for even values of n equal zero, 2) the coefficients for $n = 1, 5, 9, 13, ...$ equal $1/n!$ and 3) the coefficients for $n = 3, 7, 11, ...$ equal $-1/n!$. How do we put all this information together in a unique expression? Here are three possible (and equally good) answers:

- $\sin(x) = \sum_{n=0}^{\infty} (-1)^n \frac{1}{(2n+1)!} x^{2n+1}$
- $\sin(x) = \sum_{n=1}^{\infty} (-1)^{(n+1)} \frac{1}{(2n-1)!} x^{2n-1}$
- $\sin(x) = \sum_{n=0}^{\infty} cos(n\pi) \frac{1}{(2n+1)!} x^{2n+1}$

This may look impossibly hard to figure out, but let me share a few tricks with you. First, we notice that the sign in Equation 10.2.1.7 alternates, starting with a "+". A mathematical way of doing this is with a term $(-1)^n$ if your sum starts with $n = 0$, or $(-1)^{(n+1)}$ if you sum starts with $n = 1$. Note that $\cos(n\pi)$ does the same trick.

n	$(-1)^n$	$(-1)^{n+1}$	$\cos(n\pi)$
0	1	-1	1
1	-1	1	-1
2	1	-1	1
3	-1	1	-1

We have the correct sign for each term, but we need to generate the numbers $1, \frac{1}{3!}, \frac{1}{5!}, \frac{1}{7!}, ...$ Notice that the number "1" can be expressed as $\frac{1}{1!}$. To do this, we introduce the second trick of the day: we will use the expression $2n + 1$ to generate odd numbers (if you start your sum with $n = 0$) or $2n - 1$ (if you start at $n = 1$). Therefore, the expression $\frac{1}{(2n+1)!}$ gives $1, \frac{1}{3!}, \frac{1}{5!}, \frac{1}{7!}, ...$, which is what we need in the first and third examples (when the sum starts at zero).

Lastly, we need to use only odd powers of x. The expression $x^{(2n+1)}$ generates the terms $x, x^3, x^5 ...$ when you start at $n = 0$, and $x^{(2n-1)}$ achieves the same when you start your series at $n = 1$.

Confused about writing sums using the sum operator ($\sum$)? This video will help: http://tinyurl.com/lvwd36q

Need help? The links below contain solved examples.

External links:

Finding the maclaurin series of a function I: http://patrickjmt.com/taylor-and-maclaurin-series-example-1/

Finding the maclaurin series of a function II: http://www.youtube.com/watch?v= dp2ovDuWhro

Finding the maclaurin series of a function III: http://www.youtube.com/watch?v= WWe7pZjc4s8

Graphical Representation

From Equation 10.2.1.5 and the examples we discussed above, it should be clear at this point that any function whose derivatives are finite at $x = 0$ can be expressed by using the same set of functions: the powers of x. We will call these functions the **basis set**. A basis set is a collection of linearly independent functions that can represent other functions when used in a linear combination.

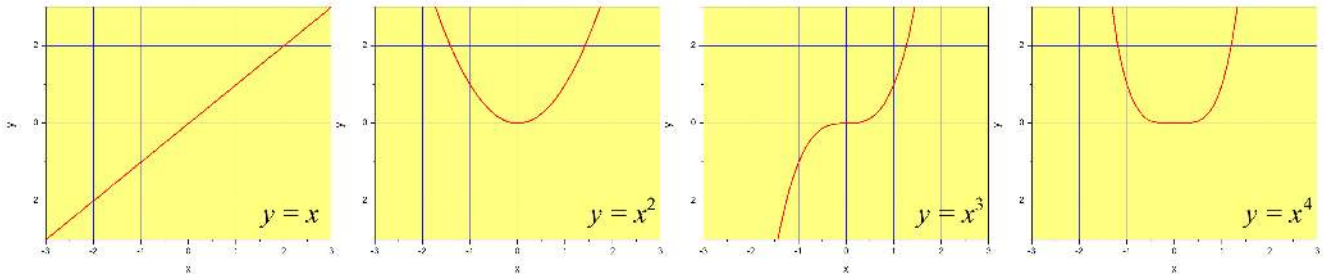


Figure 10.2.1.1: Some of the functions of the basis set for a Maclaurin expansion (CC BY-NC-SA; Marcia Levitus)

Figure 10.2.1.1 is a graphic representation of the first four functions of this basis set. To be fair, the first function of the set is $x^0 = 1$, so these would be the second, third, fourth and fifth. The full basis set is of course infinite in length. If we mix all the functions of the set with equal weights (we put the same amount of x^2 than we put x^{245} or x^0), we obtain $(1 - x)^{-1}$ (Equation 10.2.1.1. If we use only the odd terms, alternate the sign starting with a '+', and weigh each term less and less using the expression $1/(2n - 1)!$ for the $n - th$ term, we obtain $\sin x$ (Equation 10.2.1.7). This is illustrated in Figure 10.2.1.2, where we multiply the even powers of x by zero, and use different weights for the rest. Note that the 'etcetera' is crucial, as we would need to include an infinite number of functions to obtain the function $\sin x$ exactly.

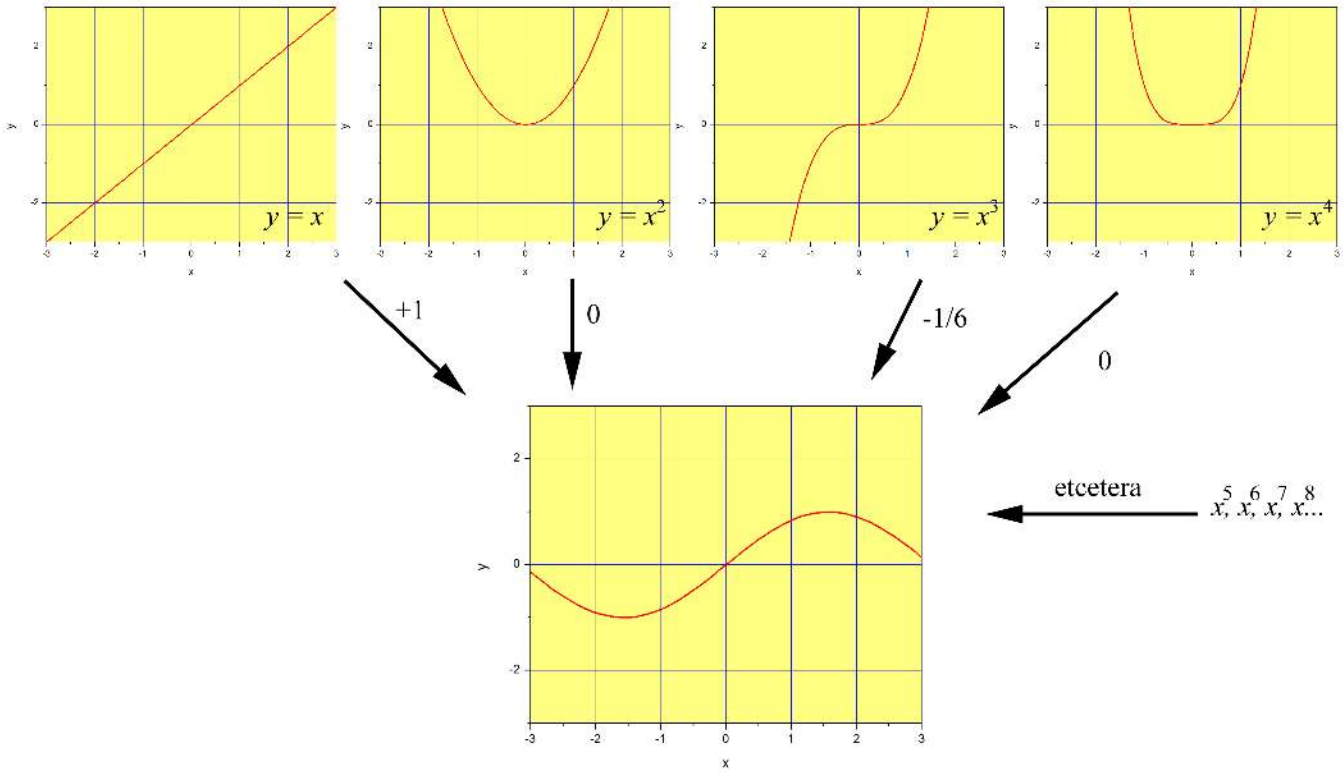


Figure 10.2.1.2: Construction of $\sin x$ using the powers of x as the basis set. (CC BY-NC-SA; Marcia Levitus)

Although we need an infinite number of terms to express a function exactly (unless the function is a polynomial, of course), in many cases we will observe that the weight (the coefficient) of each power of x gets smaller and smaller as we increase the power. For example, in the case of $\sin x$, the contribution of x^3 is $1/6th$ of the contribution of x (in absolute terms), and the contribution of x^5 is $1/120th$. This tells you that the first terms are much more important than the rest, although all are needed if we want the sum to represent $\sin x$ exactly. What if we are happy with a 'pretty good' approximation of $\sin x$? Let's see what happens if we use up to x^3 and drop the higher terms. The result is plotted in blue in Figure 10.2.1.3 together with $\sin x$ in red. We can see that the function $x - 1/6x^3$ is a very good approximation of $\sin x$ as long as we stay close to $x = 0$. As we move further away from the origin the approximation gets worse and worse, and we would need to include higher powers of x to get it better. This should be clear from eq. [series:sin], since the terms x^n get smaller and smaller with increasing n if x is a small number. Therefore, if x is small, we could write $\sin(x) \approx x - \frac{1}{3!}x^3$, where the symbol $\approx$ means approximately equal.

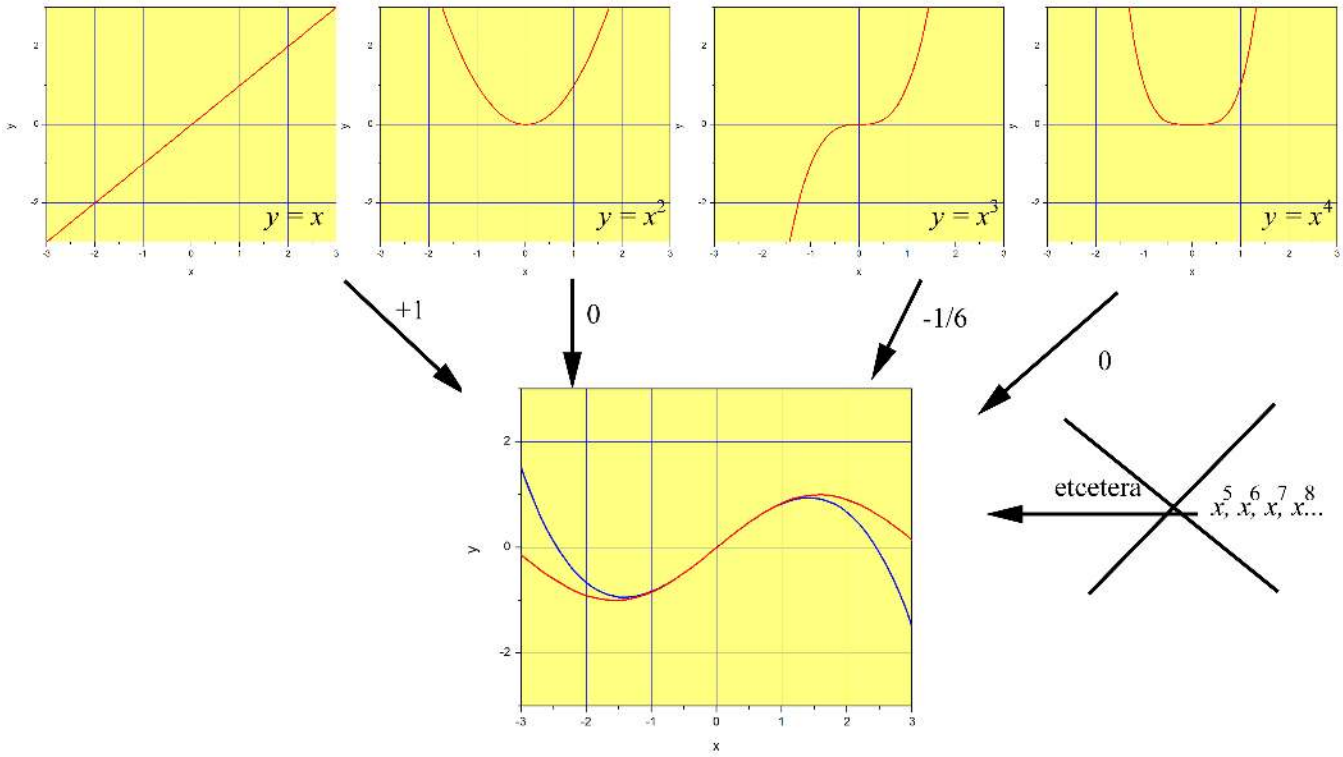


Figure 10.2.1.3: Approximation of $\sin x$ up to the third power of x. The curve in blue is the function $x - 1/6x^3$, and the curve in red is $\sin x$ (CC BY-NC-SA; Marcia Levitus)

But why stopping at $n = 3$ and not $n = 1$ or 5? The above argument suggests that the function x might be a good approximation of $\sin x$ around $x = 0$, when the term x^3 is much smaller than the term x. This is in fact this is the case, as shown in Figure 10.2.1.4.

We have seen that we can get good approximations of a function by **truncating** the series (i.e. not using the infinite terms). Students usually get frustrated and want to know how many terms are 'correct'. It takes a little bit of practice to realize there is no universal answer to this question. We would need some context to analyze how good of an approximation we are happy with. For example, are we satisfied with the small error we see at $x = 0.5$ in Figure 10.2.1.4? It all depends on the context. Maybe we are performing experiments where we have other sources of error that are much worse than this, so using an extra term will not improve the overall situation anyway. Maybe we are performing very precise experiments where this difference is significant. As you see, discussing how many terms are needed in an approximation out of context is not very useful. We will discuss this particular approximation when we learn about second order differential equations and analyze the problem of the pendulum, so hopefully things will make more sense then.

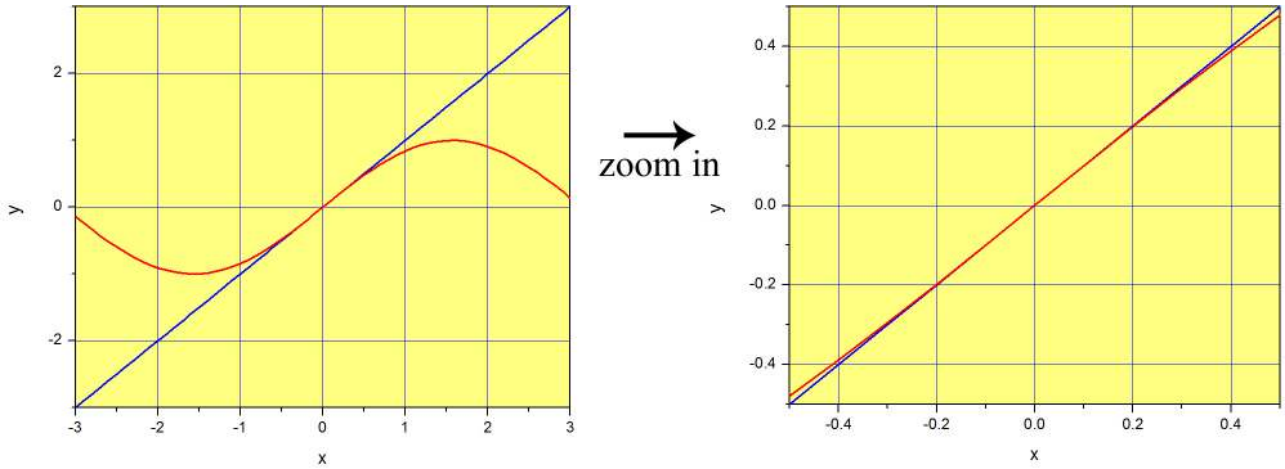


Figure **10.2.1.4**: Approximation of $\sin x$ up to the first power of x. The curve in blue is the function x, and the curve in red is $\sin x$ (CC BY-NC-SA; Marcia Levitus)

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10.2.2: Linear Approximations

If you take a look at Equation **3.1.5** you will see that we can always approximate a function as $a_0 + a_1 x$ as long as x is small. When we say 'any function' we of course imply that the function and all its derivatives need to be finite at $x = 0$. Looking at the definitions of the coefficients, we can write:

$$f(x) \approx f(0) + f'(0)x \tag{10.2.2.1}$$

We call this a linear approximation because Equation 10.2.2.1 is the equation of a straight line. The slope of this line is $f'(0)$ and the y-intercept is $f(0)$.

A fair question at this point is 'why are we even talking about approximations?' What is so complicated about the functions $\sin x$, e^x or $\ln(x+1)$ that we need to look for an approximation? Are we getting too lazy? To illustrate this issue, let's consider the problem of the pendulum, which we will solve in detail in the chapter devoted to differential equations. The problem is illustrated in Figure **10.2.2.1**, and those of you who took a physics course will recognize the equation below, which represents the law of motion of a simple pendulum. The second derivative refers to the acceleration, and the $\sin\theta$ term is due to the component of the net force along the direction of motion. We will discuss this in more detail later in this semester, so for now just accept the fact that, for this system, Newton's law can be written as:

$$\frac{d^2\theta(t)}{dt^2} + \frac{g}{l}\sin\theta(t) = 0$$

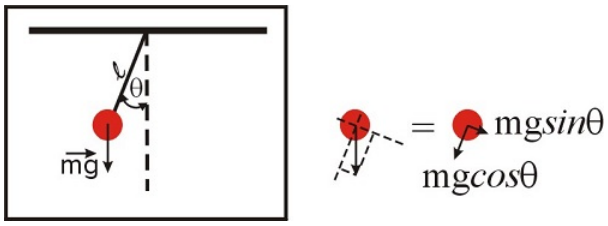


Figure **10.2.2.1**: A rigid pendulum with massless and inextensible cord of length l. The motion is assumed to occur in two dimensions, and the friction is assumed to be negligible. The mass of the object is m, and g is the acceleration due to gravity. (CC BY-NC-SA; Marcia Levitus)

This equation should be easy to solve, right? It has only a few terms, nothing too fancy other than an innocent sine function...How difficult can it be to obtain $\theta(t)$? Unfortunately, this differential equation does not have an analytical solution! An analytical solution means that the solution can be expressed in terms of a finite number of elementary functions (such as sine, cosine, exponentials, etc). Differential equations are sometimes deceiving in this way: they look simple, but they might be incredibly hard to solve, or even impossible! The fact that we cannot write down an analytical solution does not mean there is no solution to the problem. You can swing a pendulum and measure $\theta(t)$ and create a table of numbers, and in principle you can be as precise as you want to be. Yet, you will not be able to create a function that reflects your numeric results. We will see that we can solve equations like this numerically, but not analytically. Disappointing, isn't it? Well... don't be. A lot of what we know about molecules and chemical reactions came from the work of physical chemists, who know how to solve problems using numerical methods. The fact that we cannot obtain an analytical expression that describes a particular physical or chemical system does not mean we cannot solve the problem numerically and learn a lot anyway!

But what if we are interested in small displacements only (that is, the pendulum swings close to the vertical axis at all times)? In this case, $\theta << 1$, and as we saw $\sin\theta \approx \theta$ (see Figure **3.1.4**). If this is the case, we have now:

$$\frac{d^2\theta(t)}{dt^2} + \frac{g}{l}\theta(t) = 0$$

As it turns out, and as we will see in Chapter 2, in this case it is very easy to obtain the solution we are looking for:

$$\theta(t) = \theta(t=0)\cos\left((\frac{g}{l})^{1/2}t\right)$$

This solution is the familiar 'back and forth' oscillatory motion of the pendulum you are familiar with. What you might have not known until today is that this solution assumes $\sin\theta \approx \theta$ and is therefore valid only if $\theta << 1$!

There are lots of 'hidden' linear approximations in the equations you have learned in your physics and chemistry courses. You may recall your teachers telling you that a give equation is valid only at low concentrations, or low pressures, or low... you hopefully get the point. A pendulum is of course not particularly interesting when it comes to chemistry, but as we will see through many examples during the semester, oscillations, generally speaking, are. The example below illustrates the use of series to a problem involving diatomic molecules, but before discussing it we need to provide some background.

The vibrations of a diatomic molecule are often modeled in terms of the so-called *Morse potential*. This equation does not provide an exact description of the vibrations of the molecule under any condition, but it does a pretty good job for many purposes.

$$V(R) = D_e \left(1 - e^{-k(R-R_e)}\right)^2 \tag{10.2.2.2}$$

Here, R is the distance between the nuclei of the two atoms, R_e is the distance at equilibrium (i.e. the equilibrium bond length), D_e is the dissociation energy of the molecule, k is a constant that measures the strength of the bond, and V is the potential energy. Note that R_e is the distance at which the potential energy is a minimum, and that is why we call this the equilibrium distance. We would need to apply energy to separate the atoms even more, or to push them closer (Figure 10.2.2.2).

At room temperature, there is enough thermal energy to induce small vibrations that displace the atoms from their equilibrium positions, but for stable molecules, the displacement is very small: $R - R_e \to 0$. In the next example we will prove that under these conditions, the potential looks like a parabola, or in mathematical terms, $V(R)$ is proportional to the square of the displacement. This type of potential is called a 'harmonic potential'. A vibration is said to be simple harmonic if the potential is proportional to the square of the displacement (as in the simple spring problems you may have studied in physics).

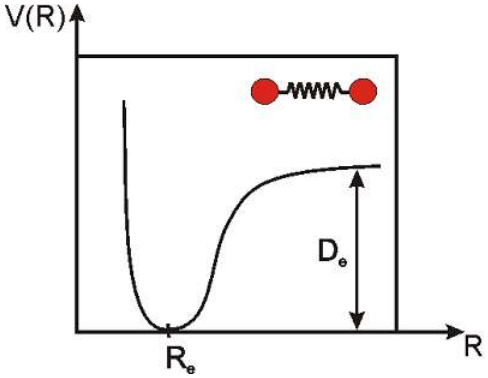


Figure 10.2.2.2: The Morse potential (CC BY-NC-SA; Marcia Levitus)

Example 10.2.2.1

Expand the Morse potential as a power series and prove that the vibrations of the molecule are approximately simple harmonic if the displacement $R - R_e$ is small.

Solution

The relevant variable in this problem is the displacement $R - R_e$, not the actual distance R. Let's call the displacement $R - R_e = x$, and let's rewrite Equation 10.2.2.2 as

$$V(R) = D_e \left(1 - e^{-kx}\right)^2 \tag{10.2.2.3}$$

The goal is to prove that $V(R) = cx^2$ (i.e. the potential is proportional to the square of the displacement) when $x \to 0$. The constant c is the proportionality constant. We can approach this in two different ways. One option is to expand the function shown in Equation 10.2.2.3 around zero. This would be correct, but it but involve some unnecessary work. The variable x appears only in the exponential term, so a simpler option is to expand the exponential function, and plug the result of this expansion back in Equation 10.2.2.3. Let's see how this works:

We want to expand e^{-kx} as $a_0 + a_1 x + a_2 x^2 ... a_n x^n$, and we know that the coefficients are $a_n = \frac{1}{n!}\left(\frac{d^n f(x)}{dx^n}\right)_0$.
The coefficient a_0 is $f(0) = 1$. The first three derivatives of $f(x) = e^{-kx}$ are

- $f'(x) = -ke^{-kx}$

- $f''(x) = k^2 e^{-kx}$
- $f'''(x) = -k^3 e^{-kx}$

When evaluated at $x = 0$ we obtain, $-k, k^2, -k^3$...

and therefore $a_n = \frac{(-1)^n k^n}{n!}$ for $n = 0, 1, 2$....

Therefore,

$$e^{-kx} = 1 - kx + k^2x^2/2! - k^3x^3/3! + k^4x^4/4!...$$

and

$$1 - e^{-kx} = +kx - k^2x^2/2! + k^3x^3/3! - k^4x^4/4!...$$

From the last result, when $x << 1$, we know that the terms in x^2, x^3... will be increasingly smaller, so $1 - e^{-kx} \approx kx$ and $(1 - e^{-kx})^2 \approx k^2x^2$.

Plugging this result in Equation 10.2.2.3 we obtain $V(R) \approx D_e k^2 x^2$, so we demonstrated that the potential is proportional to the square of the displacement when the displacement is small (the proportionality constant is $D_e k^2$). Therefore, stable diatomic molecules at room temperatures behave pretty much like a spring! (Don't take this too literally. As we will discuss later, microscopic springs do not behave like macroscopic springs at all).

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10.2.3: Taylor Series

Before discussing more applications of Maclaurin series, let's expand our discussion to the more general case where we expand a function around values different from zero. Let's say that we want to expand a function around the number h. If $h = 0$, we call the series a Maclaurin series, and if $h \neq 0$ we call the series a Taylor series. Because Maclaurin series are a special case of the more general case, we can call all the series Taylor series and omit the distinction. The following is true for a function $f(x)$ as long as the function and all its derivatives are finite at h:

$$f(x) = a_0 + a_1(x-h) + a_2(x-h)^2 + ... + a_n(x-h)^n = \sum_{n=0}^{\infty} a_n(x-h)^n \tag{10.2.3.1}$$

The coefficients are calculated as

$$a_n = \frac{1}{n!}\left(\frac{d^n f}{dx^n}\right)_h \tag{10.2.3.2}$$

Notice that instead of evaluating the function and its derivatives at $x = 0$ we now evaluate them at $x = h$, and that the basis set is now $1, (x-h), (x-h)^2, ..., (x-h)^n$ instead of $1, x, x^2, ..., x^n$. A Taylor series will be a good approximation of the function at values of x close to h, in the same way Maclaurin series provide good approximations close to zero.

To see how this works let's go back to the exponential function. Recall that the Maclaurin expansion of e^x is shown in Equation **3.1.3**. We know what happens if we expand around zero, so to practice, let's expand around $h = 1$. The coefficient a_0 is $f(1) = e^1 = e$. All the derivatives are e^x, so $f'(1) = f''(1) = f'''(1) ... = e$. Therefore, $a_n = \frac{e}{n!}$ and the series is therefore

$$e\left[1 + (x-1) + \frac{1}{2}(x-1)^2 + \frac{1}{6}(x-1)^3 + ...\right] = \sum_{n=0}^{\infty} \frac{e}{n!}(x-1)^n \tag{10.2.3.3}$$

We can use the same arguments we used before to conclude that $e^x \approx ex$ if $x \approx 1$. If $x \approx 1$, $(x-1) \approx 0$, and the terms $(x-1)^2, (x-1)^3$ will be smaller and smaller and will contribute less and less to the sum. Therefore,

$$e^x \approx e\,[1 + (x-1)] = ex.$$

This is the equation of a straight line with slope e and y-intercept 0. In fact, from Equation **3.1.7** we can see that all functions will look linear at values close to h. This is illustrated in Figure **10.2.3.1**, which shows the exponential function (red) together with the functions $1 + x$ (magenta) and ex (blue). Not surprisingly, the function $1 + x$ provides a good approximation of e^x at values close to zero (see Equation **3.1.3**) and the function ex provides a good approximation around $x = 1$ (Equation 10.2.3.3).

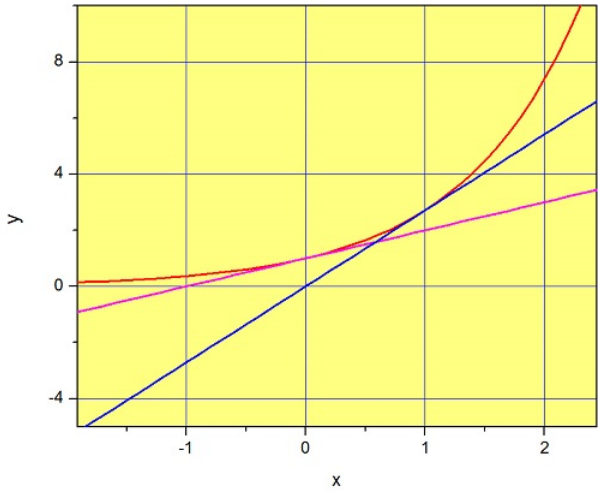


Figure **10.2.3.1**: Two linear approximations of the exponential function. The function e^x is plotted in red together with the function $y = 1 + x$ (magenta) and $y = ex$ (blue). (CC BY-NC-SA; Marcia Levitus)

Example 10.2.3.1:

Expand $f(x) = \ln x$ about $x = 1$

Solution

$$f(x) = a_0 + a_1(x-h) + a_2(x-h)^2 + \ldots + a_n(x-h)^n, a_n = \frac{1}{n!}\left(\frac{d^n f}{dx^n}\right)_h$$

$$a_0 = f(1) = \ln(1) = 0$$

The derivatives of $\ln x$ are:

$$f'(x) = 1/x, f''(x) = -1/x^2, f'''(x) = 2/x^3, f^{(4)}(x) = -6/x^4, f^{(5)}(x) = 24/x^5 \ldots$$

and therefore,

$$f'(1) = 1, f''(1) = -1, f'''(1) = 2, f^{(4)}(1) = -6, f^{(5)}(1) = 24 \ldots.$$

To calculate the coefficients, we need to divide by $n!$:

- $a_1 = f'(1)/1! = 1$
- $a_2 = f''(1)/2! = -1/2$
- $a_3 = f'''(1)/3! = 2/3! = 1/3$
- $a_4 = f^{(4)}(1)/4! = -6/4! = -1/4$
- $a_n = (-1)^{n+1}/n$

The series is therefore:

$$f(x) = 0 + 1(x-1) - 1/2(x-1)^2 + 1/3(x-1)^3 \ldots = \sum_{n=1}^{\infty} \frac{(-1)^{n+1}}{n}(x-1)^n$$

Note that we start the sum at $n = 1$ because $a_0 = 0$, so the term for $n = 0$ does not have any contribution.

Need help? The links below contain solved examples.

External links:

Finding the Taylor series of a function I: http://patrickjmt.com/taylor-and-maclaurin-series-example-2/

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10.2.4: Other Applications of Mclaurin and Taylor series

So far we have discussed how we can use power series to approximate more complex functions around a particular value. This is very common in physical chemistry, and you will apply it frequently in future courses. There are other useful applications of Taylor series in the physical sciences. Sometimes, we may use relationships to derive equations or prove relationships. Example **10.2.4.1** illustrates this last point.

Example 10.2.4.1

Calculate the following sum (λ is a positive constant)

$$\sum_{k=0}^{\infty} \frac{\lambda^k e^{-\lambda}}{k!}$$

Solution

Let's 'spell out' the sum:

$$\sum_{k=0}^{\infty} \frac{\lambda^k e^{-\lambda}}{k!} = e^{-\lambda}\left[1 + \frac{\lambda^1}{1!} + \frac{\lambda^2}{2!} + \frac{\lambda^3}{3!} \ldots\right]$$

The sum within the brackets is exactly e^{λ}. This is exact, and not an approximation, because we have all infinite terms.

Therefore,

$$\sum_{k=0}^{\infty} \frac{\lambda^k e^{-\lambda}}{k!} = e^{-\lambda} e^{\lambda} = 1$$

This would require that you recognize the term within brackets as the Maclaurin series of the exponential function. One simpler version of the problem would be to ask you to prove that the sum equals 1.

There are more ways we can use Taylor series in the physical sciences. We will see another type of application when we study differential equations. In fact, power series are extremely important in finding the solutions of a large number of equations that arise in quantum mechanics. The description of atomic orbitals, for example, require that we solve differential equations that involve expressing functions as power series.

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10.2.5: Problems

Problem 10.2.5.1

Expand the following functions around the value of x indicated in each case.

In each case, write down at least four terms of the series, and write down the result as an infinite sum.

- $\sin(ax)$, $x = 0$, a is a constant
- $\cos(ax)$, $x = 0$, a is a constant
- e^{ax}, $x = 0$, a is a real constant
- e^{-ax}, $x = 0$, a is a real constant
- $\ln(ax)$, $x = 1$, a is a real constant

Problem 10.2.5.2

Use the results of the previous problem to prove Euler's relationship:

$$e^{ix} = \cos x + i \sin x$$

Problem 10.2.5.3

The osmotic pressure (π) of a solution is given by

$$-RT \ln x_A = \pi V_m$$

where V_m is the molar volume of the pure solvent, and x_a is the mole fraction of the solvent.

Show that in the case of a dilute solution

$$RT x_B \approx \pi V_m$$

where x_B is the mole fraction of the solute. Remember that the mole fractions of the solute and the solvent need to add up to 1.

Note: you may use any of the results you obtained in Problem 10.2.5.1.

Problem 10.2.5.4

The following expression is known as the Butler-Volmer equation, and it is used in electrochemistry to describe the kinetics of an electrochemical reaction controlled solely by the rate of the electrochemical charge transfer process.

$$j = j_0(e^{(1-\alpha)f\eta} - e^{-\alpha f\eta}),\ 0 < \alpha < 1 \text{ and } f > 0, \eta > 0$$

Show that $j \approx j_0 f\eta$ when $f\eta << 1$.

Note: you may use any of the results you obtained in Problem 10.2.5.1.

Problem 10.2.5.5

The energy density of black-body radiation (ρ) at temperature T is given by Plank's formula:

$$\rho(\lambda) = \frac{8\pi hc}{\lambda^5}[e^{hc/\lambda kT} - 1]^{-1}$$

where λ is the wavelength, h is Plank's constant, and c is the speed of light. Show that the formula reduces to the classical Rayleigh-Jeans law $\rho = 8\pi kT/\lambda^4$ for long wavelengths ($\lambda \to \infty$).

Hint: Define a variable $\nu = \lambda^{-1}$ and solve the problem for $\nu \to 0$.

Note: you may use any of the results you obtained in Problem 10.2.5.1.

? Problem 10.2.5.6

Use series to prove that $\sum_{k=0}^{\infty} \frac{\lambda^k e^{-\lambda}}{k!} = 1$, λ is a positive real constant.

? Problem 10.2.5.7

Write down the equation of a straight line that provides a good approximation of the function e^x at values close to $x = 2$.

? Problem 10.2.5.8

Use a Taylor expansion around a to prove that $\ln x = \ln a + \sum_{n=1}^{\infty} \frac{(-1)^{n+1}}{na^n}(x-a)^n$

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SECTION OVERVIEW

10.3: Calculus in More than One Variable

Chapter Objectives

- Review the concept of partial derivative.
- Review the properties of partial derivatives.
- Be able to use the properties of partial derivatives in the context of physical chemistry problems.
- Review the concept of double and triple integrals.
- Learn the concept of equation of state. Understand the concept of a van der Waals gas from the molecular point of view.
- Learn about phase transitions and critical phenomena.

10.3.1: Functions of Two Independent Variables

10.3.2: The Equation of State

10.3.3: The Chain Rule

10.3.4: Double and Triple Integrals

10.3.5: Real Gases

10.3.6: Problems

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10.3.1: Functions of Two Independent Variables

A (real) function of one variable, $y = f(x)$, defines a curve in the plane. The first derivative of a function of one variable can be interpreted graphically as the slope of a tangent line, and dynamically as the rate of change of the function with respect to the variable Figure 10.3.1.1.

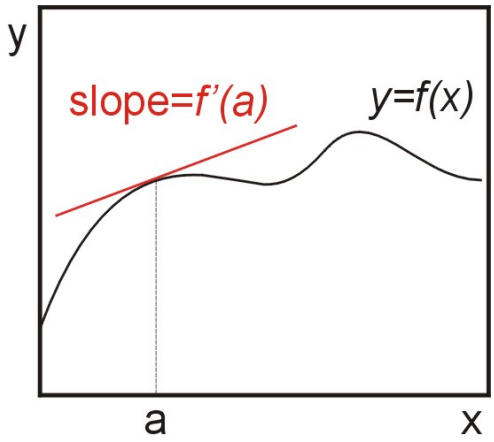


Figure 10.3.1.1: Geometric interpretation of a derivative. (CC BY-NC-SA; Marcia Levitus)

A function of two independent variables, $z = f(x, y)$, defines a surface in three-dimensional space. For a function of two or more variables, there are as many independent first derivatives as there are independent variables. For example, we can differentiate the function $z = f(x, y)$ with respect to x keeping y constant. This derivative represents the slope of the tangent line shown in Figure 10.3.1.2A. We can also take the derivative with respect to y keeping x constant, as shown in Figure 10.3.1.2B.

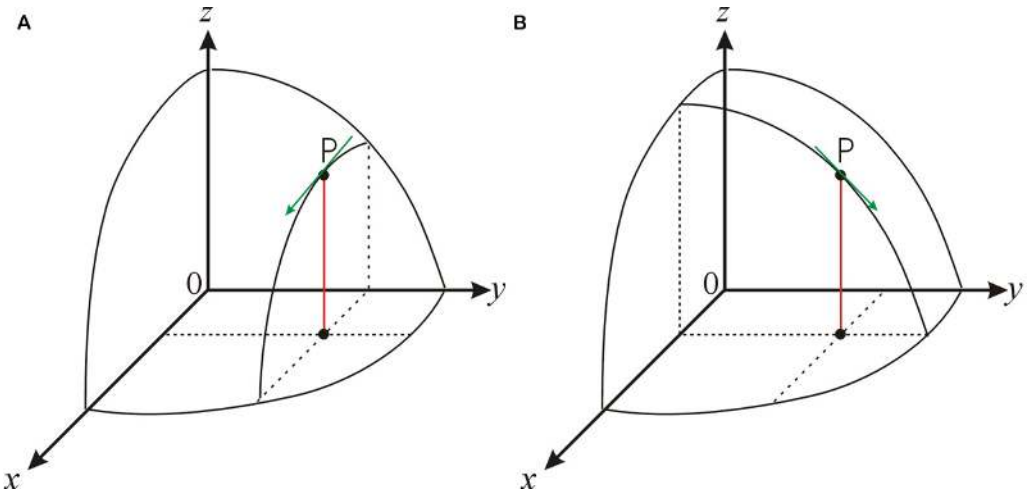


Figure 10.3.1.2: Geometric interpretation of a partial derivative. (CC BY-NC-SA; Marcia Levitus)

For example, let's consider the function $z = 3x^2 - y^2 + 2xy$. We can take the derivative of this function with respect to x treating y as a constant. The result is $6x + 2y$. This is the partial derivative of the function with respect to x, and it is written:

$$\left(\frac{\partial z}{\partial x}\right)_y = 6x + 2y$$

where the small subscripts indicate which variables are held constant. Analogously, the partial derivate of z with respect to y is:

$$\left(\frac{\partial z}{\partial y}\right)_x = 2x - 2y$$

We can extend these ideas to functions of more than two variables. For example, consider the function $f(x, y, z) = x^2y/z$. We can differentiate the function with respect to x keeping y and z constant to obtain:

$$\left(\frac{\partial f}{\partial x}\right)_{y,z} = 2x\frac{y}{z}$$

We can also differentiate the function with respect to z keeping x and y constant:

$$\left(\frac{\partial f}{\partial z}\right)_{x,y} = -x^2y/z^2$$

and differentiate the function with respect to y keeping x and z constant:

$$\left(\frac{\partial f}{\partial y}\right)_{x,z} = \frac{x^2}{z}$$

Functions of two or more variables can be differentiated partially more than once with respect to either variable while holding the other constant to yield second and higher derivatives. For example, the function $z = 3x^2 - y^2 + 2xy$ can be differentiated with respect to x two times to obtain:

$$\left(\frac{\partial}{\partial x}\left(\frac{\partial z}{\partial x}\right)_y\right)_y = \left(\frac{\partial^2 z}{\partial x^2}\right)_y = 6$$

We can also differentiate with respect to x first and y second:

$$\left(\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right)_y\right)_x = \left(\frac{\partial^2 f}{\partial y \partial x}\right) = 2$$

Check the videos below if you are learning this for the first time, or if you feel you need to refresh the concept of partial derivatives.

- Partial derivatives: http://patrickjmt.com/derivatives-finding-partial-derivatives (don't get confused by the different notation!)
- Partial derivatives: http://www.youtube.com/watch?v=vxJR5graUfI
- Higher order partial derivatives: http://www.youtube.com/watch?v=3itjTS2Y9oE

If a function of two or more variables and its derivatives are single-valued and continuous, a property normally attributed to physical variables, then the mixed partial second derivatives are equal (Euler reciprocity):

$$\left(\frac{\partial^2 f}{\partial x \partial y}\right) = \left(\frac{\partial^2 f}{\partial y \partial x}\right) \tag{10.3.1.1}$$

For example, for $z = 3x^2 - y^2 + 2xy$:

$$\left(\frac{\partial^2 f}{\partial y \partial x}\right) = \left(\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right)_y\right)_x = \left(\frac{\partial}{\partial y}(6x+2y)\right)_x = 2$$

$$\left(\frac{\partial^2 f}{\partial x \partial y}\right) = \left(\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right)_x\right)_y = \left(\frac{\partial}{\partial x}(-2y+2x)\right)_y = 2$$

Another useful property of the partial derivatives is the so-called reciprocal identity, which holds when the same variables are held constant in the two derivatives:

$$\left(\frac{\partial y}{\partial x}\right) = \frac{1}{\left(\frac{\partial x}{\partial y}\right)} \tag{10.3.1.2}$$

For example, for $z = x^2y$:

$$\left(\frac{\partial z}{\partial x}\right)_y = \left(\frac{\partial}{\partial x}x^2y\right)_y = 2xy$$

$$\left(\frac{\partial x}{\partial z}\right)_y = \left(\frac{\partial}{\partial z}\sqrt{z/y}\right)_y = \frac{1}{2y}(z/y)^{-1/2} = \frac{1}{2xy} = \frac{1}{\left(\frac{\partial z}{\partial x}\right)_y}$$

Finally, let's mention the cycle rule. For a function $z(x,y)$:

$$\left(\frac{\partial y}{\partial x}\right)_z\left(\frac{\partial x}{\partial z}\right)_y\left(\frac{\partial z}{\partial y}\right)_x=-1 \tag{10.3.1.3}$$

We can construct other versions as follows:

$$\left(\frac{\partial y}{\partial x}\right)_z\left(\frac{\partial x}{\partial z}\right)_y\left(\frac{\partial z}{\partial y}\right)_x=-1$$

$$\left(\frac{\partial x}{\partial z}\right)_y\left(\frac{\partial z}{\partial y}\right)_x\left(\frac{\partial y}{\partial x}\right)_z=-1$$

$$\left(\frac{\partial z}{\partial x}\right)_y\left(\frac{\partial x}{\partial y}\right)_z\left(\frac{\partial y}{\partial z}\right)_x=-1$$

Figure **10.3.1.3**: The chain rule: Start with any partial derivative, and follow the pattern to construct the rest (CC BY-NC-SA; Marcia Levitus)

For example, for $z=x^2y$:

$$\left(\frac{\partial y}{\partial x}\right)_z=\left(\frac{\partial}{\partial x}(z/x^2)\right)_z=-2z/x^3$$

$$\left(\frac{\partial x}{\partial z}\right)_y=\left(\frac{\partial}{\partial z}\sqrt{z/y}\right)_y=\frac{1}{2y}(z/y)^{-1/2}$$

$$\left(\frac{\partial z}{\partial y}\right)_x=\left(\frac{\partial}{\partial y}x^2y\right)_x=x^2$$

$$\left(\frac{\partial y}{\partial x}\right)_z\left(\frac{\partial x}{\partial z}\right)_y\left(\frac{\partial z}{\partial y}\right)_x=-\frac{2z}{x^3}\frac{1}{2y}\left(\frac{y}{z}\right)^{1/2}x^2=-\left(\frac{z}{y}\right)^{1/2}\frac{1}{x}=-\left(\frac{x^2y}{y}\right)^{1/2}\frac{1}{x}=-1$$

Before discussing partial derivatives any further, let's introduce a few physicochemical concepts to put our discussion in context.

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10.3.2: The Equation of State

Note

From the last section, the cycle rule is defined as follows:

$$\left(\frac{\partial y}{\partial x}\right)_z \left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x = -1 \tag{10.3.2.1}$$

The thermodynamic state of a system, such as a fluid, is defined by specifying a set of measurable properties sufficient so that all remaining properties are determined. For example, if you have a container full of a gas, you may specify the pressure, temperature and number of moles, and this should be sufficient for you to calculate other properties such as the density and the volume. In other words, the temperature (T), number of moles (n), volume (V) and pressure (P) are not all independent variables.

Ideal Gas Equation of State

To make sense of this statement, let's consider an ideal gas. You know from your introductory chemistry courses[1] that temperature, number of moles, volume and pressure are related through a universal constant R:

$$P = \frac{nRT}{V} \tag{10.3.2.2}$$

If P is expressed in atmospheres, V in liters, and T in Kelvin, then $R = 0.082\ \frac{L \times atm}{K \times mol}$

This expression tells you that the four variables cannot be changed independently. If you know three of them, you also know the fourth.

Equation 10.3.2.2 is one particular case of what is known as an **equation of state**. An equation of state is an expression relating the density of a fluid with its temperature and pressure. Note that the density is related to the number of moles and the volume, so it takes care of these two variables together. There is no single equation of state that predicts the behavior of all substances under all conditions. Equation 10.3.2.2, for example, is a good approximation for non polar gases at low densities (low pressures and high temperatures). Other more sophisticated equations are better suited to describe other systems in other conditions, but there is no universal equation of state.

In general, for a simple fluid, an equation of state will be a relationship between P and the variables T, V and n:

$$P = P(T, V, n) = P(T, V_m),$$

where V_m is the molar volume, V/n. The molar volume is sometimes written as $\bar{V}$. For example, Equation 10.3.2.2 can be rerwritten as

$$P = \frac{RT}{\bar{V}}.$$

Let's 'play' with the equation of state for an ideal gas. The partial derivative $\left(\frac{\partial P}{\partial T}\right)_{V,n}$ represents how the pressure changes as we change the temperature of the container at constant volume and constant n:

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

It is a relief that the derivative is positive, because we know that an increase in temperature causes an increase in pressure! This also tells us that if we increase the temperature by a small amount, the increase in pressure will be larger in a small container than in a large container.

The partial derivative $\left(\frac{\partial P}{\partial V}\right)_{T,n}$ represents how the pressure changes as we change the volume of the container at constant temperature and constant n:

$$\left(\frac{\partial P}{\partial V}\right)_{T,n} = -\frac{nRT}{V^2}$$

Again, we are happy to see the derivative is negative. If we increase the volume we should see a decrease in pressure as long as the temperature is held constant. This is not too different from squeezing a balloon (don't try this at home!).

We can also write an equation that represents how the volume changes with a change in pressure: $\left(\frac{\partial V}{\partial P}\right)_{T,n}$. From Equation 10.3.2.2,

$$V = \frac{nRT}{P}$$

and therefore:

$$\left(\frac{\partial V}{\partial P}\right)_{T,n} = -\frac{nRT}{P^2}$$

Let's compare these two derivatives:

$$\left(\frac{\partial V}{\partial P}\right)_{T,n} = -\frac{nRT}{P^2} = -\frac{nRT}{(nRT/V)^2} = -\frac{V^2}{nRT} = \frac{1}{\left(\frac{\partial P}{\partial V}\right)_{T,n}}$$

Surprised? You shouldn't be based on the inverse rule! (Equation ???). Note that this works because we hold the same variables constant in both cases.

Now, you may argue that the inverse rule is not particularly useful because it doesn't take a lot of work to solve for V and perform $\left(\frac{\partial V}{\partial P}\right)_{T,n}$.

Dieterici's Equation of State

Let's consider a more complex equation of state known as Dieterici's equation of state for a real gas:

$$P = \frac{RT}{\bar{V} - b} e^{-a/(R\bar{V}T)}$$

Here, a and b are constants that depend on the particular gas (e.g. whether we are considering $\mathbf{H_2}$ or $\mathbf{CO_2}$). Let's say you are asked to obtain $\left(\frac{\partial V}{\partial P}\right)_{T,n}$. What do you do? Do you find the inverse rule useful now?

Let's go back to the ideal gas, and calculate other partial derivatives:

$$\left(\frac{\partial P}{\partial V}\right)_{T,n} = -\frac{nRT}{V^2} \tag{10.3.2.3}$$

$$\left(\frac{\partial V}{\partial T}\right)_{P,n} = \frac{nR}{P} \tag{10.3.2.4}$$

$$\left(\frac{\partial T}{\partial P}\right)_{V,n} = \frac{V}{nR} \tag{10.3.2.5}$$

Let's calculate the product:

$$\left(\frac{\partial P}{\partial V}\right)_{T,n}\left(\frac{\partial V}{\partial T}\right)_{P,n}\left(\frac{\partial T}{\partial P}\right)_{V,n} = -\frac{nRT}{V^2}\frac{nR}{P}\frac{V}{nR} = -\frac{nRT}{VP} = -1$$

In the last step, we used Equation 10.3.2.2. Surprised? You shouldn't be based on the cycle rule! (Equation 10.3.2.1). Again, this is not particularly useful for an ideal gas, but let's think about Dieterici's equation again and let's assume that you are interested in calculating $\left(\frac{\partial V}{\partial T}\right)_{P,n}$. What would you do?

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10.3.3: The Chain Rule

We all know that the position of a point in space can be specified with two coordinates, x and y, called the cartesian coordinates. We also know that we can choose instead to specify the position of the point using the distance from the origin (r) and the angle that the vector makes with the x axis (θ). The latter are what we call plane polar coordinates, which we will cover in much more detail in Chapter 10.

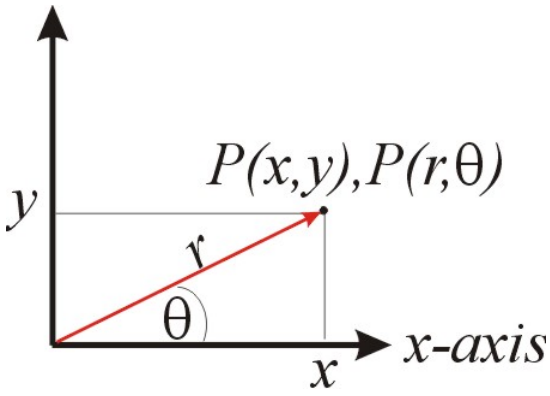


Figure **10.3.3.1**: Cartesian and polar coordinates. (CC BY-NC-SA; Marcia Levitus)

The two coordinate systems are related by:

$$x = r\cos\theta; \;\; y = r\sin\theta \tag{10.3.3.1}$$

$$r = \sqrt{x^2+y^2}; \;\; \theta = tan^{-1}(y/x) \tag{10.3.3.2}$$

Let's assume that we are given a function in polar coordinates, for example $f(r,\theta) = e^{-3r}\cos\theta$, and we are asked to find the partial derivatives in cartesian coordinates, $(\partial f/\partial x)_y$ and $(\partial f/\partial y)_x$. We can of course re-write the function in terms of x and y and find the derivatives we need, but wouldn't it be wonderful if we had a universal formula that converts the derivatives in polar coordinates ($(\partial f/\partial r)_\theta$ and $(\partial f/\partial \theta)_r$) to the derivatives in cartesian coordinates? This would allow us to take the derivatives in the system the equation is expressed in (which is easy), and then translate the derivatives to the other system without thinking too much. The chain rule will allow us to create these 'universal ' relationships between the derivatives of different coordinate systems.

Before using the chain rule, let's obtain $(\partial f/\partial x)_y$ and $(\partial f/\partial y)_x$ by re-writing the function in terms of x and y. I want to show you how much work this would involve, so you can appreciate how useful using the chain rule is. Using Equations 10.3.3.1 and 10.3.3.2, we can rewrite $f(r,\theta) = e^{-3r}\cos\theta$ as

$$f(x,y) = \frac{e^{-3(x^2+y^2)^{1/2}}x}{(x^2+y^2)^{1/2}}$$

We can easily obtain $(\partial f/\partial x)_y$ and $(\partial f/\partial y)_x$, but it is certainly quite a bit of work. What if I told you that $(\partial f/\partial x)_y$ is simply

$$\left(\frac{\partial f}{\partial x}\right)_y = \cos\theta\left(\frac{\partial f}{\partial r}\right)_\theta - \frac{\sin\theta}{r}\left(\frac{\partial f}{\partial \theta}\right)_r \tag{10.3.3.3}$$

independently of the function f? We will derive this result shortly, but for now let me just mention that the procedure involves using the chain rule. You are probably sighing in relief, because the derivatives $(\partial f/\partial r)_\theta$ and $(\partial f/\partial \theta)_r$ are much easier to obtain:

$$\left(\frac{\partial f}{\partial r}\right)_\theta = -3e^{-3r}\cos\theta$$

$$\left(\frac{\partial f}{\partial \theta}\right)_r = -e^{-3r}\sin\theta$$

and using Equation 10.3.3.3, we can obtain the derivative we are looking for:

$$\left(\frac{\partial f}{\partial x}\right)_y = -\cos\theta \times 3e^{-3r}\cos\theta + \frac{\sin\theta}{r}e^{-3r}\sin\theta$$

$$\left(\frac{\partial f}{\partial x}\right)_y = -\cos^2\theta \times 3e^{-3r} + \frac{\sin^2\theta}{r}e^{-3r} = e^{-3r}\left(\frac{\sin^2\theta}{r} - 3\cos^2\theta\right)$$

$$\left(\frac{\partial f}{\partial x}\right)_y = e^{-3(x^2+y^2)^{1/2}}\left(\frac{y^2}{(x^2+y^2)^{3/2}} - 3\frac{x^2}{(x^2+y^2)}\right)$$

Hopefully this wasn't too painful, or at least, less tedious that it would have been hadn't we used the chain rule. What about $(\partial f/\partial y)_x$? We can create an expression similar to Equation 10.3.3.3 and use it to relate $(\partial f/\partial y)_x$ with $(\partial f/\partial r)_\theta$ and $(\partial f/\partial \theta)_r$.

At this point you may be thinking that this all worked well because the function we had was easier to derive in polar coordinates than in cartesian coordinates. True, but this is the whole point. Many physical systems are described in polar coordinates more naturally than in cartesian coordinates (especially in three dimensions). This has to do with the symmetry of the system. For an atom, for example, it is much more natural to use spherical coordinates than cartesian coordinates. We could use cartesian, but the expressions would be much more complex and hard to work with. If we have equations that are more easily expressed in polar coordinates, getting the derivatives in polar coordinates will always be easier. But why would we want the derivatives in cartesian coordinates then? A great example is the Schrödinger equation, which is at the core of quantum mechanics. We will talk more about this when we discuss operators, but for now, the Schrödinger equation is a partial differential equation (unless the particle moves in one dimension) that can be written as:

$$E\psi(\vec{r}) = -\frac{\hbar}{2m}\nabla^2\psi(\vec{r}) + V(\vec{r})\psi(\vec{r})$$

Because of the symmetry of the system, for atoms and molecules it is simpler to express the position of the particle ($\vec{r}$) in spherical coordinates. However, the operator ∇^2 (known as the Laplacian) is defined in cartesian coordinates as:

$$\nabla^2 f(x,y,z) = \left(\frac{\partial^2 f}{\partial x^2}\right)_{y,z} + \left(\frac{\partial^2 f}{\partial y^2}\right)_{x,z} + \left(\frac{\partial^2 f}{\partial z^2}\right)_{x,y}$$

In other words, the Laplacian instructs you to take the second derivatives of the function with respect to x, with respect to y and with respect to z, and add the three together. We could express the functions $V(\vec{r})$ and $\psi(\vec{r})$ in cartesian coordinates, but again, this would lead to a terribly complex differential equation. Instead, we can express the Laplacian in spherical coordinates, and this is in fact the best approach. To do this, we would need to relate the derivatives in spherical coordinates to the derivatives in cartesian coordinates, and this is done using the chain rule.

Hopefully all this convinced you of the uses of the chain rule in the physical sciences, so now we just need to see how to use it for our purposes. In two dimensions, the chain rule states that if we have a function in one coordinate system $u(x,y)$, and these coordinates are functions of two other variables (e.g. $x = x(\theta, r)$ and $y = y(\theta, r)$) then:

$$\left(\frac{\partial u}{\partial r}\right)_\theta = \left(\frac{\partial u}{\partial x}\right)_y \left(\frac{\partial x}{\partial r}\right)_\theta + \left(\frac{\partial u}{\partial y}\right)_x \left(\frac{\partial y}{\partial r}\right)_\theta$$

$$\left(\frac{\partial u}{\partial \theta}\right)_r = \left(\frac{\partial u}{\partial x}\right)_y \left(\frac{\partial x}{\partial \theta}\right)_r + \left(\frac{\partial u}{\partial y}\right)_x \left(\frac{\partial y}{\partial \theta}\right)_r$$

Some students find the following 'tree' constructions useful:

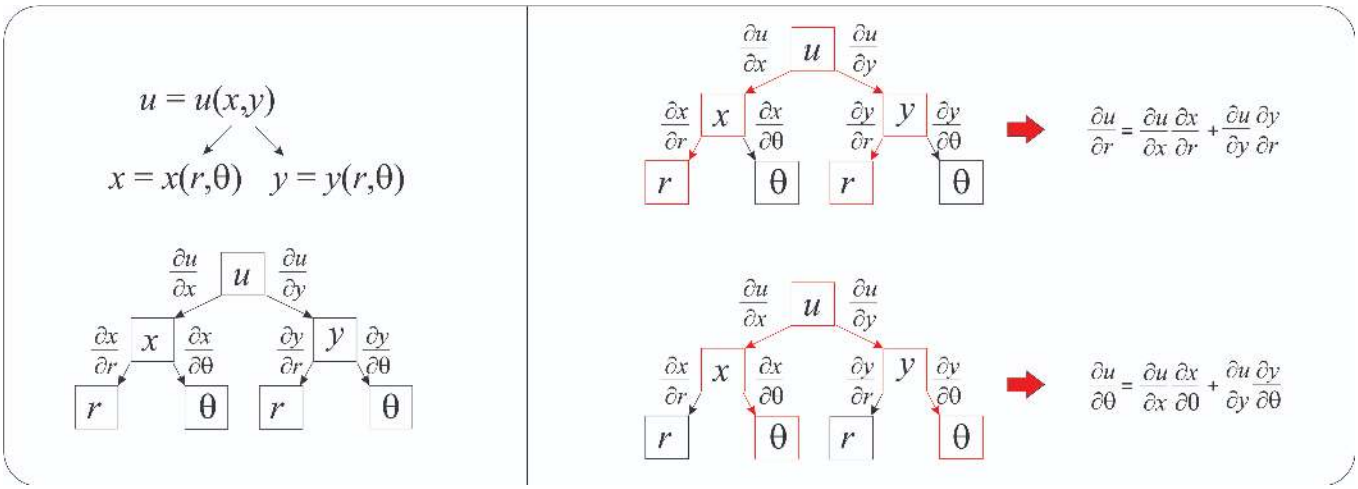


Figure **10.3.3.2**: The chain rule (CC BY-NC-SA; Marcia Levitus)

We can also consider $u = u(r, \theta)$, and $\theta = \theta(x, y)$ and $r = r(x, y)$, which gives:

$$\left(\frac{\partial u}{\partial x}\right)_y = \left(\frac{\partial u}{\partial r}\right)_\theta \left(\frac{\partial r}{\partial x}\right)_y + \left(\frac{\partial u}{\partial \theta}\right)_r \left(\frac{\partial \theta}{\partial x}\right)_y$$

$$\left(\frac{\partial u}{\partial y}\right)_x = \left(\frac{\partial u}{\partial r}\right)_\theta \left(\frac{\partial r}{\partial y}\right)_x + \left(\frac{\partial u}{\partial \theta}\right)_r \left(\frac{\partial \theta}{\partial y}\right)_x$$

Example 10.3.3.1

Derive Equation 10.3.3.3.

Solution

We need to prove $\left(\frac{\partial f}{\partial x}\right)_y = \cos\theta \left(\frac{\partial f}{\partial r}\right)_\theta - \frac{\sin\theta}{r}\left(\frac{\partial f}{\partial \theta}\right)_r$. Using the chain rule:

$$\left(\frac{\partial f}{\partial x}\right)_y = \left(\frac{\partial f}{\partial \theta}\right)_r \left(\frac{\partial \theta}{\partial x}\right)_y + \left(\frac{\partial f}{\partial r}\right)_\theta \left(\frac{\partial r}{\partial x}\right)_y$$

From Equation 10.3.3.1 and 10.3.3.2

$$\left(\frac{\partial r}{\partial x}\right)_y = \frac{1}{2}(x^2+y^2)^{-1/2}(2x) = \frac{1}{2}(r^2)^{-1/2}(2r\cos\theta) = \cos\theta$$

$$\left(\frac{\partial \theta}{\partial x}\right)_y = \frac{1}{1+(y/x)^2}\frac{(-y)}{x^2} = -\frac{1}{1+(y/x)^2}\frac{y}{x}\frac{1}{x} = -\frac{1}{1+\tan^2\theta}\tan\theta\frac{1}{r\cos\theta}$$
$$= -\frac{1}{1+\frac{\sin^2\theta}{\cos^2\theta}}\frac{\sin\theta}{\cos\theta}\frac{1}{r\cos\theta} = -\frac{\sin\theta}{r}$$

Therefore,

$$\left(\frac{\partial f}{\partial x}\right)_y = \cos\theta \left(\frac{\partial f}{\partial r}\right)_\theta - \frac{\sin\theta}{r}\left(\frac{\partial f}{\partial \theta}\right)_r$$

Need help? The videos below contain examples of how to use the chain rule for partial derivatives:

- Example 1: http://www.youtube.com/watch?v=HOYA0-pOHsg
- Example 2: http://www.youtube.com/watch?v=kCr13iTRN7E (tree diagrams)

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10.3.4: Double and Triple Integrals

We can extend the idea of a definite integral to more dimensions. If $f(x,y)$ is continuous over the rectangle $R = [a,b] \times [c,d]$ then,

$$\iint_R f(x,y)dA = \int_a^b \int_c^d f(x,y)\,dy\,dx = \int_c^d \int_a^b f(x,y)\,dx\,dy \tag{10.3.4.1}$$

If $f(x,y) \geq 0$, then the double integral represents the volume V of the solid that lies above the rectangle R and below the surface $z = f(x,y)$ (Figure 10.3.4.1).

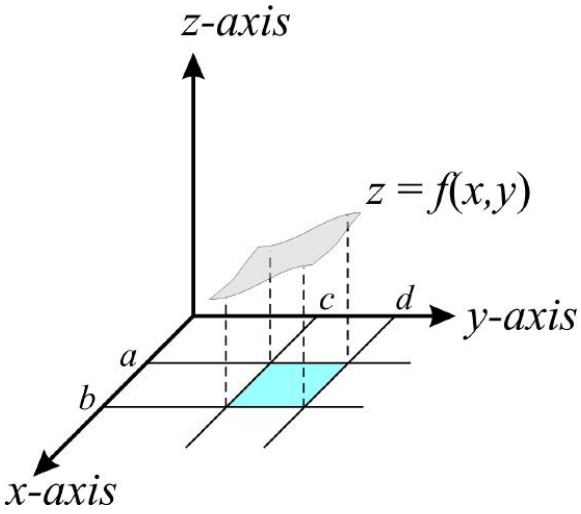


Figure 10.3.4.1: Geometric interpretation of a double integral (CC BY-NC-SA; Marcia Levitus)

We can compute the double integral of Equation 10.3.4.1 as:

$$\iint_R f(x,y)dA = \int_a^b \left[\int_c^d f(x,y)\,dy\right] dx$$

meaning that we will first compute

$$\int_c^d f(x,y)\,dy$$

holding x constant and integrating with respect to y. The result will be a function containing only x, which we will integrate between a and b with respect to x.

For example, let's solve $\int_0^3 \int_1^2 x^2 y\,dy\,dx$. We'll start by solving $\int_1^2 x^2 y\,dy$ holding x constant:

$$\int_1^2 x^2 y\,dy = x^2 \int_1^2 y\,dy = \frac{3}{2}x^2$$

Now we integrate this function from 0 to 3 with respect to x:

$$\int_0^3 \int_1^2 x^2 y\,dy\,dx = \int_0^3 \frac{3}{2}x^2\,dx = \frac{27}{2}$$

You can of course integrate from 0 to 3 first with respect to x holding y constant, and then integrate the result with respect to y from 1 to 2. Try it this way and verify you get the same result.

Triple integrals work in the same way. If $f(x,y,z)$ is continuous on the rectangular box $B = [a,b] \times [c,d] \times [r,s]$, then

$$\iiint_B f(x,y,z)dV = \int_r^s \int_c^d \int_a^b f(x,y)\,dx\,dy\,dz \tag{10.3.4.2}$$

This iterated integral means that we integrate first with respect to x (keeping y and z fixed), then we integrate with respect to y (keeping z fixed), and finally we integrate with respect to z. There are five other possible orders in which we can integrate, all of which give the same value.

Do you need a refresher on double and triple integrals? Check the videos below before moving on to the physical chemistry examples.

- Example 1: http://www.youtube.com/watch?v=RqD89-afGS0
- Example 2: http://www.youtube.com/watch?v=CPR0ZD0IYVE (check the example that starts around 3:45 min. and ends at 5:07 min)

Triple integrals are used very often in physical chemistry to normalize probability density functions. For example, in quantum mechanics, the absolute square of the wave function, $|\psi(x,y,z)|^2$, is interpreted as a *probability density*, the probability that the particle is inside the volume $dx.dy.dz$. Since the probability of finding the particle somewhere in space is 1, we require that:

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}|\psi(x,y,z)|^2\,dx\,dy\,dz = 1 \tag{10.3.4.3}$$

We already mentioned wave functions in Section 2.3, where we showed that

$$|\psi(x,y,z)|^2 = \psi^*(x,y,z)\psi(x,y,z)$$

The normalization condition, therefore, can also be written as

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\psi^*\psi\,dx\,dy\,dz = 1 \tag{10.3.4.4}$$

Example 10.3.4.1

In quantum mechanics, the lowest energy state of a particle confined in a three-dimensional box is represented by

$$\psi(x,y,z) = A\sin\frac{\pi x}{a}\sin\frac{\pi y}{b}\sin\frac{\pi z}{c}\;if\;\begin{cases}0<x<a\\0<y<b\\0<z<c\end{cases}$$

and

$$\psi(x,y,z) = 0 \text{ otherwise (outside the box).}$$

Here, A is a normalization constant, and a,b and c are the lengths of the sides of the box. Since the probability of finding the particle somewhere in space is 1, we require that

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}|\psi(x,y,z)|^2\,dx\,dy\,dz = 1$$

Find the normalization constant A in terms of a, b, c and other constants.

Solution

Because $\psi(x,y,z) = 0$ outside the box,

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}|\psi(x,y,z)|^2\,dx\,dy\,dz = \int_0^c\int_0^b\int_0^a|\psi(x,y,z)|^2\,dx\,dy\,dz$$
$$= |\psi(x,y,z)|^2 = \psi^*(x,y,z)\psi(x,y,z)$$

However, because in this case the function is real,

$$|\psi(x,y,z)|^2 = (\psi(x,y,z))^2$$

$$\int_0^c\int_0^b\int_0^a|\psi(x,y,z)|^2\,dx\,dy\,dz = \int_0^c\int_0^b\int_0^a A^2\sin^2\left(\frac{\pi x}{a}\right)\sin^2\left(\frac{\pi y}{b}\right)\sin^2\left(\frac{\pi z}{c}\right)dx\,dy\,dz = 1$$

$$\int_0^c \int_0^b \int_0^a A^2 \sin^2\left(\frac{\pi x}{a}\right) \sin^2\left(\frac{\pi y}{b}\right) \sin^2\left(\frac{\pi z}{c}\right) dx\, dy\, dz$$
$$= A^2 \int_0^a \sin^2\left(\frac{\pi x}{a}\right) dx \int_0^b \sin^2\left(\frac{\pi y}{b}\right) dy \int_0^c \sin^2\left(\frac{\pi z}{c}\right) dz$$

Using the formula sheet, we get

$$\int_0^a \sin^2\left(\frac{\pi x}{a}\right) dx = a/2$$

And therefore,

$$A^2 \int_0^a \sin^2\left(\frac{\pi x}{a}\right) dx \int_0^b \sin^2\left(\frac{\pi y}{b}\right) dy \int_0^c \sin^2\left(\frac{\pi z}{c}\right) dz = A^2 \frac{a}{2} \frac{b}{2} \frac{c}{2} = \frac{A^2 abc}{8} = 1$$

Solving for A:

$$A = \left(\frac{8}{abc}\right)^{1/2}$$

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10.3.5: Real Gases

So far in this chapter, most of you have not learned anything that you have not learned in your calculus courses. The math in this chapter is actually pretty easy, but yet, it is common that students find it very hard to apply these mathematical tools to actual problems in the physical sciences. To get you comfortable using math in chemistry we will first learn a little bit about gases and thermodynamics. Having some background will help us use the math in a context that we (chemists) can relate to.

We have already mentioned some thermodynamic variables, but in order to make more connections between chemistry and math we need to introduce some concepts that we need to start discussing real gases. You will talk about these concepts in more depth in CHM 346. An important thermodynamic variable that is used to characterize the state of a system is the internal energy (U). Let's think about a container containing a gas (e.g. O_2). The internal energy of the system is the sum of the following contributions:

- Kinetic energy: The kinetic energy is the energy that the molecules have due to their motions. It is related to their velocity, and as expected, it increases with increasing temperature, as molecules move faster.
- Vibrational and rotational energy: Molecules store energy in their bonds. As we already discussed, atoms vibrate around their equilibrium position, and there is an energy associated with these vibrations. The vibrational energy of a molecule also depends on temperature, and on the number of bonds. Atomic gases (He, Ar, etc) do not have vibrational energy. Molecules also rotate, and there is energy stored in these motions. As in the case of vibrations, atomic gases do not have contributions from rotations. You will learn about vibrational and rotational energy in CHM 345.
- Potential energy: This is the energy due to the interactions between the molecules that make up the gas. Atoms (e.g. Ar) will also interact if brought close enough. The energy of the interactions between the molecules depends obviously on the chemical nature of the molecules. We know that polar molecules will interact more strongly than non-polar molecules, and atoms with more electrons (e.g. Ar) will interact more strongly than atoms of low atomic number (e.g. He). For a given gas, these interactions depend on the distance between the molecules.

For simplicity, we will concentrate on atomic gases, where the only contributions to U are the kinetic energy (which depends on temperature only), and potential energy. You already learned about the simplest model used to describe the behavior of gases: the ideal (or perfect) gas. You learned that there are two assumptions behind the model. First the particles do not have any size, meaning that you can push them together as close as you want. In reality, atoms have a size, and if you try to push them together too hard the electronic clouds will repel each other. The other assumption is that particles do not interact with each other at any distance. In reality, this makes sense only at very low densities, when molecules are very far away from each other. However, as molecules get closer together, they experience attractive forces that in many cases are so strong that result in the formation of a liquid. Of course if we push them too close the forces become repulsive, but there is a range of distances in which attractive forces dominate. This makes sense for polar molecules, but what about atoms (e.g. Ar), that do not have a permanent dipole moment? You probably heard about London dispersive forces, without which we would never be able to liquefy a noble gas. London forces are stronger for atoms containing more electrons, and that is why the boiling point of Xe is much higher than the boiling point of Ne.

With all this in mind, let's think about what happens to an ideal gas in the three situations depicted in Figure **10.3.5.1**. The densities (molecules per unit volume) increase as we increase the pressure applied to the container. Let's assume the three containers are equilibrated at the same temperature, and let's think about how the internal energy compares among the three cases. We do not have any equations yet, so we need to think in terms of the concepts we just discussed. We have two contributions to think about. The kinetic term should be the same in the three containers because the temperature is the same, and that is the only factor that determines the velocity of the molecules. What about the potential energy? The particles do not have a size, so there are no repulsive forces that arise if we try to push them together too close. They do not have any type of attractive interactions either, so an ideal gas does not store any potential energy. We just concluded that the internal energy for an ideal gas equals the kinetic energy, and it is therefore a function of the temperature of the gas, but not its density. Now, we know that ideal gases are simplified representations of real gases, but they do not exist. In which of these three situations is a gas more likely to behave as an ideal gas? Clearly, when the density is low, the molecules are further away, the interactions between them are weaker, and we do not need to worry about potential energy much.

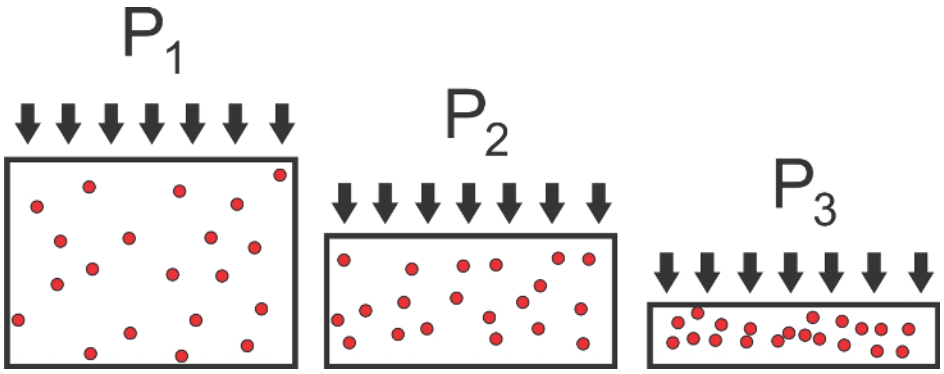


Figure 10.3.5.1: The internal energy of gases (CC BY-NC-SA; Marcia Levitus)

The van der Waals Model

Let's come back to the equation of state of an ideal gas 10.3.5.1:

$$P = \frac{nRT}{V} \tag{10.3.5.1}$$

In order to improve our description of gases we need to take into account the two factors that the ideal gas model neglects: the size of the molecules, and the interactions between them. The size of the molecules can be taken into account by assuming that the volume that the molecules have to move around is not really V, but instead $V - nb$, where nb is a measure of the volume that the molecules occupy themselves. In this context b is a measure of the volume of one molecule, so nb takes into account the volume of all molecules present in the gas. This first correction gives:

$$P = \frac{nRT}{V - nb} \tag{10.3.5.2}$$

which is known as the 'hard spheres' model. note that we have not introduced anything regarding interactions yet, so this model tells us that we can increase the density as much as we want without changing the internal energy until we get to the point where the spheres touch each other. Because they are 'hard', the force required to reduce the volume any further would be infinitely large (not too different from pushing a billiard ball inside another one). Translated into potential energy, this means that the potential energy will jump to infinity when the distance between the center of the particles equals two times their radius. This is better than nothing, but not entirely realistic. In reality molecules are not completely hard, and can be pushed against each other a little bit without an infinite force.

What about interactions? We discussed that at moderate densities, attractive interactions dominate over repulsive interactions. In order to incorporate a correction due to attractive interactions we need to recognize that the pressure of the gas needs to be smaller than the pressure of a gas without attractions (like the hard spheres model). The pressure of a gas is a measure of the collisions of the molecules with the walls of the container. Attractive forces should decrease this frequency, so the resulting pressure should be lower:

$$P = \frac{nRT}{V - nb} - C$$

where C will be a positive term, that takes into account the attractive interactions. What should this term depend on? Clearly on the chemical nature of the molecules, and should be larger for atoms with more electrons (e.g. Xe) than for atoms with less electrons (e.g. He). In addition, it should depend on the density of the gas (n/V), as attractive forces are stronger the closer the molecules are. Van der Waals proposed the following equation that satisfies everything we just said:

$$P = \frac{nRT}{V - nb} - a\left(\frac{n}{V}\right)^2 \tag{10.3.5.3}$$

Check the following examples of van der Waals constants, and see if you understand how the values of a and b make sense in terms of the sizes of the molecules, and what you know about chemical interactions from your general chemistry courses. Pay attention to the units as well.

gas	$a(L^2bar/mol^2)$	$b(L/mol)$
He	0.035	0.0237
Ar	1.35	0.0320
Kr	2.349	0.0398
H_2	0.248	0.02661
O_2	1.378	0.03183
H_2O	5.536	0.03049
CO_2	3.64	0.0427

It is worth stressing that the van der Waals model is still a model, that is, it is not the exact representation of a real gas. It improves many of the deficiencies of the real gas law, but it is still a model.

Coming back to Figure **10.3.5.1**, imagine now that the containers are filled with a van der Waals gas. The three states have different internal energy now, because the density of the molecules is different, and that changes the forces between them. The potential energy is zero if the molecules are too far for any attractive or repulsive force to be significant, or when the attractive and repulsive forces exactly cancel each other. When attractive forces dominate we would need to exert work to separate the molecules, and the potential energy is negative. When repulsive forces dominate the potential energy is positive, and we would need to exert work to push the molecules closer. With all this in mind, in which of the three situations is the potential energy lower? The answer is container number 3. Molecules are closer (but not close enough to touch each other), so attractive forces are stronger than in container number 1. Attractive forces lower that internal energy of the system. These arguments allow us to plot the potential energy for a van der Waals gas as a function of the distance between the center of the molecules:

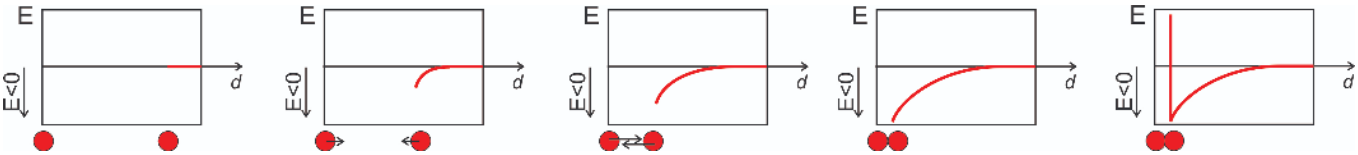


Figure **10.3.5.2**: The potential energy (E) of a van der Waals gas as two atoms or molecules are brought to close proximity (CC BY-NC-SA; Marcia Levitus)

The potential energy is zero when the distance between molecules is much longer than their diameters. If we start decreasing the density they get closer, and the attractive interactions become significant, lowering the internal energy. This continues until they touch each other. Because they are 'hard spheres' they cannot penetrate each other at all, and the potential energy jumps to infinity. This is equivalent to saying that the force required to push them closer together is infinitely large.

We discussed the difference between a real gas and a model of a real gas. How does this plot look like in reality, and how different is it from the van der Waals model? Below are examples for different gases. Notice that 'Ar_2' does not refer to a gas made up of molecules of Ar_2, but instead to the interactions between two Ar atoms. All the gases in this figure, as we know, are monoatomic.

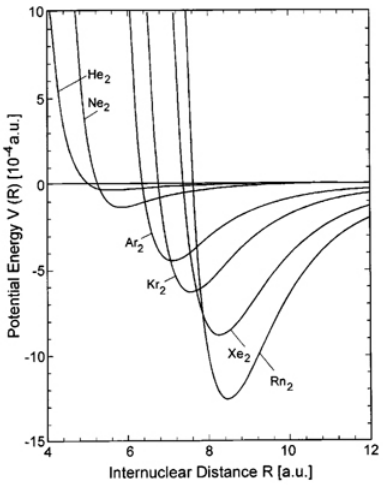


Figure **10.3.5.3**: The potential energy of real gases. (CC BY-NC-SA; Marcia Levitus)

There are a few things worth noting. First, atoms with more electrons (look at a periodic table) show a deeper well. This makes sense because more electrons result in stronger attractive London forces. Also, atoms with more electrons experience these attractive forces at longer distances than atoms with less electrons. In all cases the potential energy increases very sharply when we continue to decrease the distance between the atoms, but the potential energy does not jump to infinity suddenly, as in the case of the van der Waals gas. This means the atoms are not exactly hard spheres. As expected, we can bring two atoms of He much closer than two atoms of Rn before we see these repulsive interactions because atoms of He are much smaller than those of Rn.

Pressure-Volume Isotherms

Scientists started to study the behavior of gases back in the 1600s. As you can imagine, they had very rudimentary laboratory supplies, and their observations were mostly qualitative. One of the earliest quantitative studies in chemistry was performed by Robert Boyle, who noticed that the volume and the pressure of a fixed amount of gas at constant temperature change according to the simple law $P \propto 1/V$, where the symbol "$\propto$" means "proportional to". This is of course true for an ideal gas, whose equation of state is $P = nRT/V$, but not for a real gas. Boyle's law predicts that the volume of a gas decreases as the pressure is increased at constant temperature. Mathematically, this curve is called an hyperbola (hyperbolas are graphs where the product xy is a constant), and physically we call these plots isotherms, because they represent the behavior at constant temperature (*iso* means equal in Latin). In other words, the isotherm for an ideal gas is an hyperbola, but the isotherm for a real gas will show deviations from the hyperbolic shape.

We can of course go to the lab and measure the isotherms for any real gas in any range of temperatures we want. We know that whenever the conditions are such that the density of the gas is low, we expect interactions to be negligible, and therefore isotherms should be very close to the hyperbolas that Boyle described in the 1600s. What happens when interactions are significant? Some experimental isotherms for CO_2 are shown in Figure **10.3.5.4**. At higher temperatures (e.g. 50° C), the isotherm is close to the prediction for an ideal gas: we can compress the volume to small volumes and the pressure will increase following Boyle's law. The isotherms at higher temperatures will be even closer to the hyperbolas predicted by Boyle's law because interactions become less and less noticeable.

What happens at lower temperatures? Let's consider the isotherm at 20° C. Imagine you have a container with one mole of CO_2, and you start reducing its volume at constant temperature. The initial volume is somewhere between 0.5 and 0.6 L (point A in Figure **10.3.5.4**). As you start reducing the volume the pressure starts increasing in approximate agreement with Boyle's law, but notice that important deviations are observed as you approach point B. When the pressure reaches 60 atm (point C), the behavior of the fluid deviates greatly from that predicted by the laws of ideal gases. You continue reducing the volume of the gas, but the pressure not only does not go up as predicted by Boyle's low, but it remains constant for a while (between points C and E)! What is going on? How can we reduce the volume of a gas without increasing the pressure? The answer is that we are not dealing with a pure gas anymore: we are liquefying part of it. As we move from C to E, we increase the amount of liquid and reduce the amount of gas, and the pressure of the system remains constant as long as we have gas and liquid in equilibrium. Of course the more liquid we have the less volume the CO_2 occupies.

As we mentioned before, ideal gases are not supposed to form liquids because in principle, the molecules that make up the gas do not have any size and do not experience any interactions with the other molecules in the container. To form a liquid, molecules need to experience strong attractive forces, or otherwise the motions they experience due to their thermal energy would not allow them to stay close enough. Liquefying a gas, therefore, is a clear experimental evidence of non-ideal behavior and the existence of attractive interactions among molecules.

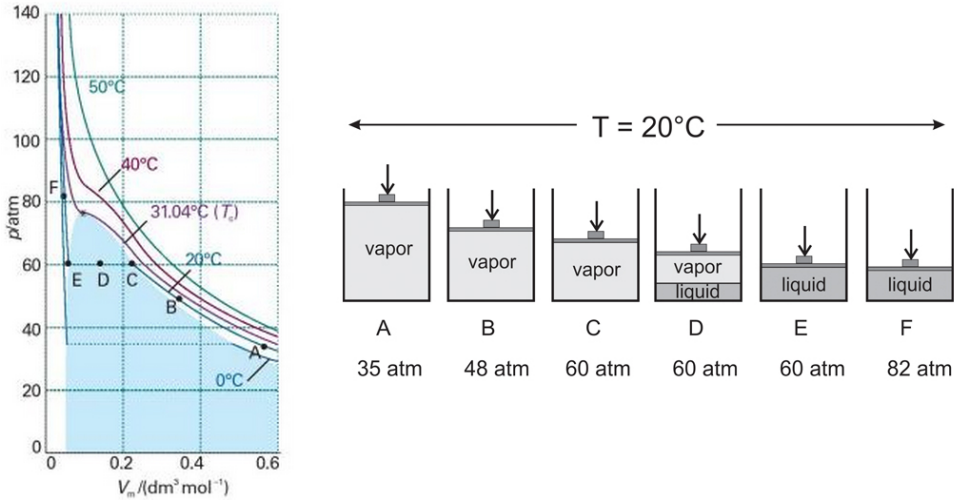


Figure **10.3.5.4**: CO_2 isotherms. (CC BY-NC-SA; Marcia Levitus)

Coming back to Figure **10.3.5.4**, any point in the horizontal line CDE represents a state where liquid and gas coexist. We call the gas "vapor" in these circumstances, but the distinction is more semantic than physical. When we reach point E, all the CO_2 molecules are part of the liquid. We can continue to reduce the volume, but the pressure of the container will go up much more dramatically than before because we would need to exert a considerable amount of force to push the molecules of liquid closer together. In more technical terms, liquids are much less compressible than gases (see the definition of compressibility in page). The area highlighted in light blue in Figure **10.3.5.4** represents the conditions under which CO_2 can exist in equilibrium between the liquid and vapor phases. For example, if we perform the experiment at 0° C, we would start seeing the first drops of liquid when the pressure of the container reaches $\approx$ 35 atm. The pressure will remain constant as we continue to reduce the volume and we form more and more liquid. When no CO_2 remains in the vapor phase, reducing the volume even further would require that we increase the pressure of the container dramatically, as we would be compressing a liquid, not a gas.

Notice that the length of the horizontal line that represents the co-existence of liquid and gas decreases as we increase the temperature. If we were to perform the experiment at 30° C (not shown), we would see that the volume at which we see the first drop of liquid is not too different from the volume at which we stop seeing CO_2 in the gas phase. Liquefying all the gas would require a small change in volume, which means that at that particular temperature and pressure, the volume that the gas occupies is not too different from the volume the liquid occupies. Pretty strange if you think about it...a mole of an ideal gas occupies 22.4L at room temperature, and a mole of liquid water occupies only 18 mL, almost a thousand times less. If we think in terms of densities, the density of water at room temperature is about 1 g/mL, or 0.056 mol/mL. The density of an ideal gas at room temperature is $n/V = P/RT \approx 4 \times 10^{-5}$ mol/L, again, around a thousand times less. Yet, at 30° C, and around 80 atm, the density of CO_2 in the liquid state is almost the same as the density of CO_2 in the gas phase. If we put CO_2 in a high pressure cell, and increase P to 80 atm, it would be hard for us to say whether the CO_2 is liquid or gas. At much lower pressures, distinguishing between liquid and gas becomes much more evident, as we are used to from our daily experience.

Critical Behavior

There is a particular isotherm where the CDE line of figure [c2v:fig:isotherms] reduces to a point. In the case of CO_2, this isotherm is the one we measure at 31.04°C, and it is so unique and important that it has a special name: the 'critical isotherm'. At temperatures below the critical isotherm, we see that the gas condenses to form liquid, and that the pressure of the system remains constant as we convert more and more gas into liquid. The lower the temperature, the more different the densities of the vapor and the liquid are. This is very intuitive for us, because it is what we are used to seeing with the liquid we know best: water. In the case

of water, we would need to increase the pressure to 218 atm and work at 374 °C to lose our ability to distinguish between liquid water and vapor. The conditions on earth are so far away from the critical point, that we can clearly distinguish liquid water from vapor from their densities. Coming back to CO_2, as we increase the temperature at high pressures (more than 60 atm), the liquid and the vapor states of the fluid become more and more similar. Right below the critical temperature we can hardly distinguish what is liquid and what is vapor, and at exactly the critical temperature, that distinction is lost. Above the critical temperature we never see a separation of phases, we just see a fluid that becomes denser as we reduce the volume of the container. Notice that the critical point is an inflection point in the critical isotherm. This happens at a particular molar volume (for CO_2 $V_c = 0.094$ L/mol) and at a particular pressure (for CO_2 $P_c = 72.9$ atm), which we call the critical molar volume and critical pressure of the fluid. If we want to liquefy CO_2, we need to do it at temperatures below its critical temperature (31.04°C). At temperatures above this value the fluid will always be a gas, although it could be a very dense gas! Chemists call this state 'supercritical fluid' just to differentiate it from a low-density gas such as CO_2 at 1 atm. Again, to give you an idea, one mole of CO_2 occupies about 25L at 1 atm and 40°C, and we call it a gas without thinking twice. From figure [c2v:fig:isotherms], at 80 atm and 40° C one mole of CO_2 occupies about 0.15L, about 170 times less than the gas we are used to seeing at 1 atm. This is a very dense fluid, but technically it is not a liquid because we are above the critical temperature. Instead, we use the term supercritical fluid. As it turns out, supercritical CO_2 is much more than a curiosity. It is used as a solvent for many industrial processes, including decaffeinating coffee and dry cleaning.

From our discussion above, it is clear that ideal gases do not display critical behavior. Again, ideal gases do not exist, so when we say that ideal gases do not display critical behavior we are just saying that 1) gases show critical behavior at conditions of temperature, pressure and molar volume that are very far from the conditions where the simple equation $PV = nRT$ describes the behavior of the gas and that 2) if we want to describe a gas close to the critical point we need an equation of state that is consistent with critical behavior. If we plot the isotherms of an ideal gas ($P = nRT/V$) we will obtain hyperbolas a any temperature. Again, this works well with gases at very low densities, but because the model does not include interactions, it cannot possibly describe the isotherms at or around the critical point.

Is the hard spheres model of Equation 10.3.5.2 consistent with the existence of the critical point? To answer this question, we could plot many isotherms according to this equation and see if the model gives one isotherm that has an inflection point as the one shown in Figure 10.3.5.4. Once again, keep in mind that the figure contains the data we measure experimentally, which is what CO_2 is actually doing in nature. Equations of state by definition are models that are meant to describe the system as close as possible, but they are by definition simplifications of the real behavior. Coming back to the model of hard spheres, you can plot as many isotherms as you want, but you will see that none of them show an inflection point. This is pretty obvious from the equation, as the isotherms are basically the same we would get with the ideal gas equation, but just shifted in the x–axis by the quantity b. Physically speaking, it is not surprising because the hard spheres model does not contain any parameter that accounts for the attractive interactions between molecules, and that is what we need to describe critical behavior.

We know that the van der Waals equation is the simplest equation that introduces a term to account for attractive forces (Equation 10.3.5.3), so it is likely that his equation might be consistent with critical behavior. Let's discuss what we mean by this in more detail. Again, van der Waals gases do not exist in nature. They are a theoretical construction where we think about molecules as hard spheres with kinetic energy that interact with each other so that the average interaction between two randomly oriented molecules is inversely proportional to the inverse of the sixth power of the distance between them. If we could create a gas whose molecules followed these exact physical laws, the gas would behave exactly as the van der Waals equation predicts. So, now we wonder: would such a gas show an isotherm with an inflection point like the one shown for the case of real CO_2? The answer is yes, and the critical constants (P_c, T_c and V_c) depend on the values of the van der Waals parameters, a and b.

Now, the fact that the van der Waals model predicts critical behavior does not mean at all that it describes the whole isotherm well. If you plot the van der Waals equation at different temperatures you will see that this model does not predict the "flat " $P - V$ part of the curve, where the liquid and the gas coexist. This is not surprising, as the treatment of the attractive interactions in the van der Waals model is too simple to describe the liquid state. In fact, you will see that the van der Waals equation predicts that the derivative $\left(\frac{\partial P}{\partial V}\right)_{T,n}$ is positive in certain regions of the isotherm, which of course does not make any physical sense. Compressing the gas will never lower the pressure as the van der Waals gas predicts, so we can clearly see how the model fails when attractive forces are important are complex. In any case, it is pretty impressive to see how such a simple equation predicts such complex behavior as the critical point.

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10.3.6: Problems

Problem 10.3.6.1

Given a generic equation of state $P = P(V, T, n)$, explain how you can obtain the derivative

$$\frac{\partial V}{\partial T}_{P,n}$$

using the properties of partial derivatives we learned in this chapter.

Problem 10.3.6.2

The thermodynamic equation:

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$$

shows how the internal energy of a system varies with the volume at constant temperature.

Prove that

1. $\left(\frac{\partial U}{\partial V}\right)_T = 0$ for an ideal gas.
2. $\left(\frac{\partial U}{\partial V}\right)_T = \frac{a}{V^2}$ for one mole of van der Waals gas (Equation 10.3.6.2)

Problem 10.3.6.3

Consider one mole of a van der Waals gas (Equation 10.3.6.2) and show that

$$\left(\frac{\partial^2 P}{\partial V \partial T}\right) = \left(\frac{\partial^2 P}{\partial T \partial V}\right)$$

Problem 10.3.6.4

Consider a van der Waals gas (Equation 10.3.6.2) and show that

$$\left(\frac{\partial V}{\partial T}\right)_{P,n} = \frac{nR}{\left(P - \frac{n^2 a}{V^2} + \frac{2n^3 ab}{V^3}\right)}$$

Hint: Calculate derivatives that are easier to obtain and use the properties of partial derivatives to get the one the problem asks for. Do not use the answer in your derivation; obtain the derivative assuming you don't know the answer and simplify your expression until it looks like the equation above.

Problem 10.3.6.5

From the definitions of expansion coefficient (α) and isothermal compressibility (κ):

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{P,n}$$

and

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,n}$$

prove that

$$\left(\frac{\partial P}{\partial T}\right)_{V,n} = \frac{\alpha}{\kappa}$$

independently of the equation of state used.

Note: A common mistake in this problem is to assume a particular equation of state. Use the cycle rule to find the required relationship independently of any particular equation of state.

Problem 10.3.6.6

Derive an equation similar to Equation 10.3.6.1, but that relates

$$\left(\frac{\partial f}{\partial y}\right)_x$$

with

$$\left(\frac{\partial f}{\partial r}\right)_\theta$$

and

$$\left(\frac{\partial f}{\partial \theta}\right)_r$$

Problem 10.3.6.7

(Extra-credit level)

The expression:

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}$$

is known as the Laplacian operator in two dimensions.

When applied to a function $f(x,y)$, we get:

$$\nabla^2 f(x,y) = \frac{\partial^2 f}{\partial x^2} + \frac{\partial^2 f}{\partial y^2}$$

Express ∇^2 in polar coordinates (2D) assuming the special case where $r = a$ is a constant.

Problem 10.3.6.8

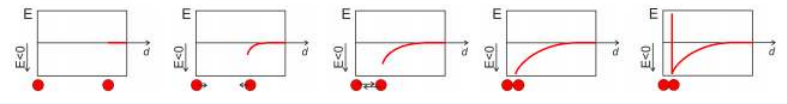
Calculate $\int_0^1 \int_1^2 \int_0^2 (x^2 + yz)\, dx\, dy\, dz$. Try three different orders of integration an verify you always get the same result.

Problem 10.3.6.9

Calculate $\int_0^{2\pi} \int_0^{\pi} \int_0^{\infty} e^{-r} r^5 \sin\theta\, dr\, d\theta\, d\phi$. Use only the formula sheet.

Problem 10.3.6.10

How would Figure 8.5.2, reproduced below, look like for an ideal gas? Sketch the potential energy as a function of the distance between the atoms.



Problem 10.3.6.11

From everything we learned in this chapter, and without doing any math, we should be able to calculate the sign (>0, <0, or 0) of the following derivatives:

For an ideal gas:

$$\left(\frac{\partial U}{\partial T}\right)_{V,n}$$

$$\left(\frac{\partial U}{\partial V}\right)_{T,n}$$

For a van der Vaals gas:

$$\left(\frac{\partial U}{\partial T}\right)_{V,n}$$

$$\left(\frac{\partial U}{\partial V}\right)_{T,n}$$

Be sure you can write a short sentence explaining your answers.

Problem 10.3.6.12

The critical point is the state at which the liquid and gas phases of a substance first become indistinguishable. A gas above the critical temperature will never condense into a liquid, no matter how much pressure is applied. Mathematically, at the critical point:

$$\left(\frac{\partial P}{\partial V}\right)_{T,n} = 0$$

and

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_{T,n} = 0$$

Obtain the critical constants of a van der Waals gas (Equation 10.3.6.2) in terms of the parameters a and b.

Hint: obtain the first and second derivatives of P with respect to V, make them equal to zero, and obtain T_c and V_c from these equations. Finally, replace these expressions in Equation 10.3.6.2 to obtain P_c.

Note

As derived in Section 8.3,

$$\left(\frac{\partial f}{\partial x}\right)_y = \cos\theta\left(\frac{\partial f}{\partial r}\right)_\theta - \frac{\sin\theta}{r}\left(\frac{\partial f}{\partial \theta}\right)_r \tag{10.3.6.1}$$

As defined in Section 8.5, the Van der Waals is defined as:

$$P = \frac{nRT}{V-nb} - a\left(\frac{n}{V}\right)^2 \tag{10.3.6.2}$$

1. If you are not familiar with this you need to read about it before moving on

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SECTION OVERVIEW

10.4: Exact and Inexact Differentials

Chapter Objectives

- Understand the concept of the total differential
- Understand the concept of exact and inexact differentials.
- Be able to test whether a differential is exact or not.
- Understand how to integrate differentials along different paths.
- Understand the role of exact and inexact differentials in thermodynamics.

10.4.1: The Total Differential

10.4.2: Exact and Inexact Differentials

10.4.3: Differentials in Thermodynamics - State and Path Functions

10.4.4: A Mathematical Toolbox

10.4.5: Line Integrals

10.4.6: Exact and Inexact Differentials (Summary)

10.4.7: Problems

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10.4.1: The Total Differential

In Chapter 8 we learned that partial derivatives indicate how the dependent variable changes with one particular independent variable keeping the others fixed. In the context of an equation of state $P = P(T, V, n)$, the partial derivative of P with respect to V at constant T and n is:

$$\left(\frac{\partial P}{\partial V}\right)_{T,n}$$

and physically represents how the pressure varies as we change the volume at constant temperature and constant n.

The partial derivative of P with respect to T at constant V and n is:

$$\left(\frac{\partial P}{\partial T}\right)_{V,n}$$

and physically represents how the pressure varies as we change the temperature at constant volume and constant n.

What happens with the dependent variable (in this case P) if we change two or more independent variables simultaneously? For an infinitesimal change in volume and temperature, we can write the change in pressure as:

$$dP = \left(\frac{\partial P}{\partial V}\right)_{T,n} dV + \left(\frac{\partial P}{\partial T}\right)_{V,n} dT \tag{10.4.1.1}$$

Equation 10.4.1.1 is called the *total differential of P*, and it simply states that the change in P is the sum of the individual contributions due to the change in V at constant T and the change in T at constant V. This equation is true for infinitesimal changes. If the changes are not infinitesimal we will integrate this expression to calculate the change in P.[differentials_position1]

Let's now consider the volume of a fluid, which is a function of pressure, temperature and the number of moles: $V = V(n, T, P)$. The total differential of V, by definition, is:

$$dV = \left(\frac{\partial V}{\partial T}\right)_{P,n} dT + \left(\frac{\partial V}{\partial P}\right)_{T,n} dP + \left(\frac{\partial V}{\partial n}\right)_{T,V} dn \tag{10.4.1.2}$$

If we want to calculate the change in volume in a fluid upon small changes in P, T and n, we could use:

$$\Delta V \approx \left(\frac{\partial V}{\partial T}\right)_{P,n} \Delta T + \left(\frac{\partial V}{\partial P}\right)_{T,n} \Delta P + \left(\frac{\partial V}{\partial n}\right)_{T,V} \Delta n \tag{10.4.1.3}$$

Of course, if we know the function $V = V(n, T, P)$, we could also calculate ΔV as $V_f - F_i$, where the final and initial volumes are calculated using the final and initial values of P, T and n. This seems easy, so why do we need to bother with Equation 10.4.1.3? The reason is that sometimes we can measure the partial derivatives experimentally, but we do not have an equation of the type $V = V(n, T, P)$ to use. For example, the following quantities are accessible experimentally and tabulated for different fluids and materials (Fig. [fig:diff_tables]):

- $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{P,n}$ (coefficient of thermal expansion)
- $\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{V,n}$ (isothermal compressibility)[differentials:compressibility]
- $V_m = \left(\frac{\partial V}{\partial n}\right)_{P,T}$ (molar volume)

Using these definitions, Equation 10.4.1.2 becomes:

$$dV = \alpha V dT - \kappa V dP + V_m dn \tag{10.4.1.4}$$

You can find tables with experimentally determined values of α and κ under different conditions, which you can use to calculate the changes in V. Again, as we will see later in this chapter, this equation will need to be integrated if the changes are not small. In any case, the point is that you may have access to information about the derivatives of the function, but not to the function itself (in this case V as a function of T, P, n).

In general, for a function $u = u(x_1, x_2 ... x_n)$, we define the total differential of u as:

$$du = \left(\frac{\partial u}{\partial x_1}\right)_{x_2 ... x_n} dx_1 + \left(\frac{\partial u}{\partial x_2}\right)_{x_1, x_3 ... x_n} dx_2 + ... + \left(\frac{\partial u}{\partial x_n}\right)_{x_1 ... x_{n-1}} dx_n \tag{10.4.1.5}$$

Example 10.4.1.1

Calculate the total differential of the function $z = 3x^3 + 3yx^2 + xy^2$.

Solution

By definition, the total differential is:

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

For the function given in the problem,

$$\left(\frac{\partial z}{\partial x}\right)_y = 9x^2 + 6xy + y^2$$

and

$$\left(\frac{\partial z}{\partial y}\right)_x = 3x^2 + 2xy$$

and therefore,

$$dz = (9x^2 + 6xy + y^2)dx + (3x^2 + 2xy)dy$$

COMPRESSIBILITY AND EXPANSION COEFFICIENTS OF LIQUIDS

This table gives data on the variation of the density of some common liquids with pressure and temperature. The pressure dependence is described to first order by the isothermal compressibility coefficient κ defined as

$$\kappa_T = -(1/V)\,(\partial V/\partial P)_T$$

where V is the volume, and the temperature dependence by the cubic expansion coefficient α,

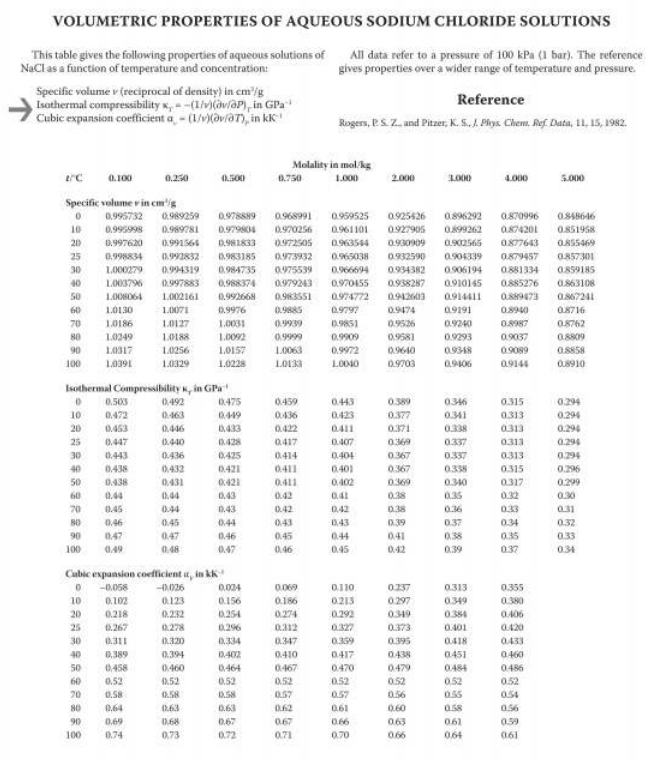
$$\alpha_V = (1/V)\,(\partial V/\partial T)_P$$

Substances are listed by molecular formula in the Hill order. More precise data on the variation of density with temperature over a wide temperature range can be found in Reference 1.

References

1. Lide, D. R., and Kehiaian, H. V., *CRC Handbook of Thermophysical and Thermochemical Data*, CRC Press, Boca Raton, FL, 1994.
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3. *Landolt-Börnstein, Numerical Data and Functional Relationships in Science and Technology, New Series, IV/4, High-Pressure Properties of Matter*, Springer-Verlag, Heidelberg, 1980.
4. Riddick, J.A., Bunger, W.B., and Sakano, T.K., *Organic Solvents, Fourth Edition*, John Wiley & Sons, New York, 1986.
5. Isaacs, N. S., *Liquid Phase High Pressure Chemistry*, John Wiley, New York, 1981.

Molecular formula	Name	Isothermal compressibility t/°C	$\kappa_T \times 10^4$/MPa^{-1}	Cubic expansion coefficient t/°C	$\alpha_V \times 10^3$/°C^{-1}
Cl_3P	Phosphorus trichloride	20	9.45	20	1.9
H_2O	Water	20	4.591	20	0.206
		25	4.524	25	0.256
		30	4.475	30	0.302
Hg	Mercury	20	0.401	20	0.1811
CCl_4	Tetrachloromethane	20	10.50	20	1.14
		40	12.20	40	1.21
		70	15.6	70	1.33
$CHBr_3$	Tribromomethane	50	8.76	25	0.91
$CHCl_3$	Trichloromethane	20	9.96	20	1.21
		50	12.9	50	1.33
CH_2Br_2	Dibromomethane	27	6.85		
CH_2Cl_2	Dichloromethane	25	10.3	25	1.39
CH_3I	Iodomethane	27	10.3	25	1.26
CH_4O	Methanol	20	12.14	20	1.49
		40	13.83	40	1.59
CS_2	Carbon disulfide	20	9.38	20	1.12
		40	10.6	35	1.16
C_2Cl_4	Tetrachloroethylene	25	7.56	25	1.02
C_2HCl_3	Trichloroethylene	25	8.57	25	1.17
$C_2H_2Cl_2$	*trans*-1,2-Dichloroethylene	25	11.2	25	1.36
$C_2H_4Cl_2$	1,1-Dichloroethane	20	7.97	25	0.93
$C_2H_4Cl_2$	1,2-Dichloroethane	30	8.46	20	1.14
$C_2H_4O_2$	Acetic acid	20	9.08	20	1.08
		80	13.7	80	1.38
C_2H_5Br	Bromoethane	20	11.53	20	1.31
C_2H_5I	Iodoethane	20	9.82	25	1.17
C_2H_6O	Ethanol	20	11.19	20	1.40
		70	15.93	70	1.67
$C_2H_6O_2$	Ethylene glycol	20	3.64	20	0.626
C_3H_6O	Acetone	20	12.62	20	1.46
		40	15.6	40	1.57
C_3H_7Br	1-Bromopropane	0	10.22	25	1.2
C_3H_7Cl	1-Chloropropane	0	12.09	20	1.4
C_3H_7I	1-Iodopropane	0	10.22	25	1.09
C_3H_8O	1-Propanol	0	8.43	0	1.22
C_3H_8O	2-Propanol	40	13.32	40	1.55
$C_3H_8O_2$	1,2-Propanediol	0	4.45	20	0.695
$C_3H_8O_2$	1,3-Propanediol	0	4.09	20	0.61
$C_3H_8O_3$	Glycerol	0	2.54	20	0.520



VOLUMETRIC PROPERTIES OF AQUEOUS SODIUM CHLORIDE SOLUTIONS

This table gives the following properties of aqueous solutions of NaCl as a function of temperature and concentration:

Specific volume v (reciprocal of density) in cm^3/g
Isothermal compressibility $\kappa_T = -(1/v)(\partial v/\partial P)_T$ in GPa^{-1}
Cubic expansion coefficient $\alpha_v = (1/v)(\partial v/\partial T)_P$ in kK^{-1}

All data refer to a pressure of 100 kPa (1 bar). The reference gives properties over a wider range of temperature and pressure.

Reference

Rogers, P. S. Z., and Pitzer, K. S., *J. Phys. Chem. Ref. Data*, 11, 15, 1982.

	Molality in mol/kg								
t/°C	0.100	0.250	0.500	0.750	1.000	2.000	3.000	4.000	5.000
Specific volume v in cm^3/g									
0	0.995732	0.989259	0.978889	0.968991	0.959525	0.925426	0.896292	0.870996	0.848646
10	0.995998	0.989781	0.979804	0.970256	0.961101	0.927905	0.899262	0.874201	0.851958
20	0.997620	0.991564	0.981833	0.972505	0.963544	0.930909	0.902565	0.877643	0.855469
25	0.998834	0.992832	0.983185	0.973932	0.965038	0.932590	0.904339	0.879457	0.857301
30	1.000279	0.994319	0.984735	0.975539	0.966694	0.934382	0.906194	0.881334	0.859185
40	1.003796	0.997883	0.988374	0.979243	0.970455	0.938287	0.910145	0.885276	0.863108
50	1.008064	1.002161	0.992668	0.983551	0.974772	0.942603	0.914411	0.889473	0.867241
60	1.0130	1.0071	0.9976	0.9885	0.9797	0.9474	0.9191	0.8940	0.8716
70	1.0186	1.0127	1.0031	0.9939	0.9851	0.9526	0.9240	0.8987	0.8762
80	1.0249	1.0188	1.0092	0.9999	0.9909	0.9581	0.9293	0.9037	0.8809
90	1.0317	1.0256	1.0157	1.0063	0.9972	0.9640	0.9348	0.9089	0.8858
100	1.0391	1.0329	1.0228	1.0133	1.0040	0.9703	0.9406	0.9144	0.8910
Isothermal Compressibility κ_T in GPa^{-1}									
0	0.503	0.492	0.475	0.459	0.443	0.389	0.346	0.315	0.294
10	0.472	0.463	0.449	0.436	0.423	0.377	0.341	0.313	0.294
20	0.453	0.446	0.433	0.422	0.411	0.371	0.338	0.313	0.294
25	0.447	0.440	0.428	0.417	0.407	0.369	0.337	0.313	0.294
30	0.443	0.436	0.425	0.414	0.404	0.367	0.337	0.313	0.294
40	0.438	0.432	0.421	0.411	0.401	0.367	0.338	0.315	0.296
50	0.438	0.431	0.421	0.411	0.402	0.369	0.340	0.317	0.299
60	0.44	0.44	0.43	0.42	0.41	0.38	0.35	0.32	0.30
70	0.45	0.44	0.43	0.42	0.42	0.38	0.36	0.33	0.31
80	0.46	0.45	0.44	0.43	0.43	0.39	0.37	0.34	0.32
90	0.47	0.47	0.46	0.45	0.44	0.41	0.38	0.35	0.33
100	0.49	0.48	0.47	0.46	0.45	0.42	0.39	0.37	0.34
Cubic expansion coefficient α_v in kK^{-1}									
0	−0.058	−0.026	0.024	0.069	0.110	0.237	0.313	0.355	
10	0.102	0.123	0.156	0.186	0.213	0.297	0.349	0.380	
20	0.218	0.232	0.254	0.274	0.292	0.349	0.384	0.406	
25	0.267	0.278	0.296	0.312	0.327	0.373	0.401	0.420	
30	0.311	0.320	0.334	0.347	0.359	0.395	0.418	0.433	
40	0.389	0.394	0.402	0.410	0.417	0.438	0.451	0.460	
50	0.458	0.460	0.464	0.467	0.470	0.479	0.484	0.486	
60	0.52	0.52	0.52	0.52	0.52	0.52	0.52	0.52	
70	0.58	0.58	0.58	0.57	0.57	0.56	0.55	0.54	
80	0.64	0.63	0.63	0.62	0.61	0.60	0.58	0.56	
90	0.69	0.68	0.67	0.67	0.66	0.63	0.61	0.59	
100	0.74	0.73	0.72	0.71	0.70	0.66	0.64	0.61	

Figure **10.4.1.1**: Tables of isothermal compressibilities and expansion coefficients of different fluids (top) and sodium chloride solutions (bottom). Source: CRC Handbook of Physics and Chemistry (CC BY-NC-SA; Marcia Levitus)

Want to see more examples?

- Example 1: http://www.youtube.com/watch?v=z0TxZ0EHzIg Notice that she calls it 'the differential', but I prefer 'the total differential'.

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10.4.2: Exact and Inexact Differentials

So far, we discussed how to calculate the total differential of a function. If you are given a function of more than one variable, you can calculate its total differential using the definition of a total differential of a function u: ($du = \left(\frac{\partial u}{\partial x_1}\right)_{x_2 \ldots x_n} dx_1 + \left(\frac{\partial u}{\partial x_2}\right)_{x_1, x_3 \ldots x_n} dx_2 + \ldots + \left(\frac{\partial u}{\partial x_n}\right)_{x_1 \ldots x_{n-1}} dx_n$). You will have one term for each independent variable. What if we are given a differential (e.g.

$$dz = (9x^2 + 6xy + y^2)dx + (3x^2 + 2xy)dy$$

see Example 9.1) and we are asked to calculate the function whose total differential is dz? This is basically working Example 9.1 backwards: we know the differential, and we are looking for the function. Things are a little bit more complicated than this, because not all differentials are the total differentials of a function. For example, from the example above we know that

$$dz = (9x^2 + 6xy + y^2)dx + (3x^2 + 2xy)dy$$

is the total differential of

$$z(x, y) = 3x^3 + 3yx^2 + xy^2.$$

However, the differential $dz = xydx + x^2dy$ is **not** the total differential of any function $z(x, y)$. You can write down every single function $z(x, y)$ in this planet, calculate their total differentials, and you will never see $dz = xydx + x^2dy$ in your list.

Therefore, the question we are addressing is the following: given a differential, 1) is it the total differential of any function? 2) if it is, which function?

To illustrate the question, let's say we are given the differential below (notice that I switched to P, V, and T, which are variables you will encounter often in thermodynamics):

$$dP = \frac{RT}{V - b}dT + \left[\frac{RT}{(V - b)^2} - \frac{a}{TV^2}\right]dV \tag{10.4.2.1}$$

The question is whether this is the total differential of a function $P = P(T, V)$ (we are told that a and b are constants, and we already know that R is a constant). By definition of total differential, if the function exists, its total differential will be:

$$dP = \left(\frac{\partial P}{\partial T}\right)_V dT + \left(\frac{\partial P}{\partial V}\right)_T dV \tag{10.4.2.2}$$

Comparing Equation 10.4.2.1 and 10.4.2.2, if the function exists, its derivatives will have to be:

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{RT}{V - b} \tag{10.4.2.3}$$

$$\left(\frac{\partial P}{\partial V}\right)_T = \left[\frac{RT}{(V - b)^2} - \frac{a}{TV^2}\right] \tag{10.4.2.4}$$

If we find a function $P = P(T, V)$ that satisfies these equations at the same time, we know that Equation 10.4.2.1 will be its total differential.

From Equation 10.4.2.3, we can calculate P by integrating with respect to T at constant V:

$$\int dP = \int \frac{RT}{V - b}dT \rightarrow P = \frac{R}{V - b}\frac{T^2}{2} + f(V) \tag{10.4.2.5}$$

where we included an integration constant ($f(V)$) that can be any function of V (we are integrating at constant V).

In order to get an expression for $P(T, V)$, we need to find out $f(V)$ so we can complete the right side of Equation 10.4.2.5. To do that, we are going to take the derivative of P (Equation 10.4.2.5 with respect to V, and compare with Equation 10.4.2.4:

$$\left(\frac{\partial P}{\partial V}\right)_T = -\frac{RT^2}{2(V - b)^2} + \frac{df(V)}{dV} \tag{10.4.2.6}$$

Looking at Equation 10.4.2.4 and 10.4.2.6, we see that the two expressions do not match, regardless of which function we chose for $f(V)$. This means that Equation 10.4.2.1 does not represent the total differential of any function $P(V, T)$. We call these differentials

inexact differentials. If a differential is the total differential of a function, we will call the differential **exact**.

What we did so far is correct, but it is not the easiest way to test whether a differential is exact or inexact. There is, in fact, a very easy way to test for exactness. We'll derive the procedure below, but in the future we can use it without deriving it each time.

Given the differential $dz = f_1(x,y)dx + f_2(x,y)dy$, the differential is exact if

$$\left(\frac{\partial f_1(x,y)}{\partial y}\right)_x = \left(\frac{\partial f_2(x,y)}{\partial x}\right)_y \tag{10.4.2.7}$$

If Equation 10.4.2.7 does not hold, the differential is inexact. For instance, if $dz = (9x^2 + 6xy + y^2)dx + (3x^2 + 2xy)dy$, the functions f_1 and f_2 are $f_1 = 9x^2 + 6xy + y^2$ and $f_2 = 3x^2 + 2xy$. To test this differential, we perform the partial derivatives

$$\left(\frac{\partial f_1(x,y)}{\partial y}\right)_x = 6x + 2y$$

and

$$\left(\frac{\partial f_2(x,y)}{\partial x}\right)_y = 6x + 2y$$

The two derivatives are the same, and therefore the differential is said to be exact.

Let's prove why the test of Equation 10.4.2.7 works. Let's consider a differential of the form $dz = f_1(x,y)dx + f_2(x,y)dy$. If the differential is exact, it is the total differential of a function $z(x,y)$, and therefore:

$$dz = f_1(x,y)dx + f_2(x,y)dy = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy \tag{10.4.2.8}$$

We know that the mixed partial derivatives of a function are independent of the order they are computed:

$$\left(\frac{\partial^2 z}{\partial y \partial x}\right) = \left(\frac{\partial^2 z}{\partial x \partial y}\right)$$

From Equation 10.4.2.8,

$$f_1(x,y) = \left(\frac{\partial z}{\partial x}\right)_y \rightarrow \left(\frac{\partial f_1(x,y)}{\partial y}\right)_x = \left(\frac{\partial^2 z}{\partial x \partial y}\right)$$

$$f_2(x,y) = \left(\frac{\partial z}{\partial y}\right)_x \rightarrow \left(\frac{\partial f_2(x,y)}{\partial x}\right)_y = \left(\frac{\partial^2 z}{\partial y \partial x}\right)$$

Because the mixed partial derivatives are the same, for an exact differential:

$$\left(\frac{\partial f_1(x,y)}{\partial y}\right)_x = \left(\frac{\partial f_2(x,y)}{\partial x}\right)_y$$

This equation is true only for an exact differential because we derived it by assuming that the function $z = z(x,y)$ exists, so its mixed partial derivatives are the same. We can use this relationship to test whether a differential is exact or inexact. If the equality of Equation 10.4.2.7 holds, the differential is exact. If it does not hold, it is inexact.

Example 10.4.2.1

Test whether the following differential is exact or inexact:

$$dz = \frac{1}{x^2}dx - \frac{y}{x^3}dy$$

Solution

To test whether dz is exact or inexact, we compare the following derivatives

$$\left(\frac{\partial(1/x^2)}{\partial y}\right)_x \stackrel{?}{=} \left(\frac{\partial(y/x^3)}{\partial x}\right)_y$$

$$\left(\frac{\partial(1/x^2)}{\partial y}\right)_x = 0$$

$$\left(\frac{\partial(y/x^3)}{\partial x}\right)_y = -3yx^{-4}$$

We conclude that dz is inexact, and therefore there is no function $z(x,y)$ whose total differential is dz.

Example 10.4.2.2

Determine whether the following differential is exact or inexact. If it is exact, determine $z = z(x,y)$.

$$dz = (2x+y)dx + (x+y)dy$$

Solution

To test whether dz is exact or inexact, we compare the following derivatives

$$\left(\frac{\partial(2x+y)}{\partial y}\right)_x \stackrel{?}{=} \left(\frac{\partial(x+y)}{\partial x}\right)_y$$

If this equality holds, the differential is exact.

$$\left(\frac{\partial(2x+y)}{\partial y}\right)_x = 1$$

$$\left(\frac{\partial(x+y)}{\partial x}\right)_y = 1$$

Therefore, the differential is exact. Because it is exact, it is the total differential of a function $z(x,y)$. The total differential of $z(x,y)$ is, by definition,

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

Comparing this expression to the differential $dz = (2x+y)dx + (x+y)dy$:

$$\left(\frac{\partial z}{\partial x}\right)_y = (2x+y)$$

$$\left(\frac{\partial z}{\partial y}\right)_x = (x+y) \tag{10.4.2.9}$$

To find $z(x,y)$, we can integrate the first expression partially with respect to x keeping y constant:

$$\int dz = z = \int (2x+y)dx = x^2 + xy + f(y)$$

So far we have

$$z = x^2 + xy + f(y) \tag{10.4.2.10}$$

so we need to find the function $f(y)$ to complete the expression above and finish the problem. To do that, we'll take the derivative of z with respect to y, and compare with Equation 10.4.2.9. The derivative of Equation 10.4.2.10 is:

$$\left(\frac{\partial z}{\partial y}\right)_x = x + \frac{df(y)}{dy}$$

comparing with Equation 10.4.2.9 we notice that $\frac{df(y)}{dy} = y$, and integrating, we obtain $f(x) = y^2/2 + c$

Therefore, $dz = (2x+y)dx + (x+y)dy$ is the total differential of $z = x^2 + xy + y^2/2 + c$.

We can check our result by working the problem in the opposite direction. If we are given $z = x^2 + xy + y^2/2 + c$ and we are asked to calculate its total differential, we would apply the definition:

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

and because

$$\left(\frac{\partial z}{\partial x}\right)_y = y + 2x$$

and

$$+\left(\frac{\partial z}{\partial y}\right)_x = y + x$$

we would write $dz = (2x + y)dx + (x + y)dy$, which is the differential we were given in the problem.

Check two extra solved examples in this video: http://tinyurl.com/kq4qecu

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10.4.3: Differentials in Thermodynamics - State and Path Functions

Distinguishing between exact and inexact differentials has very important consequences in thermodynamics. We already mentioned thermodynamic variables such as the internal energy (U), volume, pressure, and temperature, and you probably heard about entropy (S) and free energy (G). All these quantities can be used to specify the state of a system. They are properties of the current state of the system, and they do not depend on the way the system got to that state. For example, if you have a system consisting of 1 mol of He at 298 K and 1 atm, the system will have a given pressure, internal energy, entropy and free energy regardless of its history. You may have compressed the system from 2 atm, or heated the gas from 273 K. All this is irrelevant to specify the pressure, entropy, etc, because all these variables are what we call **state functions**. State functions depend only on the state of the system.

Other quantities such as work (w) and heat (q), on the other hand, are not state functions. There is no such a thing as an amount of work or heat in a system. The amounts of heat and work that "flow" during a process connecting specified initial and final states depend on how the process is carried out. Quantities that depend on the path followed between states are called **path functions**.

How is all this connected to differentials? Quantities whose values are independent of path are called state functions, and their differentials are exact (dP, dV, dG,dT...). Quantities that depend on the path followed between states are called path functions, and their differentials are inexact (dw, dq). As we will discuss in a moment, when we integrate an exact differential the result depends only on the final and initial points, but not on the path chosen. However, when we integrate an inexact differential, the path will have a huge influence in the result, even if we start and end at the same points. We'll come back to this shortly.

Knowing that a differential is exact will help you derive equations and prove relationships when you study thermodynamics in your advanced physical chemistry courses. For example, you will learn that all the state functions we mentioned above are related through these equations:

$$dU = TdS - PdV$$

$$dH = TdS + VdP$$

$$dA = -SdT - PdV$$

$$dG = -SdT + VdP$$

Here, we introduced two new state functions we haven't talked about yet: the enthalpy (H), and the Helmholtz free energy (A). You will learn about what they mean physically in CHM 346, but for now, just accept the fact that they are state functions, just as the entropy and the free energy. Although we didn't write it explicitly, T, P, V and S are not constants. When we talked about gases, we learned that P, V and T are not independent functions. If you change two of these variables you change the third, or in other words, you cannot independently vary the pressure, volume and temperature. The equation of state tells you how the three variables depend on each other. For one mole of gas, you can write the equation of state as a function $P = P(V, T)$, or as a function $V = V(T, P)$, or as a function $T = T(P, V)$. In the same way, you cannot independently change the pressure, volume, temperature and entropy of a system. If you modify the pressure and temperature, the volume and entropy will change as well. To make this clear, we can re-write the equations above as:

$$dU = T(S, V)dS - P(S, V)dV \tag{10.4.3.1}$$

$$dH = T(S, P)dS + V(S, P)dP \tag{10.4.3.2}$$

$$dA = -S(T, V)dT - P(T, V)dV \tag{10.4.3.3}$$

$$dG = -S(T, P)dT + V(T, P)dP \tag{10.4.3.4}$$

Because U, H, A and G are all state functions, their differentials are exact. We can derive a few relationships just from this fact.

For example, we see that $G = G(T, P)$, and because it's total differential, by definition, is:

$$dG = \left(\frac{\partial G}{\partial T}\right)_P dT + \left(\frac{\partial G}{\partial P}\right)_T dP \tag{10.4.3.5}$$

from Equations 10.4.3.4 and 10.4.3.5, we rapidly conclude that

$$\left(\frac{\partial G}{\partial T}\right)_P = -S$$

and

$$\left(\frac{\partial G}{\partial P}\right)_T = V$$

With minimal math, we concluded that if we change the pressure of a system at constant temperature, the rate of change of the free energy equals the volume. At this point this does not mean a lot to you, but hopefully you can appreciate how knowing that G is a state function is enough for you to derive a thermodynamic relationship! We can take this even further. Because G is a state function, dG is exact, and therefore, from Equation 10.4.3.4:

$$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P \tag{10.4.3.6}$$

We just derived one of the four Maxwell relations. You can derive the other three from Equations 10.4.3.1-10.4.3.3. Notice that once again, we derived this equation from the knowledge that G is a state function. Why are these equations useful? Let's see an example using Equation 10.4.3.6. We can integrate this expression with T constant to get:

$$\int_{P_1}^{P_2} dS = \Delta S = -\int_{P_1}^{P_2} \left(\frac{\partial V}{\partial T}\right)_P dP \text{ (constant T)}$$

This equation tells you that the change in entropy in a system can be calculated by integrating $\left(\frac{\partial V}{\partial T}\right)_P$ data. This is extremely powerful, as we can easily measure temperature, pressure and volume in the lab, but we don't have an instrument that directly measures entropy!

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10.4.4: A Mathematical Toolbox

In Chapter 8 we learned some important properties of partial derivatives, and in this chapter we learned about exact and inexact differentials. We saw many examples where these properties can be used to create relationships between thermodynamic variables. Usually we will try to calculate what we want from information we have (which is usually the information we can access experimentally). We just saw how we can calculate a change in entropy from quantities that are easy to measure in the lab: volume, temperature and pressure. In Chapter 8 we saw how we can get an expression of a partial derivative from partial derivatives that are much easier to calculate.

I will summarize some of these mathematical relationships, and call it our "toolbox". The more comfortable you get using these relationships, the easier it will be for you to derive the thermodynamic relationships you will come across in your advanced physical chemistry courses.

1. The Euler reciprocity rule (Equation 8.1.1): $\left(\frac{\partial^2 f}{\partial x \partial y}\right) = \left(\frac{\partial^2 f}{\partial y \partial x}\right)$
2. The inverse rule (Equation 8.1.2): $\left(\frac{\partial y}{\partial x}\right) = \frac{1}{\left(\frac{\partial x}{\partial y}\right)}$
3. The cycle rule (Equation 8.1.3) $\left(\frac{\partial y}{\partial x}\right)_z \left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x = -1$
4. The chain rule (Equations 8.3.4 and 8.3.5):
   $\left(\frac{\partial u}{\partial r}\right)_\theta = \left(\frac{\partial u}{\partial x}\right)_y \left(\frac{\partial x}{\partial r}\right)_\theta + \left(\frac{\partial u}{\partial y}\right)_x \left(\frac{\partial y}{\partial r}\right)_\theta$
   $\left(\frac{\partial u}{\partial \theta}\right)_r = \left(\frac{\partial u}{\partial x}\right)_y \left(\frac{\partial x}{\partial \theta}\right)_r + \left(\frac{\partial u}{\partial y}\right)_x \left(\frac{\partial y}{\partial \theta}\right)_r$
5. The definition of the total differential (Equation 9.1.7): $du = \left(\frac{\partial u}{\partial x_1}\right)_{x_2 \ldots x_n} dx_1 + \left(\frac{\partial u}{\partial x_2}\right)_{x_1, x_3 \ldots x_n} dx_2 + \ldots + \left(\frac{\partial u}{\partial x_n}\right)_{x_1 \ldots x_{n-1}} dx_n$
6. The concept of exact differential (Section 9.2)

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10.4.5: Line Integrals

In Section 9.1, we discussed that in order to properly calculate the change in pressure we would need to integrate the differential defined in Equation 10.4.5.1:

$$dP = \left(\frac{\partial P}{\partial V}\right)_{T,n} dV + \left(\frac{\partial P}{\partial T}\right)_{V,n} dT \tag{10.4.5.1}$$

This raises the question of how to integrate differentials such as this one. Before we focus on this question, let's discuss what we expect for an exact differential. Let's say that we know how to perform these integrals, and we integrate dP from initial pressure (P_i) to final pressure (P_f) to calculate ΔP for a change that is not infinitesimal:

$$\Delta P = \int_{P_i}^{P_f} dP$$

Would it surprise you that the result equals the final pressure minus the initial pressure?

$$\Delta P = P_f - P_i$$

Hopefully not; the change in pressure will obviously be the final pressure minus the initial pressure, regardless of whether we did this slowly, fast, at constant volume, constant temperature, etc. In other words, you just need the information of the state of the system at the beginning and the end of the process, but you do not need to know anything about what happened in between. All this makes sense because P is a state function, and the same argument applies to other state functions, such as entropy, internal energy, free energy, etc. We just reached an important conclusion: if we integrate an exact differential, the result will be independent of the path, and it will equal the function at the end point minus the function at the initial point. If we integrate an inexact differential this is not true, because we will be integrating the differential of a function that is *not* a state function. We'll come back to this many times, but it is important that before getting lost in the math we keep in mind what to expect.

We already mentioned the word "path", but what do we mean by that? In the example of the gas, the path would be described by the values of the temperature and volume at all times. For example, Figure 10.4.5.1 shows two possible paths that result in the same change in pressure. We could imagine an infinite number of other options, and of course we are not restricted to keeping one variable constant while changing the other.

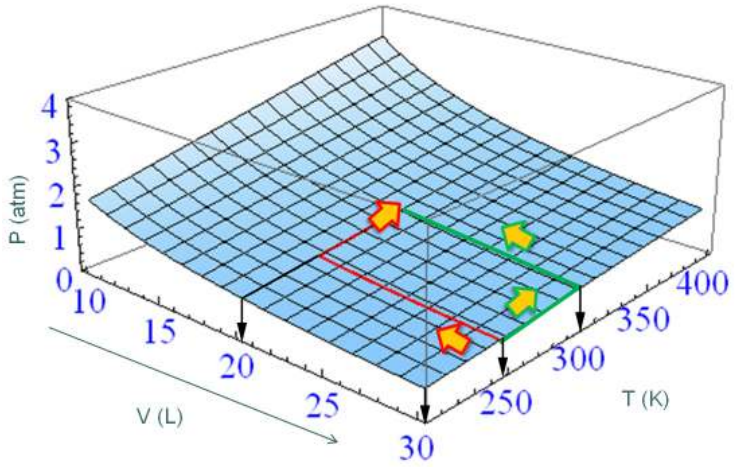


Figure 10.4.5.1: Two different paths that produce the same change in pressure in one mole of an ideal gas. In the first case (red), the volume is compressed from 30 L to 20 L at 250 K, and then the temperature is increased to 300 K at constant pressure. In the second case (green) the temperature is first raised to 300 K at a constant volume of 30L, and then the system is compressed to 20L at constant temperature The blue surface represents the function $P = RT/V$ (CC BY-NC-SA; Marcia Levitus)

We can integrate dP along one path or the other, but we already know what we will get: $\int dP = P_2 - P_1$ regardless of the path. Work and heat, on the other hand, are not state functions. There is no such a thing as an amount of work or heat in a system. The amounts of heat and work that "flow" during a process connecting specified initial and final states depend on how the process is

carried out. This means that if we want to calculate the work or the heat involved in the process, we would need to integrate the inexact differentials dw and dq indicating the particular path used to take the system from the initial to the final states:

$$q = \int_{path} dq$$

$$w = \int_{path} dw$$

For one mole of an ideal gas ($P = RT/V$),

$$dP = \left(\frac{\partial P}{\partial V}\right)_{T,n} dV + \left(\frac{\partial P}{\partial T}\right)_{V,n} dT = -\frac{RT}{V^2} dV + \frac{R}{V} dT$$

From our previous discussion, we know the result of integrating the differential

$$dP = -\frac{RT}{V^2} dV + \frac{R}{V} dT$$

along any path. The result should be the final pressure minus the initial pressure:

$$\Delta P = R(T_f/V_f - T_i/V_i) \tag{10.4.5.2}$$

where the subscripts f and i refer to the final and initial states.

Even is we know the answer, let's do it anyway so we learn how to integrate differentials. We will consider the two paths depicted in Figure 10.4.5.1. In both cases the initial temperature is 250 K, the initial volume is 30 L, the final temperature is 300 K, and the final volume is 20 L.

Let's start with the 'red' path. This path is the sum of two components, one where we change the volume at constant temperature, and another one where we change the temperature at constant volume. Let's call these individual steps path 1 and path 2, so the total path is path1 + path 2:

$$\int_{path} dP = \int_{path1} dP + \int_{path2} dP$$

$$\int_{path} \left(-\frac{RT}{V^2} dV + \frac{R}{V} dT\right) = \int_{path1} \left(-\frac{RT}{V^2} dV + \frac{R}{V} dT\right) + \int_{path2} \left(-\frac{RT}{V^2} dV + \frac{R}{V} dT\right)$$

In path 1, we keep the temperature constant, so $dT = 0$. Furthermore, the temperature equals T_i during the whole process:

$$\int_{path1} \left(-\frac{RT}{V^2} dV + \frac{R}{V} dT\right) = \int_{path1} \left(-\frac{RT_i}{V^2} dV\right) = \int_{V_i}^{V_f} -\frac{RT_i}{V^2} dV$$

in path 2 we keep the volume constant, so $dV = 0$. Furthermore, the volume equals V_f during the whole process:

$$\int_{path2} \left(-\frac{RT}{V^2} dV + \frac{R}{V} dT\right) = \int_{path2} \frac{R}{V_f} dT = \int_{T_i}^{T_f} \frac{R}{V_f} dT$$

Putting the two results together:

$$\int_{path} \left(-\frac{RT}{V^2} dV + \frac{R}{V} dT\right) = \int_{V_i}^{V_f} -\frac{RT_i}{V^2} dV + \int_{T_i}^{T_f} \frac{R}{V_f} dT$$

$$\int_{path} \left(-\frac{RT}{V^2} dV + \frac{R}{V} dT\right) = \frac{RT_i}{V}\Big|_{V_i}^{V_f} + \frac{RT}{V_f}\Big|_{T_i}^{T_f} = RT_i\left(\frac{1}{V_f} - \frac{1}{V_i}\right) + \frac{R}{V_f}(T_f - T_i)$$

$$RT_i\left(\frac{1}{V_f} - \frac{1}{V_i}\right) + \frac{R}{V_f}(T_f - T_i) = R\left(\frac{T_i}{V_f} - \frac{T_i}{V_i} + \frac{T_f}{V_f} - \frac{T_i}{V_f}\right) = R\left(\frac{T_f}{V_f} - \frac{T_i}{V_i}\right)$$

The result is, as expected, identical to Equation 10.4.5.2.

Let's now consider the two-step path depicted in green in Figure 10.4.5.1. We'll follow the same ideas we used for the path shown in red. In the first part of the path we change the temperature from T_i to T_f at constant volume, $V = V_i$. In the second part of the path we change the volume from V_i to V_f at constant temperature, $T = T_f$. In the first part, $dV = 0$ and $V = V_i$ at all times. In the second part, $dT = 0$, and $T = T_f$ at all times:

$$\int_{path}\left(-\frac{RT}{V^2}dV+\frac{R}{V}dT\right)=\int_{T_i}^{T_f}\left(\frac{R}{V_i}dT\right)+\int_{V_i}^{V_f}\left(-\frac{RT_f}{V^2}dV\right)$$

$$\int_{path}\left(-\frac{RT}{V^2}dV+\frac{R}{V}dT\right)=\frac{RT}{V_i}\Bigg|_{T_i}^{T_f}+\frac{RT_f}{V}\Bigg|_{V_i}^{V_f}$$

$$\int_{path}\left(-\frac{RT}{V^2}dV+\frac{R}{V}dT\right)=\frac{R}{V_i}(T_f-T_i)+RT_f\left(\frac{1}{V_f}-\frac{1}{V_i}\right)=R\left(\frac{T_f}{V_f}-\frac{T_i}{V_i}\right)$$

The result is, as expected, $P_f - P_i$ (Equation 10.4.5.2).

Because dP is exact, it does not matter which path we choose to go from (V_i, P_i) to (V_f, P_f), the result of the integral of dP will always the same $R\left(\frac{T_f}{V_f}-\frac{T_i}{V_i}\right)$. Let's try another path; this time one that does not keep any of the variables constant at any time. Consider the path that is the straight line that joins the points (V_i, P_i) to (V_f, P_f). In order to integrate dP along a particular path, we need the equation of the path indicating how the variables V and T are connected at all times.

In this case, $T = a + bV$, where a is the y–intercept and b is the slope. You should be able to prove that the values of a and b for this path are:

$$a = T_i - \frac{T_f - T_i}{V_f - V_i}V_i$$

$$b = \frac{T_f - T_i}{V_f - V_i}$$

Because $T = a + bV$, $dT = bdV$, $V = (T - a)/b$, and $dV = dT/b$. These relationships tell us how T and V are connected throughout the path, and we can therefore write these equivalent expressions:

$$\int_{path}\left(-\frac{RT}{V^2}dV+\frac{R}{V}dT\right)=-\int_{V_i}^{V_f}\left(-\frac{R(a+bV)}{V^2}dV\right)+\int_{T_i}^{T_f}\left(\frac{bR}{T-a}dT\right)$$

$$\int_{path}\left(-\frac{RT}{V^2}dV+\frac{R}{V}dT\right)=-\int_{V_i}^{V_f}\left(-\frac{R(a+bV)}{V^2}dV\right)+\int_{V_i}^{V_f}\left(\frac{R}{V}bdV\right)$$

$$\int_{path}\left(-\frac{RT}{V^2}dV+\frac{R}{V}dT\right)=-\int_{T_i}^{T_f}\left(-\frac{RT}{[(T-a)/b]^2}\frac{1}{b}dT\right)+\int_{T_i}^{T_f}\left(\frac{bR}{T-a}\right)dT$$

In the first case we just wrote the first integrand in terms of V only and the second integrand in terms of T only. To achieve this, we used the information from the path to see how V and T are related as we move from our initial to our final states. The same idea applies to the second and third lines, where we wrote everything in terms of V or in terms of T. The three equations will give the same result regardless of whether the differential is exact on inexact. However, because we are integrating an exact differential, the result will be identical to the result we got for the two other paths that share the same initial and final state, and also identical to $P_f - P_i$.

The three equations above are not too hard to solve, but they are more time consuming that the integrals we had to solve for the paths involving sections of the path where one or the other variable remain constant. This is powerful, because it means that if you are integrating an exact differential, you can get smart and solve the integral for a very easy path, as long as the initial and final states are the same. You know the result will be the same because the differential is exact. If, on the other hand, the differential is inexact, we are out of luck. The integral depends on the path, so we need to solve the path we are given.

Because dP is exact, the line integral equals $P_f - P_i$. A consequence of this is that the integral along a closed path (one where $P_i = P_f$) is zero. Mathematically:

$$\oint dP = 0$$

where the circle inside the integration symbol means that the path is closed. This is true for any exact differential, but not necessarily true for a differential that is inexact. Coming back to thermodynamics, imagine one mole of a gas in a container whose volume is first reduced from 30 L to 20 L at a constant temperature T= 250 K. You then heat the gas up to 300 K keeping the volume constant, then increase the volume back to 30 L keeping the temperature constant, and finally cool it down to 250 K at constant volume (see Figure **10.4.5.1**. Because the initial and final states are the same, the line integral of any state function is zero:

$$\Delta P = \oint dP = 0$$

$$\Delta G = \oint dG = 0$$

$$\Delta S = \oint dS = 0$$

etc, etc

This closed path does not involve a change in pressure, free energy or entropy, because these functions are state functions, and the final state is identical to the initial state.

On the other hand,

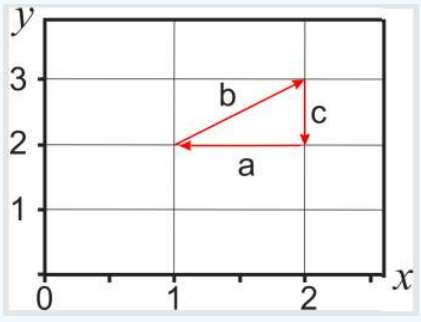
$$w = \oint dw \neq 0$$

$$q = \oint dq \neq 0$$

because we are integrating inexact differentials. Physically, you had to do work to expand the gas, heat it up, compress it, cool it down, etc. It does not matter you end up exactly where you started, work and heat were involved in the process. It may be possible for a particular closed path to yield $w = 0$ or $q = 0$, but in general this does not need to be the case.

Example 10.4.5.1

Given the following differential $dz = x\,dy + 2y\,dx$, and the closed path shown in the figure, calculate the line integral $\int_{path} dz$



Note: This problem is also available in video format: http://tinyurl.com/mszuwr7

Solution

The path is divided in three sections, so

$$\int_{path} dz = \int_a dz + \int_b dz + \int_c dz$$

In section a: $y = 2$, $dy = 0$ (y is a constant), and x changes from an initial value of 2 to a final value of 1:

$$\int_a dz = \int_2^1 4dx = 4x\,|_2^1 = 4 - 8 = -4$$

In section b: $y = 1 + x$, $dy = dx$, and x changes from an initial value of 1 to a final value of 2:

$$\begin{aligned}\int_b dz &= \int_b x\,dy + 2y\,dx = \int_1^2 x\,dx + \int_1^2 2(1+x)\,dx \\ &= \frac{x^2}{2}\bigg|_1^2 + 2\,\frac{(1+x)^2}{2}\bigg|_1^2 = \frac{3}{2} + (9-4) = \frac{13}{2}\end{aligned}$$

In section c: $x = 2$, $dx = 0$ (x is a constant), and y changes from an initial value of 3 to a final value of 2:

$$\int_c dz = \int_3^2 2dy = 2y\,|_3^2 = 4 - 6 = -2$$

Therefore,

$$\int_{path} dz = \int_a dz + \int_b dz + \int_c dz = -4 + 13/2 - 2 = 1/2$$

Notice that the integral is not zero even if the path was closed. This is not surprising given that the differential was inexact.

Example 10.4.5.2

Consider the differential

$$du = (x^2 - y^2)dx + (2xy)dy$$

a. Is du exact or inexact?
b. Explain why each of the following is true or false:
   - du is the total differential of some function $u(x, y)$. Find $u(x, y)$ if possible.
   - $\int_a du = \int_b du = \int_c du$ as long as a, b and c are paths in the (x, y) space that share the same starting and ending points.
c. Calculate $\int_{path} du$ if the path is the straight line joining the points (0,2) and (2,0).

Solution:

To test whether du is exact or inexact, we compare the following derivatives

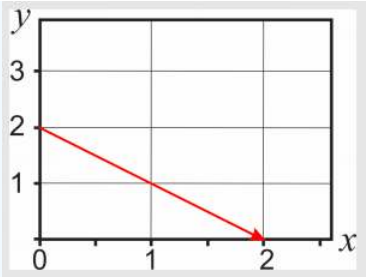
$$\left(\frac{\partial(x^2-y^2)}{\partial y}\right)_x \stackrel{?}{=} \left(\frac{\partial(2xy)}{\partial x}\right)_y$$

Because the two partial derivatives are not the same, the differential is inexact.

Because the differential is inexact, it is not the total differential of a function $u(x, y)$. We cannot find the function because it does not exist.

The line integrals $\int_a du$, $\int_b du$ and $\int_c du$ will in principle be different because the integral of an inexact differential depends not only on the initial and final states, but also on the path used to get from the initial to the final state. The statement would be true for an exact differential.

To calculate the integral along the straight line joining the points (0,2) and (2,0), we first need to find the equation $y(x)$ that describes this path. Sketching the function is not a must, but it might help:



The equation of this straight line is $y = 2 - x$. Therefore, along the path, $y = 2 - x$ and $dy = -dx$. The variable x changes from an initial value $x = 0$ to a final value $x = 2$:

$$\int_{path} du = \int_{path} (x^2 - y^2)dx + (2xy)dy$$

It is important to stress that x and y are not independent along the process, but instead, they are connected through the equation of the path. We will write the equation in terms of x (we could do it in terms of y with identical results):

$$\begin{aligned}
\int_{path} du &= \int_{path} (x^2 - y^2)dx + (2xy)dy \\
&= \int_0^2 (x^2 - (2-x)^2)dx + \int_0^2 (2x(2-x))(-dx) \\
&= \int_0^2 (x^2 - (4 + x^2 - 4x))dx - \int_0^2 (4x - 2x^2)dx \\
&= \int_0^2 (4x - 4)dx - \int_0^2 (4x - 2x^2)dx = \int_0^2 (2x^2 - 4)dx \\
&= \left(\frac{2x^3}{3} - 4x\right)\Big|_0^2 = \frac{16}{3} - 8 = -\frac{8}{3} \\
&= -\frac{8}{3}
\end{aligned}$$

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10.4.6: Exact and Inexact Differentials (Summary)

To summarize, given a function $f(x,y)$, its total differential df is, by definition:

$$df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy$$

Given an arbitrary differential

$$df = M(x,y)dx + N(x,y)dy$$

where M and N are functions of x and y, the differential is **exact** if it is the total differential of a function $f(x,y)$. To test for exactness we compare the partial derivative of $M(x,y)$ with respect to y, and the partial derivative of $N(x,y)$ with respect to x:

$$\left(\frac{\partial M(x,y)}{\partial y}\right)_x \stackrel{?}{=} \left(\frac{\partial N(x,y)}{\partial x}\right)_y$$

If the derivatives are identical, we conclude that the differential df is exact, and therefore it is the total differential of a function $f(x,y)$. To find the function, we notice that for an exact differential:

$$M(x,y) = \left(\frac{\partial f}{\partial x}\right)_y$$

$$N(x,y) = \left(\frac{\partial f}{\partial y}\right)_x$$

We can then find the function by partial integration:

$$f(x,y) = \int df = \int M(x,y)dx \text{ (at constant } y)$$

$$f(x,y) = \int df = \int N(x,y)dy \text{ (at constant } x)$$

It is important to keep in mind that the integration constant in the first case will be an arbitrary function of y, and in the second case an arbitrary function of x.

For an exact differential, the line integral does not depend on the path, but only on the initial and final points. Furthermore, because the differential is exact, it is the total differential of a state function $f(x,y)$. This means that the integral of df along any path is simply the function f evaluated at the final state minus the function f evaluated at the initial state:

$$\int_c M(x,y)dx + N(x,y)dy = \int_c df = \Delta f = f(x_2,y_2) - f(x_1,y_1)$$

where c represents the path that starts at the point (x_1,y_1) and ends at the point (x_2,y_2).

If the initial and the final states are identical, for an exact differential:

$$\oint df = 0$$

For an inexact differential, $\int_c df$ will in general depend on the path c.

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10.4.7: Problems

Problem 10.4.7.1

Determine whether the following differentials are exact or inexact. If they are exact, determine $u = u(x, y)$.

1. $du = (2ax + by)dx + (bx + 2cy)dy$
2. $du = (x^2 - y^2)dx + (2xy)dy$

Problem 10.4.7.2

Determine whether dz is exact or inexact. If it is exact, determine $z = z(P, T)$.

$$dz = -\frac{RT}{P^2}dP + \frac{R}{P}dT$$

Problem 10.4.7.3

From Equation 10.4.7.4, and using the fact that G is a state function, prove that the change in entropy (ΔS) of one mole of an ideal gas whose pressure changes from an initial value P_1 to a final value P_2 at constant temperature is:

$$\Delta S = -R \ln \frac{P_2}{P_1}$$

Problem 10.4.7.4

From Equations 10.4.7.1-10.4.7.3, and using the fact that U, H and A are state functions, derive the three corresponding Maxwell relations.

Answer

Add texts here. Do not delete this text first.

Problem 10.4.7.5

Given the following differential:

$$dz = xydx + 2ydy$$

a. Determine if it is exact or inexact. If it is, obtain $z(x, y)$

b. Calculate the line integrals $\int_c dz$ for the paths enumerated below:

1. the line $y = 2x$ from $x = 0$ to $x = 2$
2. the curve $y = x^2$ from $x = 0$ to $x = 2$
3. any other path of your choice that joins the same initial and final points.

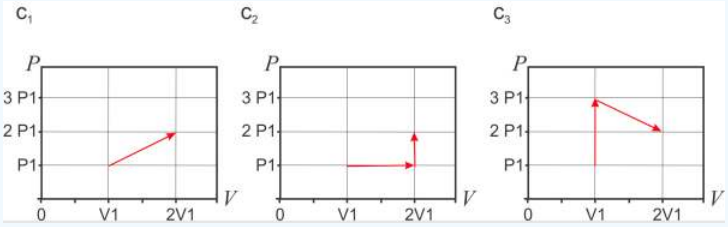
Problem 10.4.7.6

For a mole of a perfect monoatomic gas, the internal energy can be expressed as a function of the pressure and volume as

$$U = \frac{3}{2}PV$$

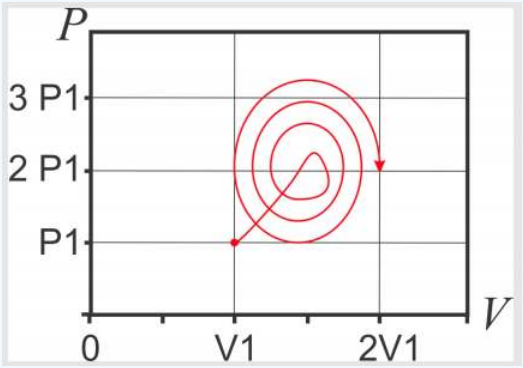
a. Write the total differential of U, dU.

b. Calculate the line integrals $\int_c dU$ for the paths shown below (c_1, c_2, c_3):



c. Calculate $U(V_f, P_f) - U(V_i, P_i)$ and compare with the results of b) (Note: f refers to the final state and i to the initial state).

d. Considering your previous results, calculate $\int_c dU$ for the path below:



As defined in Section 9.3,

$$dU = T(S,V)dS - P(S,V)dV \tag{10.4.7.1}$$

$$dH = T(S,P)dS + V(S,P)dP \tag{10.4.7.2}$$

$$dA = -S(T,V)dT - P(T,V)dV \tag{10.4.7.3}$$

$$dG = -S(T,P)dT + V(T,P)dP \tag{10.4.7.4}$$

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SECTION OVERVIEW

10.5: First Order Ordinary Differential Equations

Objectives

- Be able to identify the dependent and independent variables in a differential equation.
- Be able to identify whether an ordinary differential equation (ODE) is linear or nonlinear.
- Be able to identify the order of an ODE
- Be able to identify whether a first order ODE is separable or not.
- Be able to find the general and particular solutions of linear first order ODEs.
- Be able to find the general and particular solutions of separable first order ODEs.
- Understand how to verify that the solution you got in a problem satisfies the differential equation and initial conditions.
- Understand how to solve differential equations in the context of chemical kinetics. Understand the concept of mass balance, and half-life.

10.5.1: Definitions and General Concepts

10.5.2: 1st Order Ordinary Differential Equations

10.5.3: Chemical Kinetics

10.5.4: Problems

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10.5.1: Definitions and General Concepts

A differential equation is an equation that defines a relationship between a function and one or more derivatives of that function.

For example, this is a differential equation that relates the function $y(t)$ with its first and second derivatives:

$$\frac{d^2}{dt^2}y(t) + \frac{1}{4}\frac{d}{dt}y(t) + y(t) = \sin(t)$$

The above example is an **ordinary differential equation** (ODE) because the unknown function, $y(t)$, is a function of a single variable (in this case t). Because we are dealing with a function of a single variable, only ordinary derivatives appear in the equation. If we were dealing with a function of two or more variables, the partial derivatives of the function would appear in the equation, and we would call this differential equation a **partial differential equation** (PDE). An example of a PDE is shown below. We will discuss PDEs towards the end of the semester.

$$\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial z^2} = c^2\frac{\partial^2 u}{\partial t^2}$$

Note that in the example above we got 'lazy' and used u instead of $u(x, y, z, t)$. The fact that u is a function of x, y, z, and t is obvious from the derivatives, so you will see that often we will relax and not write the variables explicitly with the function.

Why do we need to study differential equations? The answer is simple: **Differential equations arise in the mathematical models that describe most physical processes**. Figure 10.5.1.1 illustrates three examples.

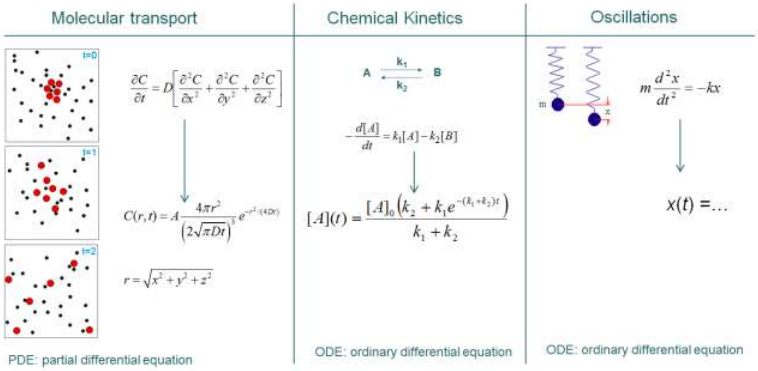


Figure 10.5.1.1: Examples of physical process that are described mathematically through differential equations (CC BY-NC-SA; Marcia Levitus)

The first column illustrates the problem of molecular transport (diffusion). Suppose the red circles represent molecules of sucrose (sugar) and the black circles molecules of water, and assume you are interested in modeling the concentration of sucrose as a function of position and time after you dissolve some sucrose right in the middle of the container. The differential equation describing the process is a partial differential equation because the concentration will be a function of two variables: r, the distance from the origin, and t, the time elapsed from the moment you started the experiment. The solution shown in the figure was obtained by assuming that all the molecules of sucrose are concentrated at the center at time zero. You could solve the differential equation with other initial conditions.

The second column illustrates a chemical system where a compound A reacts to give B. The reaction is reversible, and it could, for example, represent two different isomers of the same molecule. The differential equation models how the concentration of A, [A], changes with time. We will in fact analyze this problem in detail and find the solution shown in the figure. As we will see, in this case we are also assuming certain initial conditions.

Finally, the third column illustrates a mass attached to a spring. We will also analyze this equation, and the solution is not shown because it will be your job to get it in your homework. You may think this is a physics problem, but because molecules have chemical bonds, and atoms vibrate around their equilibrium positions, systems like these are of interest to chemists as well.

To solve the differential equation means to find the function (or family of functions) that satisfies the equation. In our first example in Figure 10.5.1.1, we would need to find the function $C(r, t)$ that satisfies the equation. In the second example we would need to

find all the functions A(t) that satisfy the equation. As we will see shortly, whether the solution is one function or a family of functions depends on whether we are restricted by initial conditions (e.g. at time zero [B] = 0) or not.

The order of a differential equation (partial or ordinary) is the highest derivative that appears in the equation. Below is an example of a first order ordinary differential equation:

$$\frac{dy}{dx} + 3y = 8e^x \tag{10.5.1.1}$$

In this example, we are looking for all the functions $y(x)$ that satisfy Equation 10.5.1.1. As usual, we will call x the independent variable, and y the dependent variable. Again, y is of course $y(x)$, but often we do not write this explicitly to save space and time. This is an ordinary differential equation because y is a function of a single variable. It is a first order differential equation because the highest derivative is of first order. It is also **a linear differential equation** because the dependent variable and all of its derivatives appear in a linear fashion. The distinction between linear and non-linear ODEs is very important because there are different methods to solve different types of differential equations. Mathematically, a first order linear ODE will have this general form:

$$\frac{dy}{dx} + f_1(x)y = f_2(x)$$

It is crucial to understand that the linearity refers to the terms that include the dependent variable (in this case y). The terms involving x ($f_1(x)$ and $f_2(x)$) can be non-linear, as in Equation 10.5.1.1. An example of a non-linear differential equation is shown below. Note that the dependent variable appears in a transcendental function (in this case an exponential), and that makes this equation non-linear:

$$\frac{dy}{dx} + 3e^y = 8x$$

Analogously, a linear second order ODE will have the general form:

$$\frac{d^2y}{dx^2} + f_1(x)\frac{dy}{dx} + f_2(x)y = f_3(x) \tag{10.5.1.2}$$

Again, we don't care whether the functions $f_1(x), f_2(x)$ and $f_3(x)$ are linear in x or not. The only thing that matters is that the terms involving the dependent variable are.

> Identifying the dependent and the independent variables: Test yourself with this short quiz. http://tinyurl.com/ll22wnv
>
> Linear or non-linear? See if you can identify the linear ODEs in this short quiz. http://tinyurl.com/msldkp3

We are still defining concepts, but we haven't said anything so far regarding how to solve differential equations! We still need to go over a few more things, so be patient.

An nth-order differential equation together with n auxiliary conditions imposed at the same value of the independent variable is called an **initial value problem**. For example, we may be interested in finding the function $y(x)$ that satisfies the following conditions:

$$y'' = e^{-x}, y(0) = 1, y'(0) = 4 \tag{10.5.1.3}$$

Notice that we are introducing different types of notations so you get used to seeing mathematical equations in different 'flavors'. Here, y'' of course means $\frac{d^2y(x)}{dx^2}$. This is an initial value problem because we have a second-order differential equation with two auxiliary conditions imposed at the same value of x (in this case $x = 0$). There are infinite functions $y(x)$ that satisfy $y'' = e^{-x}$, but only one will also satisfy the two initial conditions we imposed. If we were dealing with a first order differential equation we would need only one initial condition. We would need three for a third-order differential equation.

How do we use initial conditions to find a solution? In general, the solution of a second order ODE will contain two arbitrary constants (in the example below c_1 and c_2). This is what we will call the **general solution** of the differential equation. For example,

$y(x) = e^{-x} + c_1 x + c_2$ is the general solution of $y'' = e^{-x}$. We can verify this is true by taking the second derivative of this function. Again, we do not know yet how to get these solutions, but if we are given this solution, we know how to check if it is correct. It is clear that c_1 and c_2 can be in principle anything, so the solution of the ODE is a whole family of functions. However, if we are given initial conditions we are looking for a **particular solution**, one that not only satisfies the ODE, but also the initial conditions. Which function is that?

The first initial condition states that $y(0) = 1$. Therefore,

$$y(x) = e^{-x} + c_1 x + c_2 \Rightarrow y(0) = 1 + c_2$$

$$y(0) = 1 \Rightarrow 1 = 1 + c_2 \Rightarrow c_2 = 0$$

So far, we demonstrated that the functions $y(x) = e^{-x} + c_1 x$ satisfy not only the ODE, but also the initial condition $y(0) = 1$. We still have another initial condition, which will allow us to determine the value of c_1.

$$y'(x) = -e^{-x} + c_1 \Rightarrow y'(0) = -1 + c_1$$

$$y'(0) = 4 \Rightarrow 4 = -1 + c_1 \Rightarrow c_1 = 5$$

Therefore, the function $y(x) = e^{-x} + 5x$ is the **particular solution** of the initial value problem described in Equation 10.5.1.3. We can check our answer by verifying that this solution satisfies the three equations of the initial value problem:

1. $y'' = e^{-x} \rightarrow \frac{d^2}{dx^2}(e^{-x} + 5x) = e^{-x}$, so we know that the solution we found satisfies the differential equation.
2. $y(0) = 1 \rightarrow e^{-0} + 5 \times 0 = 1$, so we know that the solution we found satisfies one of the initial conditions.
3. $y'(0) = 4 \rightarrow \frac{d}{dx}(e^{-x} + 5x) = -e^{-x} + 5 \Rightarrow y'(0) = 4$, so we know that the solution we found satisfies the other initial condition as well.

Therefore, we demonstrated that $y(x) = e^{-x} + 5x$ is indeed the solution of the problem.

An nth-order differential equation together with n auxiliary conditions imposed at more than one value of the independent variable is called a **boundary value problem**. What is the difference between a boundary value problem and an initial value problem? In the first case, the conditions are imposed at different values of the independent variable, while in the second case, as we just saw, the conditions are imposed at the same value of the independent variable. For example, this would be a boundary value problem:

$$y'' = e^{-x}, y(0) = 1, y(1) = 0 \tag{10.5.1.4}$$

Notice that we still have two conditions because we are dealing with a second order differential equation. However, one condition deals with $x = 1$ and the other with $x = 0$. The conditions can refer to values of the first derivative, as in the previous example, or to values of the function itself, as in the example of Equation 10.5.1.4.

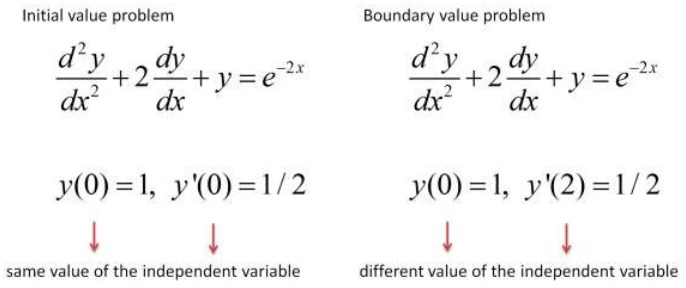


Figure 10.5.1.2: Initial vs boundary value problems (CC BY-NC-SA; Marcia Levitus)

Why do we need to distinguish between initial value and boundary value problems? The reason lies in a theorem that states that, for linear ODEs, the solution of a initial value problem exists and is unique, but a boundary value problem does not have the existence and uniqueness guarantee. The theorem is not that simple (for example it requires that the functions in x ($f_{1...3}$ in Equation 10.5.1.2) are continuous), but the bottom line is that we may find a solution whenever the conditions are imposed at the same value of x, but we may not find a solution whenever the conditions are imposed at different values. We will see examples when we discuss second order ODEs, and in particular we will discuss how boundary conditions give rise to interesting physical phenomena. For example, we will see that boundary conditions are responsible for the fact that energies in atoms and molecules are quantized.

Coming back to the boundary value problem of Equation 10.5.1.4, it is important to recognize that because the actual differential equation is the same as in the example of Equation 10.5.1.3, the **general solution** is still the same: $y(x) = e^{-x} + c_1 x + c_2$. However, the **particular solution** will be different (different values of c_1 and c_2), because we need to satisfy different conditions.

As in the first example, the first boundary condition states that $y(0) = 1$ so:

$$y(x) = e^{-x} + c_1 x + c_2 \Rightarrow y(0) = 1 + c_2$$

$$y(0) = 1 \Rightarrow 1 = 1 + c_2 \Rightarrow c_2 = 0$$

as before. However, now

$$y(1) = e^{-1} + c_1$$

where we have used the result $c_2 = 0$ so

$$y(1) = 0 \Rightarrow 0 = e^{-1} + c_1 \Rightarrow c_1 = -e^{-1}$$

and the **particular solution** is therefore $y(x) = e^{-x} - e^{-1}x$. As we did before, it is important that we check our solution. If we are right, this solution needs to satisfy all the relationships stated in Equation 10.5.1.4.

1. $y'' = e^{-x} \rightarrow \frac{d^2}{dx^2}(e^{-x} - e^{-1}x) = e^{-x}$, so the solution satisfies the differential equation.
2. $y(0) = 1 \rightarrow e^{-0} - e^{-1} \times 0 = 1$, so our solution satisfies one of the boundary conditions.
3. $y(1) = 0 \rightarrow e^{-1} - e^{-1} \times 1 = 0$, so our solution satisfies the other boundary condition as well.

Figure 10.5.1.3 illustrates the difference between the general solution and the particular solution. The general solution has two arbitrary constants, so there are an infinite number of functions that satisfy the differential equation. Three examples are shown in different colors. However, only one of these satisfies both boundary conditions (shown with the arrows).

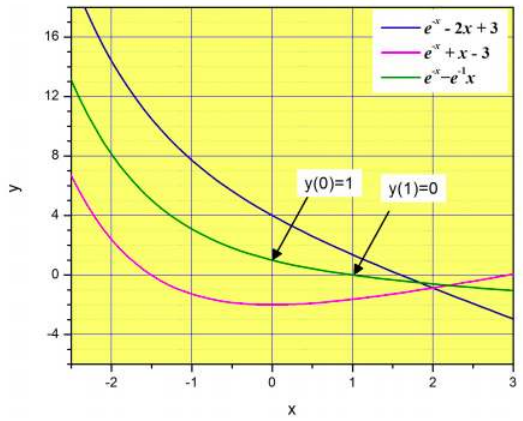


Figure 10.5.1.3: General and particular solutions of boundary value problem [eq3] (CC BY-NC-SA; Marcia Levitus)

> Using boundary conditions: see if you can obtain the particular solution of a second order ODE in this short quiz. http://tinyurl.com/lovh4x3

So far we have discussed how to:

- Identify the dependent and independent variables
- Identify the order of the differential equation.
- Identify whether the equation is linear or not
- Use initial or boundary conditions to obtain particular solutions from general solutions
- Check your results to be sure you satisfy the differential equation and all the initial or boundary conditions

We are obviously missing the most important question: How do we solve the differential equation? Unfortunately, there is no universal method, and in fact some differential equations cannot be solved analytically. We will see some examples of equations

that cannot be solved analytically and we will discuss what can be done in those cases. In this class we will only discuss some differential equations of interest in physical chemistry. It is not our intention to cover the topic in a comprehensive manner, and we will not touch on other differential equations that might be of interest in other disciplines. Yet, the background you will get in this class will allow you to teach yourself more advanced topics in differential equations if your future career demands that you have a deeper knowledge of the subject.

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10.5.2: 1st Order Ordinary Differential Equations

We will discuss only two types of 1st order ODEs, which are the most common in the chemical sciences: **linear** 1st order ODEs, and **separable** 1st order ODEs. These two categories are not mutually exclusive, meaning that some equations can be both linear and separable, or neither linear nor separable.

Separable 1st order ODEs

An ODE is called separable if it can be written as

$$\frac{dy}{dx} = \frac{g(x)}{h(y)} \tag{10.5.2.1}$$

A separable differential equation is the easiest to solve because it readily reduces to a problem of integration:

$$\int h(y)dy = \int g(x)dx \tag{10.5.2.2}$$

For example: $\frac{dy}{dx} = 4y^2x$ can be written as $y^{-2}dy = 4xdx$ or $\frac{1}{4}y^{-2}dy = xdx$. This equation is separable becuase the terms multiplying dy do not contain any terms involving x, and the terms multiplying dx do not contain any terms involving y. This allows you to integrate and solve for $y(x)$:

$$\int y^{-2}dy = \int 4xdx$$
$$-\frac{1}{y} + c_1 = 2x^2 + c_2$$
$$y = -\frac{1}{2x^2 + c_3}$$

where $c_3 = c_2 - c_1$.

Let's see how to separate other equations. If you wanted to finish these problems you would integrate both sides and solve for the dependent variable, as shown in the solved examples below. For now, let's concentrate on how to separate the terms involving the independent variable from the terms involving the dependent variable:

Example 1:

$$y' = e^{-y}(3 - x)$$

$$\frac{dy}{dx} = e^{-y}(3 - x)$$

Separated ODE:

$$e^y dy = (3 - x)dx$$

Example 2:

$$\theta' = \frac{t^2}{\theta}$$

$$\frac{d\theta}{dt} = \frac{t^2}{\theta}$$

Separated ODE:

$$\theta d\theta = t^2 dt$$

Example 3:

$$\frac{dA(t)}{dt} = \frac{2 - t}{1 - A(t)}$$

Separated ODE:

$$(1-A(t))dA = (2-t)dt$$

Example 10.5.2.1

Solve the following differential equation: $\frac{dy}{dx} = yx^2$

Solution

We first 'separate' the terms involving y from the terms involving x:

$$\frac{1}{y}dy = x^2dx$$

and then integrate both sides (it is crucial not to forget the integration constants):

$$\int \frac{1}{y}dy = \int x^2dx \rightarrow \ln y + c_1 = \frac{1}{3}x^3 + c_2$$

Remember that our goal is to find $y(x)$, so our job now is to solve for y:

$$\ln y + c_1 = \frac{1}{3}x^3 + c_2$$

$$\ln y = \frac{1}{3}x^3 + c_2 - c_1$$

$$= \frac{1}{3}x^3 + c_3$$

$$y = \exp\left(\frac{1}{3}x^3 + c_3\right) = \exp\left(\frac{1}{3}x^3\right)\exp(c_3) = Ke^{x^3/3}$$

Notice that $c_2 - c_1$ is a constant, so we re-named it c_3. In addition, $exp(c_3)$ is also a constant, so we re-named it K. The names of the constants are not important.

Just to be on the safe side, let's verify that $Ke^{x^3/3}$ is indeed the solution of this differential equation. We'll do it by substitution. On the left-hand side of the equation we have $\frac{dy}{dx}$, and on the right-hand side we have yx^2. We'll replace y by $Ke^{x^3/3}$ on both sides, and verify that the two sides are identical (the equality holds).

$$\frac{dy}{dx} = Ke^{x^3/3}x^2$$

$$yx^2 = Ke^{x^3/3}x^2$$

We just verified that the function $Ke^{x^3/3}$ satisfies $\frac{dy}{dx} = yx^2$, so we know our solution is correct!

Example **10.5.2.1** illustrates why you need to be very comfortable with the properties of the logarithmic and exponential functions. These functions appear everywhere in the physical sciences, so if you found this challenging you need to review your algebra!

Example 10.5.2.2

Solve the following differential equation: $\frac{dx}{dt} = x^2t$

This might look similar to example **10.5.2.1**, but notice that in this case, x is the dependent variable.

Solution

We first 'separate' the terms involving x from the terms involving t:

$$\frac{1}{x^2}dx = tdt$$

and then integrate both sides (it is crucial not to forget the integration constants):

$$\int \frac{1}{x^2}dx = \int tdt \rightarrow -x^{-1} + c_1 = t^2/2 + c_2$$

Remember that our goal is to find $x(t)$, so our job now is to solve for x:

$$-x^{-1} + c_1 = t^2/2 + c_2$$

$$x^{-1} = -t^2/2 + (c_1 - c_2)$$

$$x(t) = -\frac{1}{\frac{t^2}{2} + (c_2 - c_1)} = -\frac{1}{t^2/2 + c}.$$

where $c = (c_2 - c_1)$.

Just to be on the safe side, let's verify that our solution satisfies the differential equation. We'll do it by substitution. On the left-hand side of the equation we have $\frac{dx}{dt}$, and on the right-hand side we have tx^2. We'll replace x by $-\frac{1}{t^2/2 + c}$ on both sides, and verify that the two sides are identical (the equality holds).

$$\frac{dx}{dt} = \frac{t}{(t^2/2 + c)^2}$$

$$x^2 t = \frac{t}{(t^2/2 + c)^2}$$

We just verified that the function $-\frac{1}{t^2/2 + c}$ satisfies $\frac{dx}{dt} = tx^2$, so we know our solution is correct!

This example is also available as a video: http://tinyurl.com/kxdfqxq

Watch an additional solved example. http://tinyurl.com/kem7e6h

External Links:

- Example 1: http://patrickjmt.com/separable-differential-equation-example-2
- Example 2: http://www.youtube.com/watch?v=76WdBlGpxVw
- Example 3: http://www.youtube.com/watch?v=3jpiW_oueaA

Linear 1st order ODEs

A general first-order linear ODE can be written

$$\frac{dy}{dx} + p(x)y = q(x) \tag{10.5.2.3}$$

Note that the linearity refers to the y and dy/dx terms, $p(x)$ and $q(x)$ do not need to be linear in x. You may need to reorganize terms around to write your equation in the form shown in Equation 10.5.2.3. For example, $dy = (8e^x - 3y)dx$ is linear, because it can be re-organized as

$$\frac{dy}{dx} + 3y = 8e^x \tag{10.5.2.4}$$

Comparing Equations 10.5.2.3 and 10.5.2.4, we see that in this case, $p(x) = 3$ and $q(x) = 8e^x$. In this example $p(x)$ is a constant, but this need not to be the case. The term $p(x)$ can be any function of x.

First order linear ODEs can be solved by multiplying by the integrating factor $e^{\int p(x)dx}$. This sounds very strange at first sight, but we will see how it works with the example of Equation 10.5.2.4.

Our very first step is to write the equation so it looks like Equation 10.5.2.3. We then calculate the integrating factor, in this case $e^{\int 3dx} = e^{3x}$. We next multiply both sides of the equation by the integrating factor:

$$\frac{dy}{dx}e^{3x} + 3ye^{3x} = 8e^x e^{3x} = 8e^{4x}$$

In the next step, we recognize that the left-hand side is the derivative of the dependent variable multiplied by the integrating factor:

$$\frac{dy}{dx}e^{3x} + 3ye^{3x} = \frac{d}{dx}(ye^{3x})$$

This last step is the multiplication rule in reverse. If you start with $\frac{d}{dx}(ye^{3x})$, you can apply the multiplication rule to obtain $\frac{dy}{dx}e^{3x} + 3ye^{3x}$. The whole point of calculating the integrating factor is that it guarantees that the left-hand side of the equation will always be the derivative of the dependent variable multiplied by the integrating factor. This will allow us to move dx to the right side, and integrate:

$$\frac{d}{dx}(ye^{3x}) = 8e^{4x}$$

$$d(ye^{3x}) = 8e^{4x}dx$$

$$\int d(ye^{3x}) = \int 8e^{4x}dx$$

The left-side of the above equation is $\int d(ye^{3x}) = ye^{3x}$, in the same way that $\int dy = y$. The right side is $\int 8e^{4x}dx = 2e^{4x} + c$. Note that we included the integration constant only on one side. This is because we already saw that if we included integration constants in both sides we could group them into a single constant.

So far we have

$$ye^{3x} = 2e^{4x} + c$$

Now we need to solve for the dependent variable, in this case $y(x)$. Dividing both terms by e^{3x}:

$$y = 2e^{x} + ce^{-3x}$$

which is the general solution of Equation 10.5.2.4. Before moving on let's verify that this function satisfies Equation 10.5.2.4 by substituting y by $y = 2e^{x} + ce^{-3x}$:

$$\frac{dy}{dx} = 2e^{x} - 3ce^{-3x}$$

$$3y = 6e^{x} + 3ce^{-3x}$$

$$\frac{dy}{dx} + 3y = 2e^{x} - 3ce^{-3x} + 6e^{x} + 3ce^{-3x} = 8e^{x}$$

which equals the right-hand side of Equation 10.5.2.4. This verifies that $y = 2e^{x} + ce^{-3x}$ is indeed the general solution of Equation 10.5.2.4. If we were given an initial condition we could calculate the value of c and obtain the particular solution.
Let's review and list the steps we used to find the solution of a linear 1st order ODE:

1. Re-arrange the terms so the equation has the form $\frac{dy}{dx} + p(x)y = q(x)$
2. Multiply both sides of the equation by the integrating factor $e^{\int p(x)dx}$
3. Recognize that the left-hand side can be written as $\frac{d}{dx}\left(ye^{\int p(x)dx}\right)$
4. Move dx to the right-hand side and integrate. Remember the integration constants!
5. Solve for the dependent variable
6. If given, use the initial condition to calculate the value of the arbitrary constant.
7. Verify your solution is correct by substitution into the differential equation.

> See another solved example to see this method in action: http://tinyurl.com/lzluktp
>
> External Links: http://www.youtube.com/watch?v=HAb9JbBD2ig

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10.5.3: Chemical Kinetics

The term chemical kinetics refers to the study of the rates of chemical reactions. As we will see, differential equations play a central role in the mathematical treatment of chemical kinetics. We will start with the simplest examples, and then we will move to more complex cases. As you will see, in this section we will focus on a couple of reaction mechanisms. The common theme will be to find expressions that will allow us to calculate the concentration of the different species that take part of the reaction at different reaction times.

Let's start with the simplest case, in which a reactant A reacts to give the product B. We'll assume the reaction proceeds in one step, meaning there are no intermediates that can be detected.

$$A \xrightarrow{k} B \tag{10.5.3.1}$$

We'll use the following notation for the time-dependent concentrations of A and B: [A](t), [B](t), or simply [A] and [B]. We'll use $[A]_0$ and $[B]_0$ to denote the concentrations of A and B at time $t = 0$. The constant k is the rate constant of the reaction, and is a measure of how fast or slow the reaction is. It depends on the reaction itself (the chemical compounds A and B) and environmental factors such as temperature. The rate constant does not depend on the concentrations of the species involved in the reaction. The units of k depend on the particular mechanism of the reaction, as we will see through the examples. For the case described above, the units will be 1/time (e.g. s^{-1})

The rate of the reaction (r) will be defined as the number of moles of A that disappear or the number of moles of B that appear per unit of time (e.g. per second) and volume (e.g. liter). This is true because of the stoichiometry of the reaction, as we will discuss in a moment. However, because the rate is a positive quantity, we will use a negative sign if we look at the disappearance of A:

$$r = -\frac{d[A]}{dt} = \frac{d[B]}{dt}$$

The rate of the reaction, therefore, is a positive quantity with units of M.s^{-1}, or in general, concentration per unit of time. As we will see, the rate of the reaction depends on the actual concentration of reactant, and therefore will in general decrease as the reaction progresses and the reactant is converted into product. Although all the molecules of A are identical, they do not need to react at the same instant. Consider the simple mechanism of Equation 10.5.3.1, and imagine that every molecule of A has a probability $p = 0.001$ of reacting in every one-second interval. Suppose you start with 1 mole of A in a 1 L flask ($[A]_0 = 1M$), and you measure the concentration of A one second later. How many moles of A do you expect to see? To answer this question, you can imagine that you get everybody in China (about one billion people) to throw a die at the same time, and that everybody who gets a six wins the game. How many winners do you expect to see? You know that the probability that each individual gets a six is $p = 1/6$, and therefore one-sixth of the players will win in one round of the game. Therefore, you can predict that the number of winers will be $10^9/6$, and the number of losers will be $5/6 \times 10^9$. If we get the losers to play a second round, we expect that one-sixth of them will get a six, which accounts for $5/6 \times 10^9 \times 1/6$ people. After the second run, therefore, we'll still have $(5/6)^2 \times 10^9$ losers.

Following the same logic, the probability that a molecule of A reacts to give B in each one-second interval is $= 1/1000$, and therefore in the first second you expect that $6 \times 10^{23}/1000$ molecules react and $999 \times 6 \times 10^{23}/1000$ remain unreacted. In other words, during the first second of your reaction 0.001 moles of A were converted into B, and therefore the rate of the reaction was $10^{-3}Ms^{-1}$. During the second one-second interval of the reaction you expect that one-thousand of the remaining molecules will react, and so on. Imagine that you come back one hour later (3,600 s). We expect that $(999/1000)^{3,600} \times 6 \times 10^{23}$ molecules will remain unreacted, which is about 1.6×10^{22} molecules. If you measure the reaction rate in the next second, you expect that one-thousand of them (1.6×10^{19} molecules, or 2.7×10^{-5} moles) will react to give B. The rate of the reaction, therefore, decreased from $10^{-3}Ms^{-1}$ at $t = 1s$ to $2.7 \times 10^{-5}Ms^{-1}$ at $t = 1h$. You should notice that the fraction of molecules of A that react in each one-second is always the same (in this case one-thousand). Therefore, the number of molecules that react per time interval is proportional to the number of molecules of A that remain unreacted at any given time. We just concluded that the rate of the reaction is proportional to the concentration of A:

$$r = -\frac{d[A]}{dt} = \frac{d[B]}{dt} = k[A] \tag{10.5.3.2}$$

The proportionality constant, k, is related to the probability that a molecule will react in a small time interval, as we discussed above. In this class, we will concentrate on solving differential equations such as the one above. This is a very simple differential equation that can be solved using different initial conditions. Let's say that our goal is to find both [A](t) and [B](t). As chemists, we need to keep in mind that the law of mass conservation requires that

$$[A](t) + [B](t) = [A]_0 + [B]_0 \tag{10.5.3.3}$$

In plain English, the concentrations of A and B at any time need to add up to the sum of the initial concentrations, as one molecule of A converts into B, and we cannot create or destroy matter. Again, keep in mind that this equation will need to be modified according to the stoichiometry of the reaction. We will call an equation of this type a 'mass balance'.

Before solving this equation, let's look at other examples. What are the differential equations that describe this sequential mechanism?

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

In this mechanism, A is converted into C through an intermediate, B. Everything we discussed so far will apply to each of these two elementary reactions (the two that make up the overall mechanism). From the point of view of A nothing changes. Because the rate of the first reaction does not depend on B, it is irrelevant that B is converted into C (imagine you give 1 dollar per day to a friend. It does not matter whether you friend saves the money or gives it to someone else, you still lose 1 dollar per day).

$$\frac{d[A]}{dt} = -k_1[A] \tag{10.5.3.4}$$

On the other hand, the rate of change of [B], $d[B]/dt$ is the sum of the rate at which B is created ($k_1[A]$), minus the rate at which it disappears by reacting into C ($k_2[B]$):

$$\frac{d[B]}{dt} = k_1[A] - k_2[B] \tag{10.5.3.5}$$

This can be read: The rate of change of [B] equals the rate at which [B] appears from A into B, minus the rate at which [B] disappears from B into C. In each term, the rate is proportional to the reactant of the corresponding step: A for the first reaction, and B for the second step.

What about C? Again, it is irrelevant that B was created from A (if you get 1 dollar a day from your friend, you don't care if she got it from her parents, you still get 1 dollar per day). The rate at which C appears is proportional to the reactant in the second step: B. Therefore:

$$\frac{d[C]}{dt} = k_2[B] \tag{10.5.3.6}$$

The last three equations form a system of differential equations that need to be solved considering the initial conditions of the problem (e.g. initially we have A but not B or C). We'll solve this problem in a moment, but we still need to discuss a few issues related to how we write the differential equations that describe a particular mechanism. Imagine that we are interested in

$$2A + B \xrightarrow{k} 3C$$

We know that the rate of a reaction is defined as the change in concentration with time...but which concentration? is it $d[A]/dt$? or $d[B]/dt$? or $d[C]/dt$? These are all different because 3 molecules of C are created each time 1 of B and 2 of A disappear. Which one should we use? Because 2 of A disappear every time 1 of B disappears: $d[A]/dt = 2d[B]/dt$. Now, considering that rates are positive quantities, and that the derivatives for the reactants, $d[A]/dt$ and $d[B]/dt$, are negative:

$$r = -\frac{1}{2}\frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{1}{3}\frac{d[C]}{dt}$$

This example shows how to deal with the stoichiometric coefficients of the reaction. Note that in all our examples we assume that the reactions proceed as written, without any 'hidden' intermediate steps.

First order reactions

We have covered enough background, so we can start solving the mechanisms we introduced. Let's start with the easiest one (Equations 10.5.3.1, 10.5.3.2 and 10.5.3.3):

$$A \xrightarrow{k} B$$

$$r = -\frac{d[A]}{dt} = \frac{d[B]}{dt} = k[A]$$

$$[A](t) + [B](t) = [A]_0 + [B]_0$$

This mechanism is called a first order reaction because the rate is proportional to the first power of the concentration of reactant. For a second-order reaction, the rate is proportional to the square of the concentration of reactant (see Problem 4.3). Let's start by finding $[A](t)$ from $-\frac{d[A]}{dt} = k[A]$. We'll then obtain$[B](t)$ from the mass balance. This is a very simple differential equation because it is separable:

$$-\frac{d[A]}{dt} = k[A]$$

$$\frac{d[A]}{[A]} = -kdt$$

We integrate both sides of the equation, and combine the two integration constants in one:

$$\ln [A] = -kt + c$$

We need to solve for [A]:

$$[A] = e^{-kt+c} = e^c e^{-kt} = c_2 e^{-kt}$$

This is the general solution of the problem. Let's assume we are giving the following initial conditions: [A]$(t = 0) = [A]_0$, [B]$(t = 0) = 0$. We'll use this information to find the arbitrary constant c_2:

$$[A](t = 0) = c_2 e^0 = c_2$$

Therefore, the particular solution is:

$$[A](t) = [A]_0 e^{-kt} \tag{10.5.3.7}$$

What about [B]? From the mass balance, [B] = $[A]_0$ + $[B]_0$ - [A] = $[A]_0$ - $[A]_0 e^{-kt} = [A]_0 (1 - e^{-kt})$].

Figure 10.5.3.4 shows three examples of decays with different rate constants.

We can calculate the half-life of the reaction ($t_{1/2}$), defined as the time required for half the initial concentration of A to react. From Equation 10.5.3.7:

$$\frac{[A](t)}{[A]_0} = e^{-kt}$$

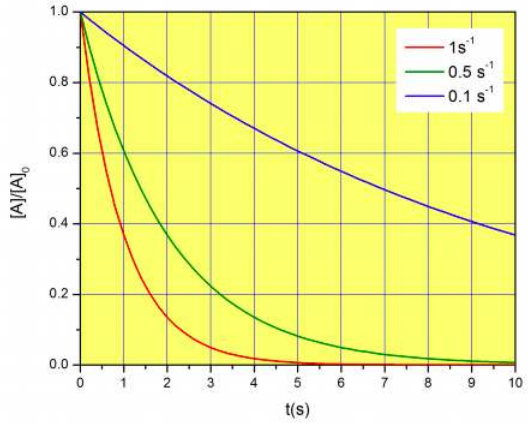


Figure 10.5.3.4: Time-dependent concentration of the reactant in the reaction $A \xrightarrow{k} B$ (CC BY-NC-SA; Marcia Levitus)

When $t = t_{1/2}$,

$$\frac{1}{2} = e^{-kt_{1/2}}$$

$$\ln 1/2 = -kt_{1/2} \rightarrow \ln 2 = kt_{1/2}$$

$$t_{1/2} = \frac{\ln 2}{k}$$

Note that in this case, the half-life does not depend on the initial concentration of A. This will not be the case for other types of mechanisms. Also, notice that we have already covered the concept of half-life in Chapter 1 (see Figure 1.3.1), so this might be a good time to read that section again and refresh what we have already learned about sketching exponential decays.

In physical chemistry, scientists often talk about the 'relaxation time' instead of the half-life. The relaxation time τ for a decay of the shape a^{-bt} is $1/b$, so in this case, the relaxation time is simply $1/k$. Notice that the relaxation time has units of time, and it represents the time at which the concentration has decayed to e^{-1} of its original value:

$$[A] = [A]_0 e^{-t/\tau} \rightarrow \frac{[A]}{[A]_0} = e^{-t/\tau} \xrightarrow{t=\tau} \frac{[A]}{[A]_0} = e^{-1} \approx 0.37$$

The half-life and relaxation time are compared in Figure 10.5.3.5 for a reaction with $k = 0.5s^{-1}$.

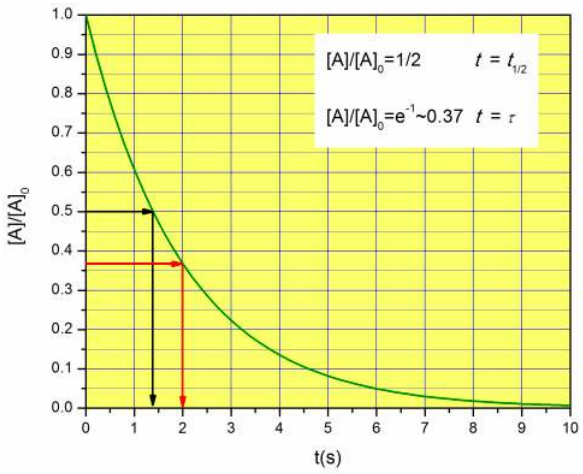


Figure 10.5.3.5: Half-life (black) and relaxation time (red) for the reaction $A \xrightarrow{k} B$ with $k = 0.5s^{-1}$ (CC BY-NC-SA; Marcia Levitus)

Consecutive First Order Processes

We will now analyze a more complex mechanism, which involves the formation of an intermediate species (B):

$$A \overset{k_1}{\rightarrow} B \overset{k_2}{\rightarrow} C$$

which is mathematically described by Equations 10.5.3.4, 10.5.3.5 and 10.5.3.6. Let's assume that initially the concentration of A is $[A]_0$, and the concentrations of B and C are zero. In addition, we can write a mass balance, which for these initial conditions is expressed as:

$$[A](t) + [B](t) + [C](t) = [A]_0$$

Let's summarize the equations we have:

$$\frac{d[A]}{dt} = -k_1[A] \tag{10.5.3.8}$$

$$\frac{d[B]}{dt} = k_1[A] - k_2[B] \tag{10.5.3.9}$$

$$\frac{d[C]}{dt} = k_2[B] \tag{10.5.3.10}$$

$$[A] + [B] + [C] = [A]_0 \tag{10.5.3.11}$$

$$[A](t=0) = [A]_0 \tag{10.5.3.12}$$

$$[B](t=0) = [C](t=0) = 0 \tag{10.5.3.13}$$

Note that Equation 10.5.3.11 is not independent from Equations 10.5.3.8-10.5.3.10. If you take the derivative of 10.5.3.11 you get $d[A]/dt + d[B]/dt + d[C]/dt = 0$, which is the same you get if you add Equations 10.5.3.8-10.5.3.10. This means that Equations 10.5.3.8-10.5.3.11 are not all independent, and three of them are enough for us to solve the problem. As you will see, the mass balance (10.5.3.11) will give us a very easy way of solving for [C] once we have [A] and [B], so we will use it instead of Equation 10.5.3.10.

We need to solve the system of Equations 10.5.3.8-10.5.3.13, and although there are methods to solve systems of differential equations (e.g. using linear algebra), this one is easy enough that can be solved with what we learned so far. This is because not all equations contain all variables. In particular, Equation 10.5.3.8 is a simple separable equation with dependent variable [A], which can be solved independently of [B] and [C]. We in fact just solved this equation in the First Order Reactions section, so let's write down the result:

$$[A](t) = [A]_0 e^{-k_1 t} \tag{10.5.3.14}$$

Equation 10.5.3.9 contains two dependent variables, but luckily we just obtained an expression for one of them. We can now re-write 10.5.3.9 as:

$$\frac{d[B]}{dt} = k_1[A]_0 e^{-k_1 t} - k_2[B] \tag{10.5.3.15}$$

Equation 10.5.3.15 contains only one dependent variable, [B], one independent variable, t, and three constants: k_1, k_2 and $[A]_0$. This is therefore an ordinary differential equation, and if it is either separable or linear, we will be able to solve it with the techniques we learned in this chapter. Recall eq. [sep], and verify that Equation 10.5.3.15 cannot be separated as

$$\frac{d[B]}{dt} = \frac{g([B])}{h(t)}$$

Equation 10.5.3.15 is not separable. Is it linear? Recall Equation ??? and check if you can write this equation as $\frac{d[B]}{dt} + p(t)[B] = q(t)$. We in fact can:

$$\frac{d[B]}{dt} + k_2[B] = k_1[A]_0 e^{-k_1 t} \tag{10.5.3.16}$$

Let's use the list of steps delineated in Section 4.2. We need to calculate the integrating factor, $e^{\int p(x)dx}$, which in this case is $e^{\int k_2 dt} = e^{k_2 t}$. We then multiply Equation 10.5.3.16 by the integrating factor:

$$\frac{d[B]}{dt} e^{k_2 t} + k_2[B] e^{k_2 t} = k_1[A]_0 e^{-k_1 t} e^{k_2 t} = k_1[A]_0 e^{(k_2 - k_1)t}$$

In the next step, we need to recognize that the left-hand side of the equation is the derivative of the product of the dependent variable times the integrating factor:

$$\frac{d}{dt}\left([B]e^{k_2 t}\right) = k_1[A]_0 e^{(k_2-k_1)t}$$

We then take 'dt' to the right side of the equation and integrate both sides:

$$\int d\left([B]e^{k_2 t}\right) = \int k_1[A]_0 e^{(k_2-k_1)t}dt$$

$$[B]e^{k_2 t} = \frac{1}{k_2-k_1}k_1[A]_0 e^{(k_2-k_1)t} + c$$

$$[B] = \frac{1}{k_2-k_1}k_1[A]_0\frac{e^{(k_2-k_1)t}}{e^{k_2 t}} + \frac{c}{e^{k_2 t}}$$

$$[B] = \frac{k_1}{k_2-k_1}[A]_0 e^{-k_1 t} + ce^{-k_2 t}$$

We have an arbitrary constant because this is a first order differential equation. Let's calculate c using the initial condition $[B](t=0) = 0$:

$$0 = \frac{k_1}{k_2-k_1}[A]_0 e^{-k_1 0} + ce^{-k_2 0} = \frac{k_1}{k_2-k_1}[A]_0 + c$$

$$c = -\frac{k_1}{k_2-k_1}[A]_0$$

And therefore,

$$[B] = \frac{k_1}{k_2-k_1}[A]_0 e^{-k_1 t} - \frac{k_1}{k_2-k_1}[A]_0 e^{-k_2 t}$$

$$[B] = \frac{k_1}{k_2-k_1}[A]_0\left(e^{-k_1 t} - e^{-k_2 t}\right) \tag{10.5.3.17}$$

Before moving on, notice that we have assumed that $k_1 \neq k_2$. We were not explicit, but we performed the integration with this assumption. If $k_1 = k_2$ the exponential term becomes 1, which is not a function of t. In this case, the integral will obviously be different, so our answer assumes $k_1 \neq k_2$. This is good news, since otherwise we would need to worry about the denominator of [eq:b(t)] being zero. You will solve the case $k_1 = k_2$ in Problem 4.4.

Now that we have [A] and [B], we can get the expression for [C]. We could use Equation 10.5.3.10:

$$\frac{d[C]}{dt} = k_2[B] = \frac{k_2 k_1}{k_2-k_1}[A]_0\left(e^{-k_1 t} - e^{-k_2 t}\right)$$

This is not too difficult because the equation is separable. However, it is easier to get [C] from the mass balance, Equation 10.5.3.11:

$$[C] = [A]_0 - [A] - [B]$$

Plugging the answers we got for [A] and [B]:

$$[C] = [A]_0 - [A]_0 e^{-k_1 t} - \frac{k_1}{k_2-k_1}[A]_0\left(e^{-k_1 t} - e^{-k_2 t}\right)$$

$$[C] = [A]_0\left[1 - e^{-k_1 t} - \frac{k_1}{k_2-k_1}\left(e^{-k_1 t} - e^{-k_2 t}\right)\right] \tag{10.5.3.18}$$

Equations 10.5.3.14, 10.5.3.17, 10.5.3.18 are the solutions we were looking for. If we had the values of k_1 and k_2 we could plot $[A](t)/[A]_0$, $[B](t)/[A]_0$ and $[C](t)/[A]_0$ and see how the three species evolve with time. If we had $[A]_0$ we could plot the actual concentrations, but notice that this does not add too much, because it just re-scales the $y-$axis but does not change the shape of the curves.

Figure 10.5.3.6 shows the concentration profiles for a reaction with $k_1 = 0.1s^{-1}$ and $k_2 = 0.5s^{-1}$. Notice that because B is an intermediate, its concentration first increases, but then decreases as B is converted into C. The product C has a 'lag phase', because we need to wait until enough B is formed before we can see the concentration of C increase (first couple of seconds in this example). As you will see after solving your homework problems, the time at which the intermediate (B) achieves its maximum concentration depends on both k_1 and k_2.

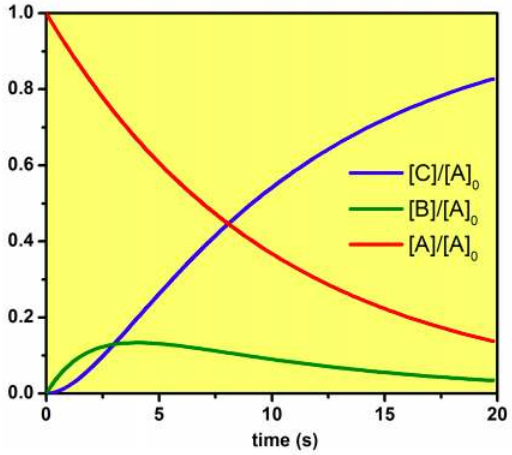


Figure 10.5.3.6: Concentration profiles for the reaction $A \xrightarrow{k_1} B \xrightarrow{k_2} C$ with $k_1 = 0.1s^{-1}$ and $k_2 = 0.5s^{-1}$ (CC BY-NC-SA; Marcia Levitus)

Reversible first order reactions

So far we have discussed irreversible reactions. Yet, we know that many reactions are reversible, meaning that the reactant and product exist in equilibrium:

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B$$

The rate of change of [A], $\frac{d[A]}{dt}$, is the rate at which A appears ($k_2[B]$) minus the rate at which A disappears ($k_1[A]$):

$$\frac{d[A]}{dt} = k_2[B] - k_1[A]$$

We cannot solve this equation as it is, because it has two dependent variables, [A] and [B]. However, we can write [B] in terms of [A], or [A] in terms of [B], by using the mass balance:

$$[A](t) + [B](t) = [A]_0 + [B]_0$$

$$\frac{d[A]}{dt} = k_2\left([A]_0 + [B]_0 - [A]\right) - k_1[A]$$

$$\frac{d[A]}{dt} = k_2\left([A]_0 + [B]_0\right) - \left(k_2 + k_1\right)[A]$$

This is an ordinary, separable, first order differential equation, so it can be solved by direct integration. You will solve this problem in your homework, so let's skip the steps and jump to the answer:

$$[A] = \frac{k_2\left([A]_0 + [B]_0\right)}{k_1 + k_2} + \frac{k_1[A]_0 - k_2[B]_0}{k_1 + k_2} e^{-(k_1+k_2)t} \tag{10.5.3.19}$$

This is a reversible reaction, so if we wait long enough it will reach equilibrium The concentration of [A] in equilibrium, $[A]_{eq}$, is the limit of the previous expression when $t \to \infty$. Because $e^{-x} \to 0$ when $x \to \infty$:

$$[A]_{eq} = \frac{k_2\left([A]_0 + [B]_0\right)}{k_1 + k_2}$$

and we can re-write Equation 10.5.3.19 as

$$[A] = [A]_{eq} + ([A]_0 - [A]_{eq})\, e^{-(k_1+k_2)t} \tag{10.5.3.20}$$

As you will do in your homework, we can calculate $[B](t)$ from the mass balance as $[B](t) = [A]_0 + [B]_0 - [A](t)$.

Equation 10.5.3.20 is not too different from Equation 10.5.3.7. In the case of an irreversible reaction, (Equation 10.5.3.7), [A] decays from an initial value $[A]_0$ to a final value $[A]_{t\to\infty} = 0$ with a relaxation time $\tau = 1/k$. For the reversible reaction, $[A] - [A]_{eq}$ decays from an initial value $[A]_0 - [A]_{eq}$ to a final value $[A]_{t\to\infty} - [A]_{eq} = 0$ with a relaxation time $\tau = (k_1 + k_2)^{-1}$. This last statement is not trivial! It says that the rate at which a reaction approaches equilibrium depends on the sum of the forward and backward rate constants.

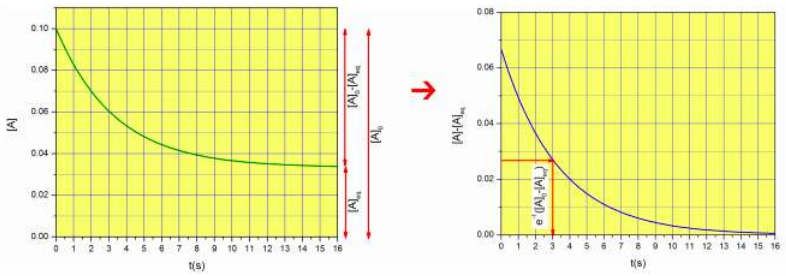


Figure 10.5.3.7: The kinetics of a reaction with $[A]_0 = 0.1M$, $k_1 = 0.1s^{-1}$ and $k_2 = 0.2s^{-1}$ approaching equilibrium. Note that the relaxation time is $3s = (k_1 + k_2)^{-1}$ (CC BY-NC-SA; Marcia Levitus)

In your homework you will be asked to prove that the ratio of the concentrations in equilibrium, $[B]_{eq}/[A]_{eq}$ is equal to the ratio of the forward and backwards rate constants. In addition, from your introductory chemistry courses you should know that the equilibrium constant of a reaction (K_{eq}) is the ratio of the equilibrium concentrations of product of reactant. Therefore:

$$\frac{[B]_{eq}}{[A]_{eq}} = K_{eq} = \frac{k_1}{k_2} \tag{10.5.3.21}$$

This means that we can calculate the ratio of k_1 and k_2 from the concentrations of A and B we observe once equilibrium has been reached (i.e. once $\frac{d[A]}{dt} = \frac{d[B]}{dt} = 0$). At the same time, we can obtain the sum of k_1 and k_2 from the relaxation time of the process. If we have the sum and the ratio, we can calculate both k_1 and k_2. This all makes sense, but it requires that we can watch the reaction from an initial state outside equilibrium. If the system is already in equilibrium, $[A]_0 = [A]_{eq}$, and $d[A]/dt = 0$ at all times. A plot of [A](t) will look flat, and we will not be able to extract the relaxation time of the reaction. If, however, we have an experimental way of shifting the equilibrium so $[A]_0 \neq [A]_{eq}$, we can measure the relaxation time by observing how the reaction returns to its equilibrium position.

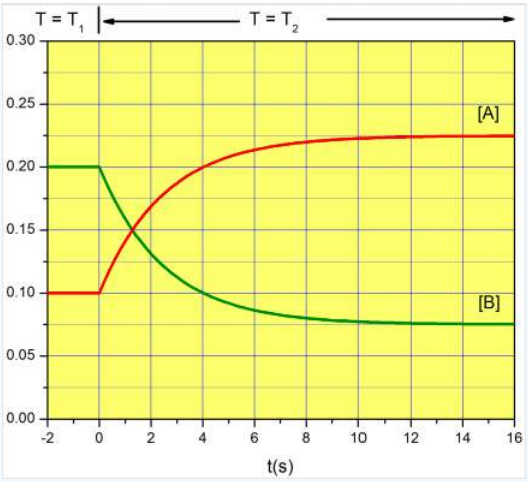
Advanced topic: How can we shift the equilibrium? One way is to produce a very quick change in the temperature of the system. The equilibrium constant of a reaction usually depends on temperature, so if a system is equilibrated at a given temperature (say $25°C$), and we suddenly increase the temperature (e.g. to $26°C$), the reaction will suddenly be away from its equilibrium condition at the new temperature. We can watch the system relax to the equilibrium concentrations at $26°C$, and measure the relaxation time. This will allow us to calculate the rate constants at $26°C$.

$$\frac{[B]_{eq}}{[A]_{eq}} = K_{eq} = \frac{k_1}{k_2}$$

Example 10.5.3.1

Advanced topic The following figure illustrates the experimental procedure known as “T-jump”, in which a sudden change in temperature is used to shift the position of a reversible reaction out of equilibrium. The experiment starts at a temperature T_1, and the temperature is increased to T_2 instantaneously at time $t = 0$. Because the equilibrium constant at T_2 is different from the equilibrium constant at T_1, the system needs to relax to the new equilibrium state. From the graph below estimate to the best of your abilities $K_{eq}(T_1)$, $K_{eq}(T_2)$, and the rate constants k_1, and k_2 at T_2.

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B$$



Solution

At T_1, $[A]_{eq} = 0.1M$ and $[B]_{eq} = 0.2M$. The equilibrium constant is $[B]_{eq}/[A]_{eq} = 2$.

At T_2, $[A]_{eq} = 0.225M$ and $[B]_{eq} = 0.075M$. The equilibrium constant is $[B]_{eq}/[A]_{eq} = 1/3$.

Because $K_{eq} = \frac{k_1}{k_2}$, at $T = T_2$, $\frac{k_1}{k_2} = 1/3$. To calculate the relaxation time let's look at the expression for $[A](t)$ (Equation 10.5.3.20).

$$[A] = [A]_{eq} + ([A]_0 - [A]_{eq})\, e^{-(k_1+k_2)t}$$

When the time equals the relaxation time ($\tau = (k_1 + k_2)^{-1}$),

$$[A](t = \tau) = [A]_{eq} + ([A]_0 - [A]_{eq})\, e^{-1}$$

$$[A](t = \tau) \approx 0.225M + (0.1M - 0.225M) \times 0.37 \approx 0.18$$

1

From the graph, $[A] = 0.18$ at $t = 2.5s$, and therefore the relaxation time is $\tau = (k_1 + k_2)^{-1} = 2.5s$.

We have $(k_1 + k_2)^{-1} = 2.5s = 5/2s$ and $\frac{k_1}{k_2} = 1/3$:

$$(k_1 + k_2) = 2/5 = (k_1 + 3k_1) = 4k_1 \rightarrow k_1 = 1/10 = 0.1s^{-1}, k_2 = 0.3s^{-1}$$

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10.5.4: Problems

Problem 10.5.4.1

In each case,

- Identify the dependent and independent variables.
- Determine if the differential equation is separable.
- Determine if the differential equation is linear.
- Find the general solution.
- Find the particular solution using the given initial condition.
- Verify that your solution satisfies the differential equation by substitution.

1. $\frac{dy}{dx} = \frac{y+2}{x-3}, y(0) = 1$
2. $x' = e^{x+t}, x'(0) = 2$
3. $\frac{dy}{dx} - \frac{3}{x}y = 2x^4, y(1) = 1$
4. $\frac{df}{dt} = \frac{3t^2}{f}, f(2) = 4$
5. $h'(t) + 2h(t) = 4, h(0) = 1$

Problem 10.5.4.2

Consider the reaction $A \xrightarrow{k} B$. The rate of disappearance of A is proportional to the concentration of A, so:

$$-\frac{d[A]}{dt} = k[A]$$

1) Obtain [A](t) and [B](t).

2) Using the definition of half-life $(t_{1/2})$, obtain an expression for $(t_{1/2})$ for this mechanism. Your result will be a function of k.

3) Sketch $[A](t)$ and $[B](t)$ for the case $k = 0.1s^{-1}$, $[B]_0 = 0$ and $[A]_0 = 10^{-3}M$. Remember that you are expected to do this without the help of a calculator.

Problem 10.5.4.3

Consider the reaction $2A \xrightarrow{k} B$. This mechanism is called a bi-molecular reaction, because the reaction involves the collision of two molecules of reactant. In this case, the rate of disappearance of A is proportional to the square of the concentration of A, so:

$$-\frac{1}{2}\frac{d[A]}{dt} = k[A]^2$$

Notice that the rate is proportional to the square of the concentration, so this is a second-order reaction.
Assume that the initial concentration of [A] is $[A]_0$, and the initial concentration of [B] is zero.

1. Obtain an expression for [A](t).
2. Write down a mass balance (a relationship relating [A](t), [B](t), $[A]_0$ and $[B]_0$) and obtain [B](t).
3. Using the definition of half-life $(t_{1/2})$, obtain an expression for $(t_{1/2})$ for this mechanism. Your result will be a function of k and $[A]_0$.

Problem 10.5.4.4

Obtain $[A](t), [B](t)$, and$[C](t)$ for the following mechanism:

$$A \xrightarrow{k} B \xrightarrow{k} C$$

Assume $[A](0) = [A]_0$, and $[B](0) = [C](0) = 0$

Note that this problem is identical to the one solved in Section 4.2 but with $k_1 = k_2$. Be sure you identify the step where the two problems become different.

? Problem 10.5.4.5

Consider the reaction

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B$$

modeled mathematically by the following ODE

$$\frac{d[A]}{dt} = k_2[B] - k_1[A]$$

The constants, k_1 and k_2 represent the kinetic constants in the forward and backward direction respectively, and [A] and [B] represent the molar concentration of A and B. Assume you start with initial concentrations $[A](t = 0) = [A]_0$ and $[B](t = 0) = [B]_0$.

Mass conservation requires that $[A](t) + [B](t) = [A]_0 + [B]_0$

1. Obtain [A](t) and [B](t) in terms of $k_1, k_2, [A]_0$ and $[B]_0$.
2. Obtain expressions for the concentrations of A and B in equilibrium: $[A]_{eq} = [A](t \to \infty)$ and $[B]_{eq} = [B](t \to \infty)$.
3. Prove that the equilibrium constant of the reaction, $\frac{[B]_{eq}}{[A]_{eq}} = K_{eq}$, can be expressed as

$$\frac{[B]_{eq}}{[A]_{eq}} = \frac{k_1}{k_2}$$

4. Assume that $k_1 = 1 min^{-1}$, $k_2 = \frac{1}{2} min^{-1}$, $[A]_0 = 0$ and $[B]_0 = 0.1M$, calculate $[A]_{eq}$ and $[B]_{eq}$, and sketch $[A](t)$ and $[B](t)$ to the best of your abilities.

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SECTION OVERVIEW

10.6: Second Order Ordinary Differential Equations

Chapter Objectives

- Be able to obtain the general solution of any homogeneous second order ODE with constant coefficients.
- Be able to obtain particular solutions when initial conditions are given.
- Understand how to solve the equation of motion of a pendulum and a spring in non-viscous and viscous media.
- Understand how to solve the Schrödinger equation for the one dimensional particle in the box. Obtain the normalized eigenfunctions and the eigenvalues.

10.6.1: Second Order Ordinary Differential Equations

10.6.2: Second Order Ordinary Differential Equations - Oscillations

10.6.3: Second Order Ordinary Differential Equations with Boundary Conditions

10.6.4: An example in Quantum Mechanics

10.6.5: Problems

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10.6.1: Second Order Ordinary Differential Equations

Solving second order ordinary differential equations is much more complex than solving first order ODEs. We just saw that there is a general method to solve any linear 1st order ODE. Unfortunately, this is not true for higher order ODEs. However, we can solve higher order ODEs if the coefficients are constants:

$$y''(x) + k_1 y'(x) + k_2 y(x) + k_3 = 0$$

The equation above is said to be homogeneous if $k_3 = 0$:

$$y''(x) + k_1 y'(x) + k_2 y(x) = 0 \tag{10.6.1.1}$$

It is possible to solve non-homogeneous ODEs, but in this course we will concentrate on the homogeneous cases. Second order linear equations occur in many important applications. For example, the motion of a mass on a spring, and any other simple oscillating system, is described by an equation of the form

$$m\frac{d^2u}{dt^2} + \gamma\frac{du}{dt} + ku = F(t)$$

We'll analyze what the different parts of this equation mean in the examples. The equation above is homogeneous if $F(t) = 0$.

Let's analyze Equation 10.6.1.1, which is linear and homogeneous. The parameters m, γ and k represent physical quantities that do not depend on the value of x, and therefore the equation has constant coefficients.This equation will be satisfied by a function whose derivatives are multiples of itself. This is the only way that we will get zero after adding a multiple of the function plus a multiple of its first derivative plus a multiple of the second derivative. You may be tempted to say that $\sin(x)$ satisfies this requirement, but its first derivative is $\cos x$, so it will not cancel out with the sine term when added together. The only functions that satisfy this requirement are the expnential functions $e^{\alpha x}$, with first and second derivatives $\alpha e^{\alpha x}$ and $\alpha^2 e^{\alpha x}$ respectively. So, let's assume that the answer we are looking for is an exponential function, $y(x) = e^{\alpha x}$, and let's plug these expressions back into Equation 10.6.1.1:

$$\alpha^2 e^{\alpha x} + k_1 \alpha e^{\alpha x} + k_2 e^{\alpha x} = 0$$

$$e^{\alpha x}\left(\alpha^2 + k_1\alpha + k_2\right) = 0$$

Thee above equation tells us that either $e^{\alpha x}$ or $\left(\alpha^2 + k_1\alpha + k_2\right)$ are zero. In the first case, this would mean that x is plus or minus infinity (depending on whether α is negative or positive). But this is too restrictive because we want to find a solution that is a function of x, so we don't want to impose restrictions on our independent variable. We therefore consider

$$\left(\alpha^2 + k_1\alpha + k_2\right) = 0$$

This is a quadratic equation in α, which we will call the auxiliary equation. The two roots are found from:

$$\alpha_{1,2} = \frac{-k_1 \pm \sqrt{k_1^2 - 4k_2}}{2}$$

This gives two answers, α_1 and α_2, which means there are at least two different exponential functions that are solutions of the differential equation: $e^{\alpha_1 x}$ and $e^{\alpha_2 x}$. We will see that any linear combination of these two functions is also a solution, but before continuing, let's look at a few examples. Notice that the argument of the square root can be positive, negative or zero, depending on the relative values of k_1 and k_2. This means that $\alpha_{1,2}$ can be imaginary, and the solutions can therefore be complex exponentials. Let's look at the three situations individually through examples.

Case I: $k_1^2 - 4k_2 > 0$

In this case, $\sqrt{k_1^2 - 4k_2} > 0$, and therefore α_1 and α_2 are both real and different.

For example: Find the solution of $y''(x) - 5y'(x) + 4y(x) = 0$ subject to initial conditions $y(0) = 1$ and $y'(0) = -1$.

As we discussed above, we'll assume the solution is $y(x) = e^{\alpha x}$, and we'll determine which values of α satisfy this particular differential equation. Let's replace $y(x), y'(x)$ and $y''(x)$ in the differential equation:

$$\alpha^2 e^{\alpha x} - 5\alpha e^{\alpha x} + 4e^{\alpha x} = 0$$

$$e^{\alpha x}\left(\alpha^2 - 5\alpha + 4\right) = 0$$

and with the arguments we discussed above:

$$\left(\alpha^2 - 5\alpha + 4\right) = 0$$

$$\alpha_{1,2} = \frac{-(-5) \pm \sqrt{(-5)^2 - 4 \times 4}}{2}$$

from which we obtain $\alpha_1 = 1$ and $\alpha_2 = 4$. Therefore, e^x and e^{4x} are both solutions to the differential equation. Let's prove this is true. If $y(x) = e^{4x}$, then $y'(x) = 4e^{4x}$ and $y''(x) = 16e^{4x}$. Substituting these expressions in the differential equation we get

$$y''(x) - 5y'(x) + 4y(x) = 16e^{4x} - 5 \times 4e^{4x} + 4 \times e^{4x} = 0$$

so $y(x) = e^{4x}$ clearly satisfies the differential equation. You can do the same with $y(x) = e^x$ and prove it is also a solution.

However, none of these solutions satisfy both initial conditions, so clearly we are not finished. We found two independent solutions to the differential equation, and now we will claim that any linear combination of these two independent solutions ($c_1 y_1(x) + c_2 y_2(x)$) is also a solution. Mathematically, this means that if $y_1(x)$ and $y_2(x)$ are solutions, then $c_1 y_1(x) + c_2 y_2(x)$ is also a solution, where c_1 and c_2 are constants (i.e. not functions of x). Coming back to our example, the claim is that $c_1 e^{4x} + c_2 e^x$ is the general solution of this differential equation. Let's see if it's true:

$$\begin{aligned} y(x) &= c_1 e^{4x} + c_2 e^x \\ y'(x) &= 4c_1 e^{4x} + c_2 e^x \\ y''(x) &= 16c_1 e^{4x} + c_2 e^x \end{aligned}$$

Substituting in the differential equation:

$$y''(x) - 5y'(x) + 4y(x) = 16c_1 e^{4x} + c_2 e^x - 5 \times \left(4c_1 e^{4x} + c_2 e^x\right) + 4 \times \left(c_1 e^{4x} + c_2 e^x\right) = 0$$

so we just proved that the linear combination is also a solution, independently of the values of c_1 and c_2. It is important to notice that our general solution has now two arbitrary constants, as expected for a second order differential equation. We will determine these constants from the initial conditions to find the particular solution.

The general solution is $y(x) = c_1 e^{4x} + c_2 e^x$. Let's apply the first initial condition: $y(0) = 1$.

$$y(0) = c_1 + c_2 = 1$$

This gives a relationship between c_1 and c_2. The second initial condition is $y'(0) = -1$.

$$y'(x) = 4c_1 e^{4x} + c_2 e^x \rightarrow y'(0) = 4c_1 + c_2 = -1$$

We have two equations with two unknowns that we can solve to get $c_1 = -2/3$ and $c_2 = 5/3$.

The particular solution is then:

$$y(x) = -\frac{2}{3} e^{4x} + \frac{5}{3} e^x$$

Case II: $k_1^2 - 4k_2 < 0$

In this case, $k_1^2 - 4k_2 < 0$, so , $\sqrt{k_1^2 - 4k_2} = i\sqrt{-k_1^2 + 4k_2}$ where $\sqrt{-k_1^2 + 4k_2}$ is a real number. Therefore, in this case,

$$\alpha_{1,2} = \frac{-k_1 \pm \sqrt{k_1^2 - 4k_2}}{2} = \frac{-k_1 \pm i\sqrt{-k_1^2 + 4k_2}}{2}$$

and then the two roots α_1 and α_2 are complex conjugates. Let's see how it works with an example.

Determine the solution of $y''(x) - 3y'(x) + \frac{9}{2}y(x) = 0$ subject to the initial conditions $y(0) = 1$ and $y'(0) = -1$.

Following the same methodology we discussed for the previous example, we assume $y(x) = e^{\alpha x}$, and use this expression in the differential equation to obtain a quadratic equation in α:

$$\alpha_{1,2} = \frac{3 \pm \sqrt{(-3)^2 - 4 \times 9/2}}{2} = \frac{3 \pm \sqrt{-9}}{2}$$

Therefore, $\alpha_1 = \frac{3}{2} + \frac{3}{2}i$ and $\alpha_2 = \frac{3}{2} - \frac{3}{2}i$, which are complex conjugates. The general solution is:

$$y(x) = c_1 e^{(\frac{3}{2}+\frac{3}{2}i)x} + c_2 e^{(\frac{3}{2}-\frac{3}{2}i)x}$$
$$y(x) = c_1 e^{\frac{3}{2}x} e^{\frac{3}{2}ix} + c_2 e^{\frac{3}{2}x} e^{-\frac{3}{2}ix}$$
$$y(x) = e^{\frac{3}{2}x}\left(c_1 e^{\frac{3}{2}ix} + c_2 e^{-\frac{3}{2}ix}\right)$$

This expression can be simplified using Euler's formula: $e^{\pm ix} = \cos(x) \pm i \sin x$ (Equation 2.2.1).

$$y(x) = e^{\frac{3}{2}x}\left[c_1\left(\cos(\frac{3}{2}x) + i\sin(\frac{3}{2}x)\right) + c_2\left(\cos(\frac{3}{2}x) - i\sin(\frac{3}{2}x)\right)\right]$$

Grouping the sines and cosines together:

$$y(x) = e^{\frac{3}{2}x}\left[\cos(\frac{3}{2}x)(c_1 + c_2) + i\sin(\frac{3}{2}x)(c_1 - c_2)\right]$$

Renaming the constants $c_1 + c_2 = a$ and $i(c_1 - c_2) = b$

$$y(x) = e^{\frac{3}{2}x}\left[a\cos(\frac{3}{2}x) + b\sin(\frac{3}{2}x)\right]$$

Our general solution has two arbitrary constants, as expected from a second order ODE. As usual, we'll use our initial conditions to determine their values. The first initial condition is $y(0) = 1$

$$y(0) = a = 1 \quad (e^0 = 1, \cos(0) = 1 \quad \text{and} \quad \sin(0) = 0)$$

So far, we have

$$y(x) = e^{\frac{3}{2}x}\left[\cos(\frac{3}{2}x) + b\sin(\frac{3}{2}x)\right]$$

The second initial condition is $y'(0) = -1$

$$y'(x) = e^{\frac{3}{2}x}\left[-\sin(\frac{3}{2}x) + b\cos(\frac{3}{2}x)\right]\frac{3}{2} + \frac{3}{2}e^{\frac{3}{2}x}\left[\cos(\frac{3}{2}x) + b\sin(\frac{3}{2}x)\right]$$

$$y'(0) = \frac{3}{2}b + \frac{3}{2} = -1 \rightarrow b = -\frac{5}{3}$$

The particular solution is, therefore:

$$y(x) = e^{\frac{3}{2}x}\left[\cos(\frac{3}{2}x) - \frac{5}{3}\sin(\frac{3}{2}x)\right]$$

Notice that the function is real even when the roots were complex numbers.

Case III: $k_1^2 - 4k_2 = 0$

The last case we will analyze is when $k_1^2 - 4k_2 = 0$, which results in

$$\alpha_{1,2} = \frac{-k_1 \pm \sqrt{k_1^2 - 4k_2}}{2} = \alpha_{1,2} = \frac{-k_1}{2}$$

Therefore, the two roots are real, and identical. This means that $e^{-k_1 x/2}$ is a solution, but this creates a problem because we need another independent solution to create the general solution from a linear combination, and we have only one. The second solution can be found using a method called reduction of order. We will not discuss the method in detail, although you can see how it is used in this case at the end of the video http://tinyurl.com/mpl69ju. The application of the method of reduction of order to this differential equation gives $(a + bx)e^{-k_1 x/2}$ as the general solution. The constants a and b are arbitrary constants that we will determine from the initial/boundary conditions. Notice that the exponential term is the one we found using the 'standard' procedure. Let's see how it works with an example.

Determine the solution of $y''(x) - 8y'(x) + 16y(x) = 0$ subject to initial conditions $y(0) = 1$ and $y'(0) = -1$.

We follow the procedure of the previous examples and calculate the two roots:

$$\alpha_{1,2} = \frac{-k_1 \pm \sqrt{k_1^2 - 4k_2}}{2} = \frac{8 \pm \sqrt{8^2 - 4 \times 16}}{2} = 4$$

Therefore, e^{4x} is a solution, but we don't have another one to create the linear combination we need. The method of reduction of order gives:

$$y(x) = (a + bx)e^{4x}$$

Since we accepted the result of the method of reduction of order without seeing the derivation, let's at least show that this is in fact a solution. The first and second derivatives are:

$$y'(x) = be^{4x} + 4(a + bx)e^{4x}$$

$$y''(x) = 4be^{4x} + 4be^{4x} + 16(a + bx)e^{4x}$$

Substituting these expressions in $y''(x) - 8y'(x) + 16y(x) = 0$:

$$\left[4be^{4x} + 4be^{4x} + 16(a + bx)e^{4x}\right] - 8\left[be^{4x} + 4(a + bx)e^{4x}\right] + 16\left[(a + bx)e^{4x}\right] = 0$$

Because all these terms cancel out to give zero, the function $y(x) = (a + bx)e^{4x}$ is indeed a solution of the differential equation.

Coming back to our problem, we need to determine a and b from the initial conditions. Let's start with $y(0) = 1$:

$$y(0) = a = 1$$

So far, we have $y(x) = (1 + bx)e^{4x}$, and therefore $y'(x) = be^{4x} + 4(1 + bx)e^{4x}$. The other initial condition is $y'(0) = -1$:

$$y'(0) = b + 4 = -1 \rightarrow b = -5$$

The particular solution, therefore, is $y(x) = (1 - 5x)e^{4x}$

> This video contains an example of each of the three cases discussed above as well as the application of the method of reduction of order to case III. Remember that you can pause, rewind and fast forward so you can watch the videos at your own pace. http://tinyurl.com/mpl69ju

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10.6.2: Second Order Ordinary Differential Equations - Oscillations

> Note
>
> This section is also available in video format: http://tinyurl.com/kq7mrcq

The motion of a frictionless pendulum

We will now use what we learned so far to solve a problem of relevance in the physical sciences. We'll start with the problem of the pendulum, and as we already discussed in Section 3.2, even if the pendulum is not particularly interesting as an application in chemistry, the topic of oscillations is of great interest due to the fact that atoms in molecules vibrate around their bonds.

The problem of the pendulum was introduced in Figure 3.5, which is reprinted again below:

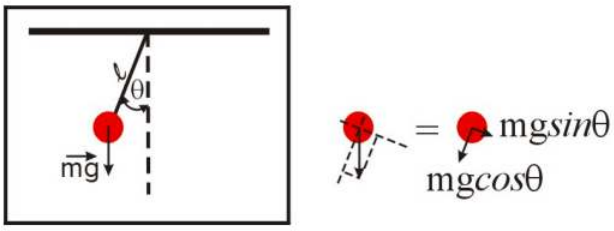


Figure **10.6.2.1**: A rigid pendulum with massless and inextensible cord of length l. The motion is assumed to occur in two dimensions, and the friction is assumed to be negligible. The mass of the object is m, and g is the acceleration due to gravity. (CC BY-NC-SA; Marcia Levitus)

If you took a university physics course, you may recognize that Newton's second law yields:

$$ml\frac{d^2\theta}{dt^2} + mg\sin\theta = 0 \tag{10.6.2.1}$$

This, unfortunately, is a non-linear differential equation (the dependent variable, θ, appears as the argument of a transcendental function). As we discussed in Section 3.2, this ODE has no analytical solution. It is possible to solve this equation numerically (and you will do it in the lab), but we cannot get an equation that is the solution of this ODE. We also discussed that we can obtain analytical solutions if we assume that the angle θ is small at all times. This means that the solution we get is valid only if the pendulum oscillates very close to the line normal to the ceiling. You may be thinking that studying such a system is boring and useless, but again, as we discussed in Section 3.2, for most molecules at moderate temperatures the displacement of the atoms around their equilibrium position is very small. That is why studying oscillations of systems close to equilibrium makes sense for a chemist.

We already discussed that if $\theta << 1$, then $\sin\theta \approx \theta$ (see Figure 3.4). Equation 10.6.2.1 can then be simplified to:

$$\frac{d^2\theta}{dt^2} + \frac{g}{l}\theta = 0$$

This equation is linear in θ, is homogeneous, and has constant coefficients (g is the acceleration of gravity and l the length of the rod). The auxiliary equation of this ODE is:

$$\alpha^2 + \frac{g}{l} = 0$$

and therefore,

$$\alpha = \pm i\sqrt{\frac{g}{l}}$$

The general solution is

$$\theta(t) = c_1 e^{\alpha_1 t} + c_2 e^{\alpha_2 t}$$

$$\theta(t) = c_1 e^{i(g/l)^{1/2}t} + c_2 e^{-i(g/l)^{1/2}t}$$

We will get the values of the arbitrary constants from the initial conditions. Let's assume that at time zero the value of θ was $\theta_0 << 1$, and the value of $d\theta/dt$, which is a measure of the velocity, was $\theta'(0) = 0$. Physically, it means that at time zero we are holding the pendulum still. At this point we can either use Euler relationships to simplify our result into a cosine and a sine, or use the initial conditions and use Euler's relationship later. Either way will work, and how you choose to proceed is a matter of personal taste. Let's apply the initial conditions now:

$$\theta(t) = c_1 e^{i(g/l)^{1/2}t} + c_2 e^{-i(g/l)^{1/2}t} \rightarrow \theta(0) = c_1 + c_2 = \theta_0$$

$$\theta'(t) = c_1 i(g/l)^{1/2} e^{i(g/l)^{1/2}t} - c_2 i(g/l)^{1/2} e^{-i(g/l)^{1/2}t}$$

$$\theta'(0) = c_1 i(g/l)^{1/2} - c_2 i(g/l)^{1/2} = 0 \rightarrow c_1 = c_2$$

Therefore, $c_1 = c_2 = \theta_0/2$, and our particular solution is:

$$\theta(t) = \frac{\theta_0}{2}\left(e^{i(g/l)^{1/2}t} + e^{-i(g/l)^{1/2}t}\right)$$

From Euler's relationship we know that $e^{ix} + e^{-ix} = 2cosx$, so

$$\theta(t) = \theta_0 \cos\left(\left(\frac{g}{l}\right)^{1/2} t\right) \tag{10.6.2.2}$$

This is of course the familiar periodic function that you saw in your physics course. Remember that we got here by assuming $\theta << 1$ at all times.

As we saw in Section 1.4, the period of the function $\cos(nx)$ is $2\pi/n$. The period of the function $\theta_0 \cos\left(\left(\frac{g}{l}\right)^{1/2} t\right)$ is therefore $P = 2\pi\left(\frac{l}{g}\right)^{1/2}$. The period has units of time, and it tells us the time that it takes for the pendulum to complete a whole cycle (see Figure 10.6.2.2).

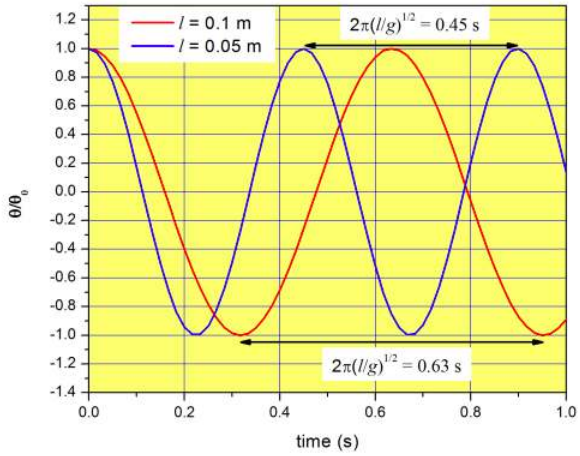


Figure 10.6.2.2: The oscillations of a pendulum in a frictionless medium (Equation 10.6.2.2). (CC BY-NC-SA; Marcia Levitus)

We can also calculate the frequency of the motion, which is just the reciprocal of the period. If the period is the amount of time you need to wait to complete a full cycle, the reciprocal is the number of cycles per unit time. For example, if it takes a pendulum with $l = 0.1m$ 0.63 seconds to complete a cycle, this means that we get 1.58 cycles per second. The frequency has units of reciprocal time.

The fact that pendula with different lengths have different periods was used by a very creative mind to produce the beautiful display showcased a the lobby of the PSF building at ASU (right across the elevators). There are some videos on YouTube demonstrating the idea (search for pendulum waves), but the one in the physics department at ASU is much more impressive, so go and check it out if you haven't done so yet.

The pendulum in a viscous medium

The problem we just saw assumed that there was no friction, so the pendulum will oscillate forever without changing the amplitude. Let's make the problem more realistic from the physical point of view and add a term that accounts for frictional

resistance. The force due to friction is usually proportional to the velocity, so this new force introduces a term that depends on the first derivative of θ:

$$\frac{d^2\theta}{dt^2} + \gamma\frac{d\theta}{dt} + \frac{g}{l}\theta = 0$$

The constant γ depends on the medium, and it will be larger in e.g. water (more friction) than in air (less friction). The auxiliary equation is now

$$\alpha^2 + \gamma\alpha + \frac{g}{l} = 0$$

and the two roots are:

$$\alpha_{1,2} = \frac{-\gamma \pm \sqrt{\gamma^2 - 4g/l}}{2}$$

and we see that the result will depend on the relative values of γ^2 and $4g/l$. We will analyze the case $\gamma^2 < 4g/l$ first (low friction regime). It is useful to always think about what one expects before doing any math. Think about the pendulum without friction, and imagine you do the same experiment in air (small friction). How do you think the plot of $\theta(t)$ vs t would look like?

Coming back to the math, let's call $a = \sqrt{4g/l - \gamma^2}$ to simplify notation. In the low friction case, a will be a real number. The two roots will therefore be:

$$\alpha_{1,2} = \frac{-\gamma \pm ia}{2}$$

and the general solution will be

$$\theta(t) = c_1 e^{\alpha_1 t} + c_1 e^{\alpha_2 t}$$

$$\theta(t) = c_1 e^{-\gamma t/2} e^{iat/2} + c_2 e^{-\gamma t/2} e^{-iat/2}$$

$$\theta(t) = e^{-\gamma t/2}\left(c_1 e^{iat/2} + c_2 e^{-iat/2}\right)$$

At this point we can either use the initial conditions and use Euler's relationship later, or we can use Euler's equations now and the initial conditions later. Either way should work.

$$\theta(t) = e^{-\gamma t/2}\left[(c_1 \cos(ta/2) + c_1 i \sin(ta/2) + c_2 \cos(ta/2) - c_2 i \sin(ta/2))\right]$$

$$\theta(t) = e^{-\gamma t/2}\left[(c_1 + c_2)\cos(ta/2) + (c_1 - c_2) i \sin(ta/2)\right]$$

and grouping and re-naming constants:

$$\theta(t) = e^{-\gamma t/2}\left[c_3 \cos(ta/2) + c_4 \sin(ta/2)\right]$$

We will now evaluate c_3 and c_4 from the initial conditions. Let's assume again that $\theta(0) = \theta_0$ and $\theta'(0) = 0$. Evaluating the previous equation at $t = 0$:

$$\theta(0) = c_3 = \theta_0$$

so we have

$$\theta(t) = e^{-\gamma t/2}\left[\theta_0 \cos\left(\frac{ta}{2}\right) + c_4 \sin\left(\frac{ta}{2}\right)\right]$$

$$\theta'(t) = e^{-\gamma t/2}\left[-\frac{\theta_0 a}{2}\sin\left(\frac{ta}{2}\right) + \frac{c_4 a}{2}\cos\left(\frac{ta}{2}\right)\right] - \frac{\gamma}{2}e^{-\gamma t/2}\left[\theta_0 \cos\left(\frac{ta}{2}\right) + c_4 \sin\left(\frac{ta}{2}\right)\right]$$

$$\theta'(0) = c_4\frac{a}{2} - \theta_0\frac{\gamma}{2} = 0$$

$$c_4 = \frac{\gamma\theta_0}{a}$$

and therefore

$$\theta(t) = e^{-\gamma t/2}\left[\theta_0 \cos\left(\frac{ta}{2}\right) + \frac{\gamma\theta_0}{a}\sin\left(\frac{ta}{2}\right)\right]$$

$$\theta(t) = \theta_0 e^{-\gamma t/2}\left[\cos\left(\frac{ta}{2}\right) + \frac{\gamma}{a}\sin\left(\frac{ta}{2}\right)\right]$$

If everything went well this equation should simplify to Equation 10.6.2.2 for the case $\gamma = 0$. Recall that $a = \sqrt{4g/l - \gamma^2}$, so if $\gamma = 0$:

$$\theta(t) = \theta_0\left[\cos\left(\frac{ta}{2}\right)\right]$$

$$\theta(t) = \theta_0\left[\cos\left(\sqrt{\frac{g}{l}}t\right)\right]$$

This of course does not prove that our solution is correct, but it is always good to see that we recover a known equation for a particular case (in this case $\gamma = 0$).

Figure 10.6.2.3 shows $\theta(t)/\theta_0$ for three cases with $g/l = 1$ (i.e. a cord of length 9.8 m) and increasing values of friction. Remember that we are assuming that θ is small.

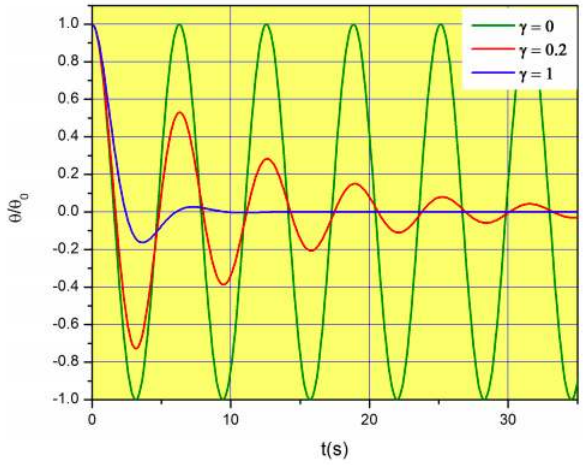


Figure 10.6.2.3: A pendulum in low-friction media ($l = 9.8$m) (CC BY-NC-SA; Marcia Levitus)

So far we have analyzed the case $\gamma^2 < 4g/l$. As we increase the friction coefficient, we will reach the point where $\gamma^2 = 4g/l$. Look at Figure 10.6.2.3, and think about what you would see when this happens. Mathematically, we will have two repeated roots:

$$\alpha_{1,2} = \frac{-\gamma \pm \sqrt{\gamma^2 - 4g/l}}{2} = -\frac{\gamma}{2}$$

so $\theta(t) = e^{-\gamma t/2}$ is a solution, but we need to find an independent solution through the method of reduction of order. We know that the general solution will be (Section 2.2):

$$\theta(t) = (c_1 + c_2 t)e^{-\gamma t/2}$$

The arbitrary constants will be calculated from the initial conditions:

$$\theta(0) = (c_1) = \theta_0$$

$$\theta'(t) = -\frac{\gamma}{2}(\theta_0 + c_2 t)e^{-\gamma t/2} + c_2 e^{-\gamma t/2}$$

$$\theta'(0) = -\frac{\gamma}{2}(\theta_0) + c_2 = 0$$

$$c_2 = \frac{\gamma}{2}\theta_0$$

Therefore,

$$\theta(t) = (c_1 + c_2 t)e^{-\gamma t/2}$$

$$\theta(t) = (\theta_0 + \frac{\theta_0 \gamma}{2} t) e^{-\gamma t/2} = \theta_0 (1 + \frac{\gamma}{2} t) e^{-\gamma t/2}$$

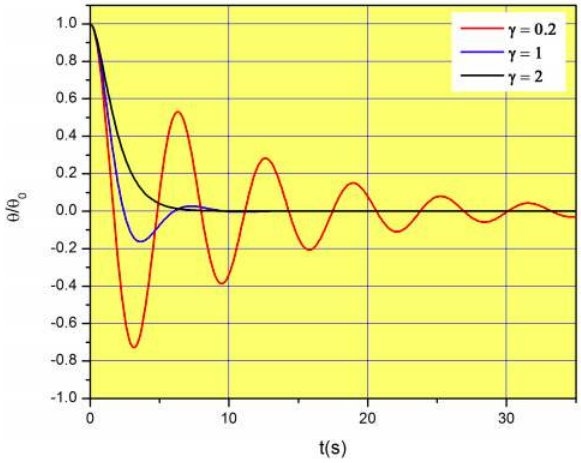


Figure **10.6.2.4**: A critically damped pendulum with $l = 9.8$m (black) (CC BY-NC-SA; Marcia Levitus)

The behavior of $\theta(t)$ is shown in Figure **10.6.2.4** in black. This regime is called critically damped because it represents the point where the oscillations no longer occur as γ increases. If we continue increasing the frictional coefficient, the pendulum will approach $\theta = 0$ slower and slower, but will never cross to the other side ($\theta < 0$). Let's find the mathematical expression for $\theta(t)$ for the case $\gamma^2 > 4g/l$. The two roots are now different and real:

$$\alpha_{1,2} = \frac{-\gamma \pm \sqrt{\gamma^2 - 4g/l}}{2}$$

and the general solution is therefore

$$\theta(t) = c_1 e^{\alpha_1 t} + c_2 e^{\alpha_2 t}$$

$$\theta(t) = c_1 e^{(-\gamma + b)t/2} + c_2 e^{(-\gamma - b)t/2};\ b = \sqrt{\gamma^2 - 4g/l}$$

The first initial condition is $\theta(0) = \theta_0$:

$$\theta(0) = c_1 + c_2 = \theta_0$$

The second initial condition is $\theta'(t) = 0$:

$$\theta'(t) = c_1 \left(\frac{-\gamma + b}{2}\right) e^{(-\gamma + b)t/2} + c_2 \left(\frac{-\gamma - b}{2}\right) e^{(-\gamma - b)t/2}$$

$$\theta'(0) = c_1 \left(\frac{-\gamma + b}{2}\right) + c_2 \left(\frac{-\gamma - b}{2}\right) = 0$$

$$\theta'(0) = -(c_1 + c_2)\gamma + (c_1 - c_2)b = 0$$

the first initial condition yielded $c_1 + c_2 = \theta_0$ so

$$\theta'(0) = -\theta_0 \gamma + (c_1 - c_2)b = 0$$

$$(c_1 - c_2) = \theta_0 \gamma / b$$

The two initial conditions gave two relationships between c_1 and c_2:

$$c_1 + c_2 = \theta_0$$

$$(c_1 - c_2) = \theta_0 \gamma / b$$

Solving this system of two equations with two unknowns:

$$c_1 = \frac{\theta_0}{2} \left(1 + \frac{\gamma}{b}\right)$$

$$c_2 = \frac{\theta_0}{2}\left(1 - \frac{\gamma}{b}\right)$$

And finally we can write the particular solution as:

$$\theta(t) = c_1 e^{(-\gamma+b)t/2} + c_2 e^{(-\gamma-b)t/2};\ b = \sqrt{\gamma^2 - 4g/l}$$

$$\theta(t) = \frac{\theta_0}{2}\left(1 + \frac{\gamma}{b}\right) e^{(-\gamma+b)t/2} + \frac{\theta_0}{2}\left(1 - \frac{\gamma}{b}\right) e^{(-\gamma-b)t/2};\ b = \sqrt{\gamma^2 - 4g/l}$$

$$\theta(t) = \frac{\theta_0}{2} e^{-\gamma t/2}\left[\left(1 + \frac{\gamma}{b}\right) e^{bt/2} + \left(1 - \frac{\gamma}{b}\right) e^{-bt/2}\right]$$

Figure **10.6.2.5** shows results with $g/l = 1$, and three different values of γ. Notice that $\gamma = 2$ corresponds to the critically damped regime.

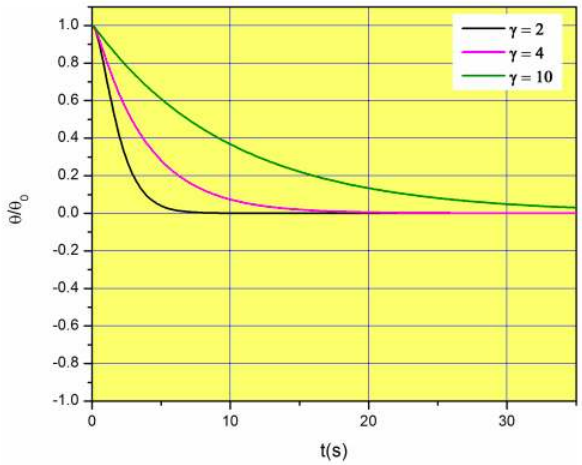


Figure **10.6.2.5**: The high friction regime ($\gamma^2 > 4g/l$) (CC BY-NC-SA; Marcia Levitus)

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10.6.3: Second Order Ordinary Differential Equations with Boundary Conditions

Note

This section is also available in video format: http://tinyurl.com/n8tgbf6

You may have noticed that all the examples we discussed so far in this chapter involve initial conditions, or in other words, conditions evaluated at the same value of the independent value. We will see now how boundary conditions give rise to important consequences in the solutions of differential equations, which are extremely important in the description of atomic and molecular systems. Let's start by asking ourselves whether all boundary value problems involving homogeneous second order ODEs have non-trivial solutions. The trivial solution is $y(x) = 0$, which is a solution to any homogeneous ODE, but this solution is not particularly interesting from the physical point of view. For example, let's solve the following problem:

$$y''(x) + 3y(x) = 0;\ y('0) = 0;\ y(1) = 0$$

Following the same procedure we have used in previous examples, we get the following general solution:

$$y(x) = a\cos(\sqrt{3}x) + b\sin(\sqrt{3}x)$$

The first boundary condition is $y'(0) = 0$:

$$y'(x) = -\sqrt{3}a\sin(\sqrt{3}x) + \sqrt{3}b\cos(\sqrt{3}x) \rightarrow y'(0) = \sqrt{3}b = 0 \rightarrow b = 0$$

Therefore, so far we have $y(x) = a\cos(\sqrt{3}x)$. The second boundary condition is $y(1) = 0$, so

$$y(1) = a\cos\sqrt{3} = 0 \rightarrow a = 0$$

Therefore, the only particular solution for these particular boundary conditions is $y(x) = 0$, the trivial solution. Let's change the question and ask ourselves now if there is any number λ, so that the equation

$$y''(x) + \lambda y(x) = 0;\ y'(0) = 0;\ y(1) = 0$$

has a non-trivial solution. Our general solution depends on whether λ is positive or negative. If $\lambda > 0$ we have

$$y(x) = a\cos(\sqrt{\lambda}x) + b\sin(\sqrt{\lambda}x)$$

Notice that we are using results be obtained in previous sections, but you would need to show all your work!

If $\lambda < 0$ we have

$$y(x) = ae^{\sqrt{|\lambda|}x} + be^{-\sqrt{|\lambda|}x}$$

where $|\lambda|$ is the absolute value of λ.

Let's look at the case $\lambda < 0$ first. The first boundary condition implies

$$y'(x) = \sqrt{|\lambda|}ae^{\sqrt{|\lambda|}x} - \sqrt{|\lambda|}be^{-\sqrt{|\lambda|}x} \rightarrow y'(0) = \sqrt{|\lambda|}(a-b) = 0 \rightarrow a = b$$

and therefore $y(x) = a\left(e^{\sqrt{|\lambda|}x} + e^{-\sqrt{|\lambda|}x}\right)$. Using the second boundary condition:

$$y(1) = a\left(e^{\sqrt{|\lambda|}} + e^{-\sqrt{|\lambda|}}\right) = 0 \rightarrow a = 0$$

Therefore, if $\lambda < 0$, the solution is always $y(x) = 0$, the trivial solution.

Let's see what happens if $\lambda > 0$. The general solution is $y(x) = a\cos(\sqrt{\lambda}x) + b\sin(\sqrt{\lambda}x)$, and applying the first boundary condition:

$$y'(x) = -\sqrt{\lambda}a\sin(\sqrt{\lambda}x) + \sqrt{\lambda}b\cos(\sqrt{\lambda}x) \rightarrow y'(0) = \sqrt{\lambda}b = 0 \rightarrow b = 0$$

Therefore, so far we have $y(x) = a\cos\sqrt{\lambda}x$. The second boundary condition is $y(1) = 0$, so

$$y(1) = a\cos(\sqrt{\lambda}) = 0$$

As before, $a = 0$ is certainly a possibility, but this again would give the trivial solution, which we are trying to avoid. However, this is not our only option, because there are some values of λ that also make $y(1) = 0$. These are $\sqrt{\lambda} = \frac{\pi}{2}, \frac{3\pi}{2}, \frac{5\pi}{2}$, or in terms of λ:

$$\lambda = \frac{\pi^2}{4}, \frac{9\pi^2}{4}, \frac{25\pi^2}{4}$$

This means that

$$y''(x) + 3y(x) = 0;\ y'(0) = 0;\ y(1) = 0$$

does not have a non-trivial solution, but

$$y''(x) + (\pi^2/4)y(x) = 0;\ y'(0) = 0;\ y(1) = 0$$

does. The values of λ that guarantee that the differential equation has non-trivial solutions are called the **eigenvalues** of the equation. The non-trivial solutions are called the **eigenfunctions** of the equation. We just found the eigenvalues, but what about the eigenfunctions?

We just concluded that the solutions are $y(x) = a\cos\sqrt{\lambda}x$, and now we know that $\sqrt{\lambda} = \frac{\pi}{2}, \frac{3\pi}{2}, \frac{5\pi}{2}$. We can write the eigenfunctions as:

$$y(x) = a\cos\frac{(2n-1)\pi}{2}x \quad n = 1, 2, 3...$$

We could also use $(2n + 1)$ with $n = 0, 1, 2...$. Notice that we do not have any information that allows us to calculate the constant a, so we leave it as an arbitrary constant.

Also, notice that although we have infinite eigenvalues, the eigenvalues are discrete. The term discrete means that the variable can take values for a countable set (like the natural numbers). The opposite of discrete is continuous (like the real numbers). These discrete eigenvalues have very important consequences in quantum mechanics. In fact, you probably know from your introductory chemistry classes that atoms and molecules have energy levels that are discrete. Electrons can occupy one orbital or the next, but cannot be in between. These energies are the eigenvalues of differential equations with boundary conditions, so this is an amazing example of what boundary conditions can do!

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10.6.4: An example in Quantum Mechanics

The main postulate of quantum mechanics establishes that the state of a quantum mechanical system is specified by a function called *the wave function*. The wave function is a function of the coordinates of the particle (the position) and time. We often deal with *stationary states*, i.e. states whose energy does not depend on time. For example, at room temperature and in the absence of electromagnetic radiation such as UV light, the energy of the only electron in the hydrogen atom is constant (the energy of the 1s orbital). In this case, all the information about the state of the particle is contained in a time-independent function, $\psi(\mathbf{r})$, where $\mathbf{r}$ is a vector that defines the position of the particle. In Section 2.3 we briefly mentioned that $|\psi|^2 = \psi^*\psi$ can be interpreted in terms of the probability of finding the electron in different regions of space. Because the probability of finding the particle somewhere in the universe is 1, the wave function needs to be normalized (that is, the integral of $|\psi|^2$ over all space has to equal 1).

The fundamental equation in quantum mechanics is known as the Schrödinger equation, which is a differential equation whose solutions are the wave functions. For a particle of mass m moving in one dimension in a potential field described by $U(x)$ the Schrödinger equation is:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + U(x)\psi(x) = E\psi(x)$$

Notice that the position of the particle is defined by x, because we are assuming one-dimensional movement. The constant $\hbar$ (pronounced “h-bar”) is defined as $h/(2\pi)$, where h is Plank’s constant. $U(x)$ is the potential energy the particle is subjected to, and depends on the forces involved in the system. For example, if we were analyzing the hydrogen atom, the potential energy would be due to the force of interaction between the proton (positively charged) and the electron (negatively charged), which depends on their distance. The constant E is the total energy, equal to the sum of the potential and kinetic energies.

This will be confusing until we start seeing a few examples, so don’t get discouraged and be patient. Let’s start by discussing the simplest (from the mathematical point of view) quantum mechanical system. Our system consists of a particle of mass m that can move freely in one dimension between two “walls”. The walls are impenetrable, and therefore the probability that you find the particle outside this one-dimensional box is zero. This is not too different from a ping-pong ball bouncing inside a room. It does not matter how hard you bounce the ball against the wall, you will never find it on the other side. However, we will see that for microscopic particles (small mass), the system behaves very different than for macroscopic particles (the ping-pong ball). The behavior of macroscopic systems is described by the laws of what we call classical mechanics, while the behavior of molecules, atoms and sub-atomic particles is described by the laws of quantum mechanics. The problem we just described is known as the “particle in the box” problem, and can be extended to more dimensions (e.g. the particle can move in a 3D box) or geometries (e.g. the particle can move on the surface of a sphere, or inside the area of a circle).

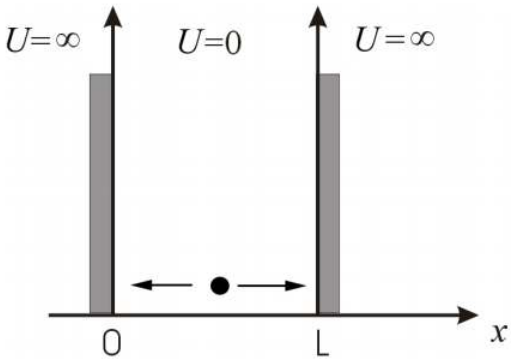


Figure **10.6.4.1**: The problem of a particle in a one-dimensional box (CC BY-NC-SA; Marcia Levitus)

The particle in a one-dimensional box

We will start with the simplest case, which is a problem known as ’the particle in a one-dimensional box’ (Figure **10.6.4.1**). This is a simple physical problem that, as we will see, provides a rudimentary description of conjugated linear molecules. In this problem, the particle is allowed to move freely in one dimension inside a ’box’ of length L. In this context, ’freely’ means that the particle is not subject to any force, so the potential energy inside the box is zero. The particle is not allowed to move outside the box, and

physically, we guarantee this is true by impossing an infinite potential energy at the edges of the box ($x = 0$ and $x = L$) and outside the box ($x < 0$ and $x > L$).

$$U(x) = \begin{cases} \infty & x < 0 \\ 0 & 0 < x < L \\ \infty & x > L \end{cases}$$

Because the potential energy outside the box is infinity, the probability of finding the particle in these regions is zero. This means that $\psi(x) = 0$ if $x > L$ or $x < 0$. What about $\psi(x)$ inside the box? In order to find the wave functions that describe the states of a system, we have to solve Schrödinger's equation:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + U(x)\psi(x) = E\psi(x)$$

Inside the box $U(x) = 0$, so:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} = E\psi(x)$$

$$\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + E\psi(x) = 0 \tag{10.6.4.1}$$

Remember that $\hbar$ is a constant, m is the mass of the particle (also constant), and E the energy. The energy of the particle is a constant in the sense that it is not a function of x. We will see that there are many (in fact infinite) possible values for the energy of the particle, but these are numbers, not functions of x. With all this in mind, hopefully you will recognize that the Schrödinger equation for the one-dimensional particle in a box is a homogeneous second order ODE with constant coefficients. Do we have any initial or boundary conditions? In fact we do, because the wave function needs to be a continuous function of x. This means that there cannot be sudden jumps of probability density when moving though space. In particular in this case, it means that $\psi(0) = \psi(L) = 0$, because the probability of finding the particle outside the box is zero.

Let's solve Equation 10.6.4.1. We need to find the functions $\psi(x)$ that satisfy the ODE. The auxiliary equation is (remember that $m, \hbar, E$ are positive constants):

$$\frac{\hbar^2}{2m}\alpha^2 + E = 0$$

$$\alpha = \pm i\sqrt{\frac{2mE}{\hbar^2}}$$

and the general solution is therefore:

$$\psi(x) = c_1 e^{i\sqrt{\frac{2mE}{\hbar^2}}x} + c_2 e^{-i\sqrt{\frac{2mE}{\hbar^2}}x}$$

Because $\psi(0) = 0$:

$$\psi(x) = c_1 + c_2 = 0 \rightarrow c_1 = -c_2$$

$$\psi(x) = c_1\left(e^{i\sqrt{\frac{2mE}{\hbar^2}}x} - e^{-i\sqrt{\frac{2mE}{\hbar^2}}x}\right)$$

This can be simplified using Euler's relationships: $e^{ix} - e^{-ix} = 2i\sin x$

$$\psi(x) = c_1(2i)\sin\left(\sqrt{\frac{2mE}{\hbar^2}}x\right)$$

$$\psi(x) = A\sin\left(\sqrt{\frac{2mE}{\hbar^2}}x\right)$$

In the last step we recognized that $2ic_1$ is a constant, and called it A.

The second boundary condition is $\psi(L) = 0$:

$$\psi(L) = A\sin\left(\sqrt{\frac{2mE}{\hbar^2}}L\right) = 0$$

We can make $A = 0$, but this will result in the wave function being zero at all values of x. This is what we called the 'trivial solution' before, and although it is a solution from the mathematical point of view, it is not when we think about the physics of the problem. If $\psi(x) = 0$ the probability of finding the particle inside the box is zero. However, the problem states that the particle cannot be found outside, so it has to be found inside with a probability of 1. This means that $\psi(x) = 0$ is not a physically acceptable solution inside the box, and we are forced to consider the situations where

$$\sin\left(\sqrt{\frac{2mE}{\hbar^2}}L\right) = 0$$

We know the function $\sin x$ is zero at values of x that are zero, or multiples of π:

$$\left(\sqrt{\frac{2mE}{\hbar^2}}L\right) = \pi, 2\pi, 3\pi... = n\pi\ (n = 1, 2, 3..\infty)$$

This means that our solution is:

$$\psi(x) = A\sin\left(\frac{n\pi}{L}x\right)\ (n = 1, 2, 3...\infty)$$

Notice that we didn't consider $n = 0$ because that would again cause $\psi(x)$ to vanish inside the box. The functions $\psi(x)$ contain information about the state of the system, and are called the *eigenfunctions*. What about the energies?

$$\left(\sqrt{\frac{2mE}{\hbar^2}}L\right) = n\pi \rightarrow E = \left(\frac{n\pi}{L}\right)^2\frac{\hbar^2}{2m}\ (n = 1, 2, 3...\infty)$$

The energies are the *eigenvalues* of this equation. Notice that there are infinite eigenfunctions, and each one has a defined eigenvalue.

n	$\psi(x)$	E
1	$A\sin\left(\frac{\pi}{L}x\right)$	$\left(\frac{\pi}{L}\right)^2\frac{\hbar^2}{2m}$
2	$A\sin\left(\frac{2\pi}{L}x\right)$	$\left(\frac{2\pi}{L}\right)^2\frac{\hbar^2}{2m}$
3	$A\sin\left(\frac{3\pi}{L}x\right)$	$\left(\frac{3\pi}{L}\right)^2\frac{\hbar^2}{2m}$

The lowest energy state is described by the wave function $\psi = A\sin\left(\frac{\pi}{L}x\right)$, and its energy is $\left(\frac{\pi}{L}\right)^2\frac{\hbar^2}{2m}$.

What about the constant A? Mathematically, any value would work, and none of the boundary conditions impose any restriction on its value. Physically, however, we have another restriction we haven't fulfilled yet: the wave function needs to be normalized. The integral of $|\psi|^2$ over all space needs to be 1 because this function represents a probability.

$$\int_{-\infty}^{\infty}|\psi(x)|^2dx = 1$$

However, $\psi(x) = 0$ outside the box, so the ranges $x < 0$ and $x > L$ do not contribute to the integral. Therefore:

$$\int_0^L|\psi(x)|^2dx = \int_0^L A^2\sin^2\left(\frac{n\pi}{L}x\right)dx = 1$$

We will calculate A from this normalization condition. Using the primitives found in the formula sheet, we get:

$$\int_0^L\sin^2\left(\frac{n\pi}{L}x\right)dx = L/2$$

and therefore

$$A = \sqrt{\frac{2}{L}}$$

We can now write down our normalized wave function as:

$$\psi(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}x\right) \; (n = 1, 2, 3...\infty)$$

We solved our first problem in quantum mechanics! Let's discuss what we got, and what it means. First, because the potential energy inside the box is zero, the total energy equals the kinetic energy of the particle (i.e. the energy due to the fact that the particle is moving from left to right or from right to left). A ping-pong ball inside a macroscopic box can move at any speed we want, so its kinetic energy is not quantized. However, if the particle is an electron, its kinetic energy inside the box can adopt only quantized values of energy: $E = (\frac{n\pi}{L})^2 \frac{\hbar^2}{2m}$ $(n = 1, 2, 3...\infty)$. Interestingly, the particle cannot have zero energy ($n = 0$ is not an option), so it cannot be at rest (our ping-pong ball can have zero kinetic energy without violating any physical law). If a ping-pong ball moves freely inside the box we can find it with equal probability close to the edges or close to the center. Not for an electron in a one-dimensional box! The function $|\psi(x)|^2$ for the lowest energy state ($n = 1$) is plotted in Figure **10.6.4.2**. The probability of finding the electron is greater at the center than it is at the edges; nothing like what we expect for a macroscopic system. The plot is symmetric around the center of the box, meaning the probability of finding the particle in the left side is the same as finding it in the right side. That is good news, because the problem is truly symmetric, and there are no extra forces attracting or repelling the particle on the left or right half to the box.

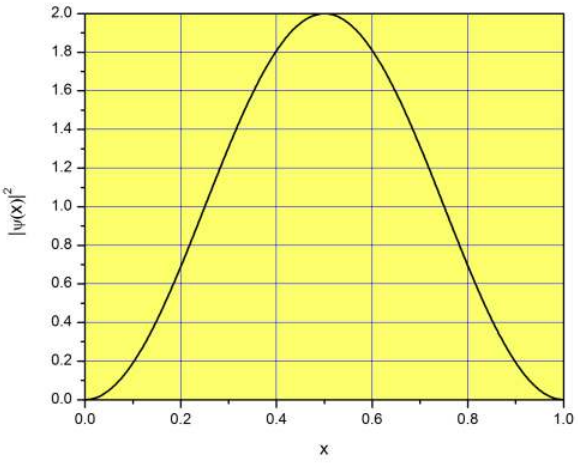


Figure **10.6.4.2**: The lowest energy state of a particle in a one-dimensional box of length $L = 1$ (CC BY-NC-SA; Marcia Levitus)

Looking at Figure **10.6.4.2**, you may think that the probability of finding the particle at the center really 2. How can this be? Probabilities cannot be greater than 1! This is a major source of confusion among students, so let's clarify what it means. The function $|\psi(x)|^2$ is not a probability, but a probability density. Technically, this means that $|\psi(x)|^2 dx$ is the probability of finding the particle between x and $x + dx$ (see page for more details). For example, the probability of finding the particle between $x = 0.5$ and 0.5001 is $\approx |\psi(0.5)|^2 \times 0.0001 = 0.0002$. This is approximate because $\Delta x = 0.0001$ is small, but not infinitesimal. What about the probability of finding the particle between $x = 0.5$ and 0.6? We need to integrate $|\psi(x)|^2 dx$ between $x = 0.5$ and $x = 0.6$:

$$p(0.5 < x < 0.6) = \int_{0.5}^{0.6} |\psi(x)|^2 dx \approx 0.2$$

Importantly,

$$p(0 < x < 1) = \int_{0}^{1} |\psi(x)|^2 dx = 1$$

as it should be the case for a normalized wave function. Notice that these probabilities refer to the lowest energy state ($n = 1$), and will be different for states of increasing energy.

> The particle in the box problem is also available in video format: http://tinyurl.com/mjsmd2a

Where is the chemistry?

So far we talked about a system that sounds pretty far removed from anything we (chemists) care about. We understand electrons in atoms, but electrons moving in a one-dimensional box? To see why this is not such a crazy idea, let's consider the molecule of carotene (the orange pigment in carrots). We know that all those double bonds are conjugated, meaning that the π electrons are delocalized and relatively free to move around the bonds highlighted in red in Figure **10.6.4.3**.

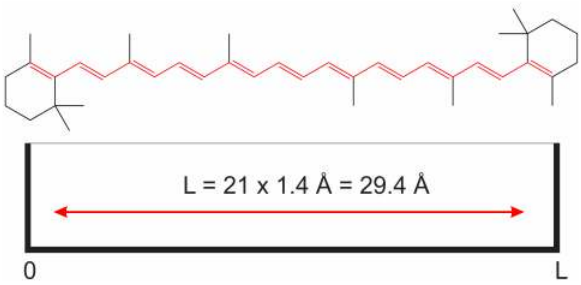


Figure **10.6.4.3**: The particle in a box model applied to carotene. (CC BY-NC-SA; Marcia Levitus)

Because the length of each carbon-carbon bond is around 1.4 Å (Å stands for angstrom, and equals $10^{-10}m$), we can assume that the π electrons move inside a one dimensional box of length $L = 21 \times 1.4\,\text{Å} = 29.4\,\text{Å}$. This is obviously an approximation, as it is not true that the electrons move freely without being subject to any force. Yet, we will see that this simple model gives a good semi-quantitative description of the system.

We already solved the problem of the particle in a box, and obtained the following eigenvalues:

$$E = \left(\frac{n\pi}{L}\right)^2 \frac{\hbar^2}{2m} \; (n = 1, 2, 3...\infty) \tag{10.6.4.2}$$

These are the energies that the particle in the box is allowed to have. In this case, the particle in question is an electron, so m is the mass of an electron. Notice that we have everything we need to use Equation 10.6.4.2: $\hbar = 1.0545 \times 10^{-34} m^2 kg\ s^{-1}$, $m = 9.109 \times 10^{-31} kg$, and $L = 2.94 \times 10^{-9} m$. This will allow us to calculate the allowed energies for the π electrons in carotene. For $n = 1$ (the lowest energy state), we have:

$$E_1 = \left(\frac{\pi}{L}\right)^2 \frac{\hbar^2}{2m} = 6.97 \times 10^{-21} J$$

Joule is the unit of energy, and $1J = kg \times m^2 \times s^{-2}$. A very easy way of remembering this is to recall Einstein's equation: $E = mc^2$, which tells you that energy is a mass times the square of a velocity (hence, $1J = 1kg(1m/s)^2$). Coming back to Equation 10.6.4.2, the allowed energies for the π electrons in carotene are:

$$E_n = n^2 \times 6.97 \times 10^{-21} J \; (n = 1, 2, 3...\infty)$$

Notice that the energies increase rapidly. The energy of the tenth level (E_{10}) is one hundred times the energy of the first! The number of levels is inifinite, but of course we know that the electrons will fill the ones that are lower in energy. This is analogous to the hydrogen atom. We know there are an infinite number of energy levels, but in the absence of an external energy source we know the electron will be in the 1s orbital, which is the lowest energy level. This electron has an infinite number of levels available, but we need an external source of energy if we want the electron to occupy a higher energy state. The same concepts apply to molecules. As you have learned in general chemistry, we cannot have more than two electrons in a given level, so we will put our 22 π electrons (2 per double bond) in the first 11 levels (Figure **10.6.4.4**, left).

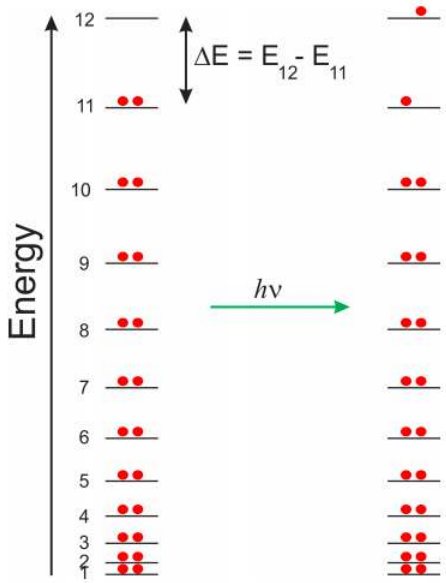


Figure **10.6.4.4**: The particle in a box model applied to carotene (CC BY-NC-SA; Marcia Levitus)

We can promote an electron to the first unoccupied level (in this case $n = 12$) by using light of the appropriate frequency (ν). The energy of a photon is $E = h\nu$, where h is Plank's constant. In order for the molecule to absorb light, the wavelength of the light beam needs to match exactly the gap in energy between the highest occupied state (in this case $n = 11$) and the lowest unoccupied state. The wavelength of light is related to the frequency as: $\lambda = c/\nu$, where c is the speed of light. Therefore, in order to produce the excited state shown in the right side of Figure **10.6.4.4**, we have to use light of the following wavelength:

$$E = E_{12} - E_{11} = h\nu = hc/\lambda \rightarrow \lambda = hc/(E_{12} - E_{11})$$

Recall that $E_n = n^2 \times 6.97 \times 10^{-21} J$, so $(E_{12} - E_{11}) = (144 - 121) \times 6.97 \times 10^{-21} J = 1.60 \times 10^{-19} J$. Therefore,

$$\lambda = \frac{6.626 \times 10^{-34} J\,s \times 3 \times 10^{8} m\,s^{-1}}{1.60 \times 10^{-19} J} = 1.24 \times 10^{-6} m = 1,242 nm$$

In the last step we expressed the result in nanometers ($1nm = 10^{-9} m$), which is a common unit to describe the wavelength of light in the visible and ultraviolet regions of the electromagnetic spectrum. It is actually fairly easy to measure the absorption spectrum of carotene. You just need to have a solution of carotene, shine the solution with light of different colors (wavelengths), and see what percentage of the light is transmitted. The light that is not transmitted is absorbed by the molecules due to transitions such as the one shown in Figure **10.6.4.4**. In reality, the absorption of carotene actually occurs at 497 nm, not at 1,242 nm. The discrepancy is due to the huge approximations of the particle in the box model. Electrons are subject to interactions with other electrons, and with the nuclei of the atoms, so it is not true that the potential energy is zero. Although the difference seems large, you should not be too disappointed about the result. It is actually pretty impressive that such a simple model can give a prediction that is not that far from the experimental result. Nowadays chemists use computers to analyze more sophisticated models that cannot be solved analytically in the way we just solved the particle in the box. Yet, there are some qualitative aspects of the particle in the box model that are useful despite the approximations. One of these aspects is that the wavelength of the absorbed light gets lower as we reduce the size of the box. From Equation 10.6.4.2, we can write:

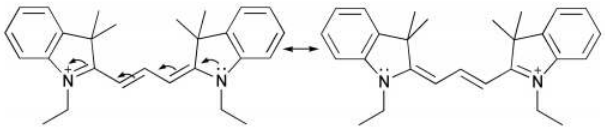
$$hc/\lambda = \left(\frac{\pi}{L}\right)^2 \frac{\hbar^2}{2m}(n_2^2 - n_1^2)$$

where n_2 is the lowest unoccupied level, and n_1 is the highest occupied level. Because $n_2 = n_1 + 1$,

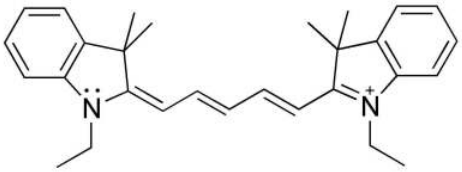
$$hc/\lambda = \left(\frac{\pi}{L}\right)^2 \frac{\hbar^2}{2m}((n_1 + 1)^2 - n_1^2) = \left(\frac{\pi}{L}\right)^2 \frac{\hbar^2}{2m}(2n_1 + 1)$$

Molecules that have a longer conjugated system will absorb light of longer wavelengths (less energy), and molecules with a shorter conjugated system will absorb light of shorter wavelengths (higher energy). For example, consider the following molecule, which is a member of a family of fluorescent dyes known as cyanines. The conjugated system contains 8 π electrons, and the molecule

absorbs light of around 550 nm. This wavelength corresponds to the green region of the visible spectrum. The solution absorbs green and lets everything else reach your eye. Red is the complementary color of green, so this molecule in solution will look red to you.



Now look at this other cyanine, which has two extra π electrons:



The particle in a box model tells you that this cyanine should absorb light of longer wavelengths (less energy), so it should not surprise you to know that a solution of this compound absorbs light of about 670 nm. This corresponds to the orange-red region of the spectrum, and the solution will look blue to us. If we instead shorten the conjugated chain we will produce a compound that absorbs in the blue (450 nm), and that will be yellow when in solution. We just connected differential equations, quantum mechanics and the colors of things... impressive!

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10.6.5: Problems

Problem 10.6.5.1

Solve the following initial value problems:

1. $\frac{d^2x}{dt^2} + \frac{dx}{dt} - 2x = 0;\ x(0) = 1;\ x'(0) = 0$
2. $\frac{d^2x}{dt^2} + 6\frac{dx}{dt} + 9x = 0;\ x(1) = 0;\ x'(1) = 1$
3. $\frac{d^2x}{dt^2} + 9x = 0;\ x(\pi/3) = 0;\ x'(\pi/3) = -1$
4. $\frac{d^2x}{dt^2} - 2\frac{dx}{dt} + 2x = 0;\ x(0) = 1;\ x'(0) = 0$

Problem 10.6.5.2

The simple harmonic oscillator consists of a body moving in a straight line under the influence of a force whose magnitude is proportional to the displacement x of the body from the point of equilibrium, and whose direction is towards this point.

$$F = -k(x - x_0) \tag{10.6.5.1}$$

The force acts in the direction opposite to that of the displacement. The constant k is a measure of how hard or soft the spring is.

Newton's law of motion states that the force applied on an object equals its mass multiplied by its acceleration. The variable $h = x - x_0$ represents the displacement of the spring from its undistorted length, and the acceleration is the second derivative of the displacement. Therefore:

$$F = m\frac{d^2h(t)}{dt^2} \tag{10.6.5.2}$$

Combining equations 10.6.5.1 and 10.6.5.2 we obtain:

$$m\frac{d^2h(t)}{dt^2} = -kh(t) \tag{10.6.5.3}$$

which is a second order differential equation. Notice that m (the mass of the body) and k (the spring constant) are not functions of x.

Assume that the displacement h and the velocity h' at time $t = 0$ are: $h(0) = A$ and $h'(0) = 0$. Physically, this means that the displacement at time zero is A, and the body is at rest.

• Obtain an expression for $h(t)$.

• What is the period of the function you found above?

In the example above we assumed that the forces due to friction were negligible. If the oscillator moves in a viscous medium, we need to include a frictional term in Newton's equation. The force due to friction is proportional to the velocity of the mass ($h'(t)$), and the direction is opposite to the displacement. Therefore:

$$m\frac{d^2h(t)}{dt^2} = -kh(t) - \gamma\frac{dh(t)}{dt} \tag{10.6.5.4}$$

where γ is a constant that depends on the viscosity of the medium.

• Obtain an expression for $h(t)$. You will have to consider the cases $\gamma^2 < 4mk$, $\gamma^2 = 4mk$ and $\gamma^2 > 4mk$ separately. The answers are printed below so you can check your results. Be sure you show all your work step by step.

- $\gamma^2 < 4mk$:

$$h(t) = Ae^{-\gamma t/2m}\left[\cos\left(\frac{at}{2m}\right) + \frac{\gamma}{a}\sin\left(\frac{at}{2m}\right)\right], a = \sqrt{4mk - \gamma^2}$$

- $\gamma^2 = 4mk$:

$$h(t) = A\left(1 + \frac{\gamma}{2m}t\right)e^{-\gamma t/2m}$$

- $\gamma^2 > 4mk$:

$$h(t) = \frac{A}{2}e^{-\gamma t/2m}\left[\left(e^{at/2m} + e^{-at/2m}\right) + \frac{\gamma}{a}\left(e^{at/2m} - e^{-at/2m}\right)\right], a = \sqrt{\gamma^2 - 4mk}$$

? Problem 10.6.5.3

Find the eigenfunctions ($f(x)$) and eigenvalues λ of the following boundary value problems:

- $-\frac{d^2}{dx^2}f(x) = \lambda f(x)$, $f(0) = 0, f'(1) = 0$
- $-\frac{d^2}{dx^2}f(x) = \lambda f(x)$, $f'(0) = 0, f(\pi) = 0$

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