GENERAL PHYSICAL CHEMISTRY I



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This text was compiled on 04/28/2026

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CHAPTER OVERVIEW

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1.1: Properties of Gas

Learning Objectives

Make sure you thoroughly understand the following essential ideas:

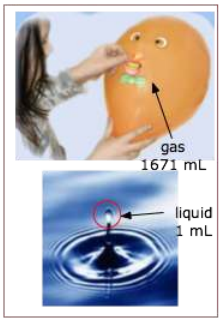
- State the ***three major properties of gases*** that distinguish them from condensed phases of matter.
- Define ***pressure***, and explain why a gas exerts pressure on the walls of a container.
- Explain the operation of a simple *barometer*, and why its invention revolutionized our understanding of gases.
- Explain why a barometer that uses water as the barometric fluid is usually less practical than one which employs mercury.
- How are the Celsius and Fahrenheit *temperature scales* defined? How do the magnitudes of the "degree" on each scale related?
- Why must the temperature and pressure be specified when reporting the *volume* of a gas?

The invention of the sensitive *balance* in the early seventeenth century showed once and for all that gases have weight and are therefore matter. Guericke's invention of air pump (which led directly to his discovery of the *vacuum*) launched the “pneumatic era" of chemistry long before the existence of atoms and molecules had been accepted. Indeed, the behavior of gases was soon to prove an invaluable tool in the development of the atomic theory of matter.

Introduction

The study of gases allows us to understand the behavior of matter at its simplest: individual particles, acting independently, almost completely uncomplicated by interactions and interferences between each other. This knowledge of gases will serve as the pathway to our understanding of the far more complicated *condensed phases* (liquids and solids) in which the theory of gases will no longer give us correct answers, but it will still provide us with a useful *model* that will at least help us to rationalize the behavior of these more complicated states of matter.

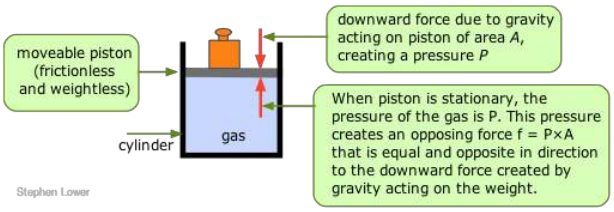
First, we know that a gas has **no definite volume or shape**; a gas will fill whatever volume is available to it. Contrast this to the behavior of a liquid, which always has a distinct upper surface when its volume is less than that of the space it occupies. The other outstanding characteristic of gases is their **low *densities***, compared with those of liquids and solids. One mole of liquid water at 298 K and 1 atm pressure occupies a volume of 18.8 cm^3, whereas the same quantity of water vapor at the same temperature and pressure has a volume of 30200 cm^3, more than 1000 times greater.



The most remarkable property of gases, however, is that to a very good approximation, **they all *behave the same way*** in response to changes in temperature and pressure, expanding or contracting by predictable amounts. This is very different from the behavior of liquids or solids, in which the properties of each particular substance must be determined individually. We will see later that each of these three *macroscopic* characteristics of gases follows directly from the *microscopic* view— that is, from the *atomic* nature of matter.

The Pressure of a Gas

The molecules of a gas, being in continuous motion, frequently strike the inner walls of their container. As they do so, they immediately bounce off without loss of kinetic energy, but the reversal of direction (*acceleration*) imparts a *force* to the container walls. This force, divided by the total surface area on which it acts, is the *pressure* of the gas.



The pressure of a gas is observed by measuring the pressure that must be applied externally in order to keep the gas from expanding or contracting. To visualize this, imagine some gas trapped in a cylinder having one end enclosed by a freely moving piston. In order to keep the gas in the container, a certain amount of weight (more precisely, a *force*, *f*) must be placed on the piston so as to exactly balance the force exerted by the gas on the bottom of the piston, and tending to push it up. The pressure of the gas is simply the quotient *f/A*, where *A* is the cross-section area of the piston.

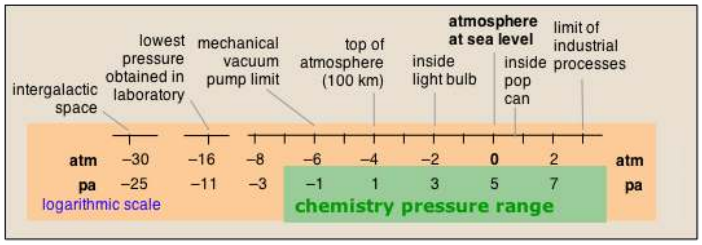
Pressure Units

The unit of pressure in the SI system is the *pascal* (Pa), defined as a force of one newton per square meter (1 Nm^{-2} = 1 kg m^{-1} s^{-2}.) At the Earth's surface, the force of gravity acting on a 1 kg mass is 9.81 N. Thus if the weight is 1 kg and the surface area of the piston is 1 M^2, the pressure of the gas would be 9.81 Pa. A 1-gram weight acting on a piston of 1 cm^2 cross-section would exert a pressure of 98.1 pA. (If you wonder why the pressure is higher in the second example, consider the number of cm^2 contained in 1 m^2.)

In chemistry, it is often common to express pressures in units of *atmospheres* or *torr*: 1 atm = 101325 Pa = 760 torr. The older unit *millimeter of mercury* (mm Hg) is almost the same as the torr and is defined as one mm of level difference in a mercury barometer at 0°C. In meteorology, the pressure unit most commonly used is the *bar*:

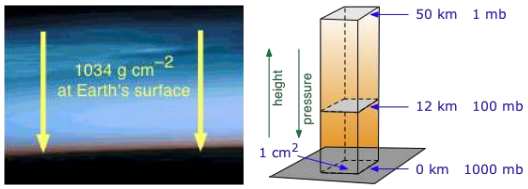
$$1 \text{ bar} = 10^5 \text{ N m}^{-2} = 750.06 \text{ torr} = 0.987 \text{ atm}.$$

The pressures of gases encountered in nature span an exceptionally wide range, only part of which is ordinarily encountered in chemistry. Note that in the chart below, the pressure scales are logarithmic; thus 0 on the atm scale means 10^0 = 1 atm.



Atmospheric Pressure

The column of air above us exerts a force on each 1-cm^2 of surface equivalent to a weight of about 1034 g. The higher into the air you go, the lower the mass of air above you, hence the lower the pressure (right).



This figure is obtained by solving Newton's law $\mathbf{F} = m\mathbf{a}$ for m, using the acceleration of gravity for $\mathbf{a}$:

$$m = \frac{101375\ kg\,m^{-1}\,s^{-2}}{9.8\,m\,s^{-2}} = 10340\,kg\,m^{-1} = 1034\ g\ cm^{-2} \tag{1.1.1}$$

Example 1.1.1

If several kilos of air are constantly pressing down on your body, why do you not feel it?

Solution

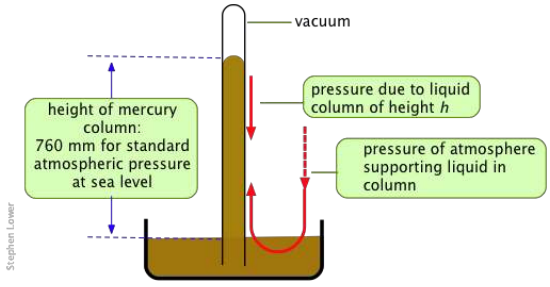
Because every other part of your body (including within your lungs and insides) also experiences the same pressure, so there is no net force (other than gravity) acting on you.

This was the crucial first step that led eventually to the concept of gases and their essential role in the early development of Chemistry. In the early 17th century the Italian Evangelista Torricelli invented a device — the *barometer* — to measure the pressure of the atmosphere. A few years later, the German scientist and some-time mayor of Magdeburg Otto von Guericke devised a method of pumping the air out of a container, thus creating which might be considered the opposite of air: the *vacuum*.

As with so many advances in science, idea of a vacuum — a region of nothingness — was not immediately accepted. Torricelli's invention overturned the then-common belief that air (and by extension, all gases) are weightless. The fact that we live at the bottom of a sea of air was most spectacularly demonstrated in 1654, when two teams of eight horses were unable to pull apart two 14-inch copper hemispheres (the "Magdeburg hemispheres") which had been joined together and then evacuated with Guericke's newly-invented vacuum pump.



The classical barometer, still used for the most accurate work, measures the height of a column of liquid that can be supported by the atmosphere. As indicated below, this pressure is exerted directly on the liquid in the reservoir, and is transmitted hydrostatically to the liquid in the column.



Metallic mercury, being a liquid of exceptionally high density and low vapor pressure, is the ideal barometric fluid. Its widespread use gave rise to the "millimeter of mercury" (now usually referred to as the "torr") as a measure of pressure.

Example 1.1.2: Water Barometer

How is the air pressure of 1034 g cm^{-3} related to the 760-mm height of the mercury column in the barometer? What if water were used in place of mercury?

Solution

The density of Hg is 13.6 g cm^{-3}, so in a column of 1-cm^2 cross-section, the height needed to counter the atmospheric pressure would be (1034 g × 1 cm^2) / (13.6 g cm^{-3}) = 76 cm.

The density of water is only 1/13.6 that of mercury, so standard atmospheric pressure would support a water column whose height is 13.6 x 76 cm = 1034 cm, or 10.3 m. You would have to read a water barometer from a fourth-story window!

Water barometers were once employed to measure the height of the ground and the heights of buildings before more modern methods were adopted.

A modification of the barometer, the *U-tube manometer*, provides a simple device for measuring the pressure of any gas in a container. The U-tube is partially filled with mercury, one end is connected to container, while the other end can either be opened to the atmosphere. The pressure inside the container is found from the difference in height between the mercury in the two sides of the U-tube. The illustration below shows how the two kinds of manometer work.

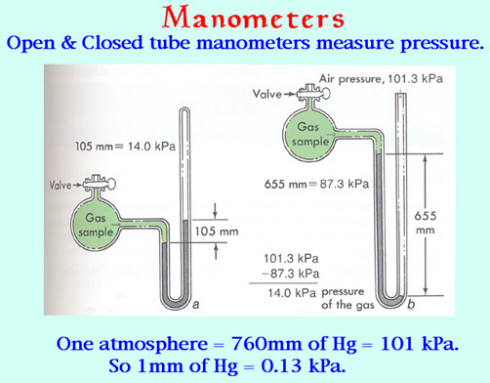


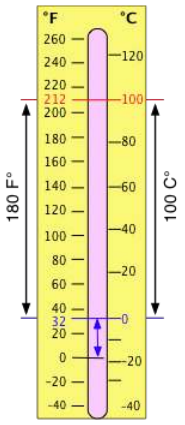
Figure **1.1.3**: In the open-tube manometer on the right, the atmosphere pushes the mercury column down in the open side, and again the pressure in torr is found from the difference in the levels. When using this method, the atmospheric pressure must be determined by means of a barometer.

The manometers ordinarily seen in the laboratory come in two flavors: closed-tube and open-tube. In the closed-tube unit shown at the left, the longer limb of the J-tube is evacuated by filling it with mercury and then inverting it. If the sample container is also evacuated, the mercury level will be the same in both limbs. When gas is let into the container, its pressure pushes the mercury down on one side and up on the other; the difference in levels is the pressure in torr. For practical applications in engineering and industry, especially where higher pressures must be monitored, many types of mechanical and electrical *pressure gauges* are available.

The Temperature of a Gas

If two bodies are at different temperatures, heat will flow from the warmer to the cooler one until their temperatures are the same. This is the principle on which *thermometry* is based; the temperature of an object is measured indirectly by placing a calibrated device known as a *thermometer* in contact with it. When thermal equilibrium is obtained, the temperature of the thermometer is the same as the temperature of the object.

A *thermometer* makes use of some temperature-dependent quantity, such as the density of a liquid, to allow the temperature to be found indirectly through some easily measured quantity such as the length of a mercury column. The resulting scale of temperature is entirely arbitrary; it is defined by locating its zero point, and the size of the *degree* unit. At one point in the 18th century, 35 different temperature scales were in use! The Celsius temperature scale (formally called centigrade) locates the zero point at the freezing temperature of water; the Celsius degree is defined as 1/100 of the difference between the freezing and boiling temperatures of water at 1 atm pressure.



The older *Fahrenheit* scale placed the zero point at the coldest temperature it was possible to obtain at the time (by mixing salt and ice.) The 100° point was set with body temperature (later found to be 98.6°F.) On this scale, water freezes at 32°F and boils at 212°F. The Fahrenheit scale is a finer one than the Celsius scale; there are 180 Fahrenheit degrees in the same temperature interval that contains 100 Celsius degrees, so 1 F° = 5/9 C°. Since the zero points are also different by 32F°, conversion between temperatures expressed on the two scales requires the addition or subtraction of this offset, as well as multiplication by the ratio of the degree size.

> *You should be able to derive the formulas for this conversion.*

Absolute Temperature

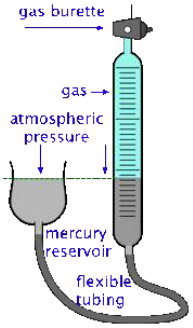
In 1787 the French mathematician and physicist Jacques Charles discovered that for each Celsius degree that the temperature of a gas is lowered, the volume of the gas will diminish by 1/273 of its volume at 0°C. The obvious implication of this is that if the temperature could be reduced to –273°C, the volume of the gas would contract to zero. Of course, all real gases condense to liquids before this happens, but at sufficiently low pressures their volumes are linear functions of the temperature (*Charles' Law*), and extrapolation of a plot of volume as a function of temperature predicts zero volume at -273°C. This temperature, known as *absolute zero*, corresponds to the total absence of thermal energy.

The temperature scale on which the zero point is –273.15°C was suggested by Lord Kelvin, and is usually known as the *Kelvin* scale. Since the size of the Kelvin and Celsius degrees are the same, conversion between the two scales is a simple matter of adding or subtracting 273.15; thus room temperature, 20°, is about 293 K.

Because the Kelvin scale is based on an absolute, rather than on an arbitrary zero of temperature, it plays a special significance in scientific calculations; most fundamental physical relations involving temperature are expressed mathematically in terms of absolute temperature. In engineering work, an absolute scale based on the Fahrenheit degree is sometimes used; this is known as the **Rankine scale**.

The volume occupied by a gas

The *volume* of a gas is simply the space in which the molecules of the gas are free to move. If we have a mixture of gases, such as air, the various gases will coexist within the same volume. In these respects, gases are very different from liquids and solids, the two condensed states of matter. The volume of a gas can be measured by trapping it above mercury in a calibrated tube known as a *gas burette*. The SI unit of volume is the cubic meter, but in chemistry we more commonly use the *liter* and the *milliliter* (mL). The *cubic centimeter* (cc) is also frequently used; it is very close to 1 milliliter (mL).



It's important to bear in mind, however, that the volume of a gas varies with both the temperature and the pressure, so reporting the volume alone is not very useful. A common practice is to measure the volume of the gas under the ambient temperature and atmospheric pressure, and then to correct the observed volume to what it would be at standard atmospheric pressure and some fixed temperature, usually 0° C or 25°C.

Contributors and Attributions

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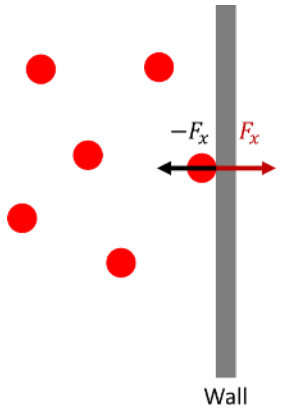
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1.2: All Dilute Gases Behave Ideally

Ideal gases have 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

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

Since the particles have no forces acting upon them, except for when they collide iwht the wall container, 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 the average force over area:

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

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 $a^3 = V$:

$$\begin{aligned} P &= \frac{Nk_B T}{V} \\ &= \frac{nRT}{V} \end{aligned} \tag{1.2.9}$$

which is the ideal gas law. It relates the pressure, volume, and temperature of an ideal gas and is referred to as an equation of state. An equation of state is a relation between variables and describes the state of matter under a set of given physical conditions. One way to visualize any equation of state is to plot *isotherms*, which are graphs of P vs. V at fixed values of T . For the ideal-gas equation of state, 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.

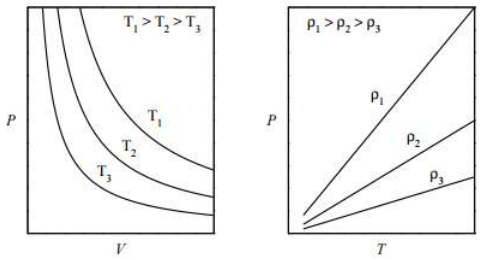


Figure 16.1.1 : (Left) Pressure vs. volume for different temperatures (isotherms of the ideal-gas equation of state. (Right) Pressure vs. temperature for different densities $\rho = N/V$.

We can rearrange the ideal gas equation of state to put all the constants and variables on one side:

$$\frac{PV}{nRT} = 1 = Z \tag{1.2.10}$$

Z is called the *compressibility* of the gas. In an ideal gas, if we compress the gas by increasing P , the volume decreases 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.

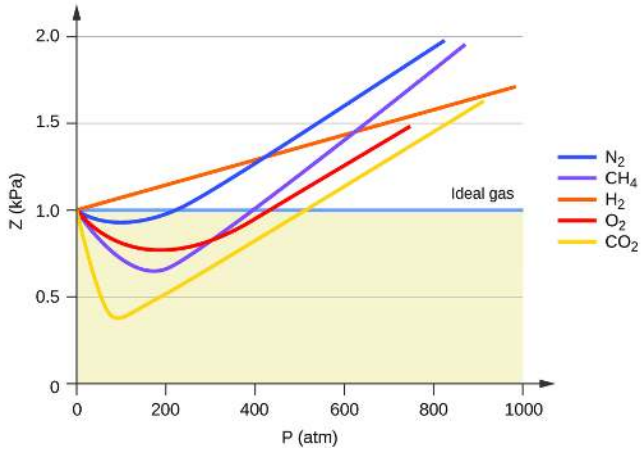


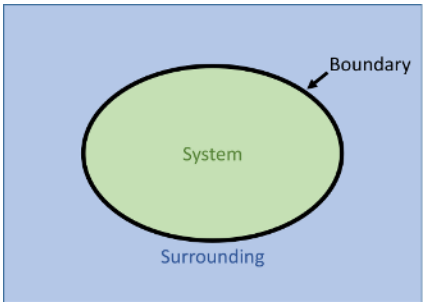
Figure 16.1.2 : A graph of the compressibility factor (Z) vs. pressure shows that gases can exhibit significant deviations from the behavior predicted by the ideal gas law. from Openstax (CC-BY)

Figure 16.1.2 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.

1.2.1: Extensive and Intensive Properties in Thermodynamics

Before we discuss ensembles and how we construct them, we need to introduce an important distinction between different types of thermodynamic properties that are used to characterize the ensemble. This distinction is *extensive* and *intensive* properties.

Thermodynamics always divides the universe into a *system* and its *surroundings* with a *boundary* between them. The unity of all three of these is the thermodynamic *universe*.



Now suppose we allow the system to grow in such a way that both the number of particles and the volume grow with the ratio N/V remaining constant. Any property that increases as we grow the system in this way is called an *extensive* property. Any property that remains the same as we grow the system in this way is called *intensive*.

The ideal gas equation of state can be written in an extensive form:

$$\begin{aligned} PV &= nRT \\ P\bar{V} &= RT \\ P &= \rho RT \end{aligned} \tag{1.2.11}$$

where $\bar{V} = V/n$ is called the molar volume and $\rho = N/V$ is called density. Unlike V , which increases as the number of moles increases (an *extensive* quantity, $\bar{V}$ and ρ do not exhibit this dependence and, therefore, are called *intensive*. Compressibility can also be written in an intensive form:

$$\begin{aligned} Z &= \frac{PV}{nRT} \\ &= \frac{P\bar{V}}{RT} \\ &= \frac{P}{\rho RT} \end{aligned}$$

Some examples of intensive and extensive properties include:

- Extensive: number of particles (N), moles (n), volume (V), mass (m), energy, free energy
- Intensive: pressure (P), density (ρ), molar heat capacity (C), temperature (T)

Contributors and Attributions

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1.3: van der Waals and Redlich-Kwong Equations of State

The ideal gas law is valid for low pressures, where the finite volume of particles and intermolecular attractions do not have a large impact. At higher pressures, we must account for these factors. The van der Waals and Redlich-Kwong equations of states are equations of state that attempt to account for real gas behavior by modifying the ideal gas law with two additional parameters.

1.3.1: The Van der Waals Equation of State

The van der Waals Equation of State is an equation relating the density of gases and liquids to the pressure, volume, and temperature conditions (i.e., it is a thermodynamic equation of state). It can be viewed as an adjustment to the ideal gas law that takes into account the non-zero volume of gas molecules and inter-particle attraction using correction terms a and b. It was derived in 1873 by Johannes Diderik van der Waals, who received the Nobel Prize in 1910 for this work. The van der Waals equation of state is:

$$P = \frac{nRT}{V - nb} - \frac{an^2}{V^2} \tag{1.3.1}$$

Equation 1.3.1 can also be rewritten as

$$\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$$

If the correction terms a and b go to zero, the equation reduces to the ideal gas equation of state:

$$PV = nRT$$

Let's first look first at the correction term b, which represents the volumes of the particles and assumes a hard-wall potential, $u_o(r)$. This potential energy term describes a system of hard sphere "billiard balls" of diameter σ. Figure 16.2.1 shows two of these billiard ball type particles at the point of contact (i.e, the distance of closest approach). At this point, they undergo a collision and separate, so they cannot be closer than that distance.

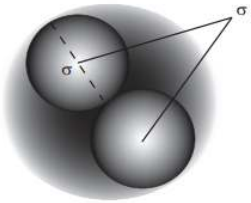


Figure 16.2.1 : Two hard spheres of diameter σ at closest contact. The distance between their centers is also σ. A sphere of radius σ just containing the two particles is shown in cross-section.

The distance between their centers is also σ. Because of this distance of closest approach, the total volume available to the particles is not the volume of the container, V, but some volume less than V. This reduction in volume can be calculated. Figure 16.2.1 shows a shaded sphere that just contains the pair of billiard ball particles. The volume of this sphere is the volume excluded from any two particles. The radius of the sphere is σ and the excluded volume for the two particles is $4\pi\sigma^3/3$, which is the volume of the shaded sphere. From this, we see that the excluded volume for any *one* particle is just half of this or $\frac{2}{3}\pi\sigma^3$. The excluded volume for a mole of such particles is the parameter b:

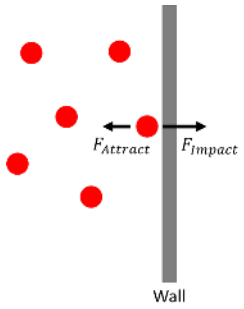
$$b = \frac{2}{3}\pi\sigma^3 N_0$$

Given n moles of gas, the total excluded volume is then nb, so that the total *available* volume is $V - nb$.

Let's turn our attention the a, which represents the intermolecular attractions of the particles. Molecular attractions tend to make the P exerted by the gas less than that predicted by the ideal gas law at low pressures. P is force over area:

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

Pressure is proportion to the net force on the wall of the container:



The net force is the force of the molecules impacting the container wall minus the intermolecular attraction of the molecules:

$$\bar{F}_{Net} = \bar{F}_{Impact} - \bar{F}_{Attract}$$

Therefore, the pressure will be less for the real gas than the ideal gas. We can add a correction term to pressure to account for intermolecular attractions:

$$P_{VDW} = P_{Real} + a\,(?)$$

V does influence the amount of intermolecular attraction because P is reduced as V is increased:

$$P \propto \frac{1}{V}$$

And pressure is proportional to the number of attractive interactions:

of molecular interactions $\propto P^2$

of molecular interactions $\propto \frac{1}{V^2}$

We now have an expression for the van der Waals P:

$$P = P_{Real} + \frac{an^2}{V^2}$$

The constants a and b depend on the substance. Some typical values are:[1]

Molecule	a $\left(\frac{L^2 \cdot bar}{mol^2}\right)$	b $\left(\frac{L}{mole}\right)$
H_2O	5.536	0.03049
N_2	1.43	0.03913
CH_4	2.283	0.04278
C_2H_6	5.562	0.0638

1. *R. C. Weast (1972). Handbook of Chemistry and Physics 53rd Edition. Chemical Rubber Pub.*

1.3.2: Redlich-Kwong Equation of State

The van der Waals Equation of State had to wait almost 100 years before a real, successful improvement was introduced to it. This progress occurred once researchers committed themselves to finding the empirical temperature dependency of the attraction parameter a proposed by van der Waals. In contrast, very little attention has been paid to modifying the parameter b for co-volume. It makes a lot of sense that b would not be modified by temperature, because it represents the *volume* of the molecules, which should not be affected by their kinetic energy (measured in terms of temperature). The very first noteworthy successful modification to the attraction parameter came with the publication of the equation of state of Redlich-Kwong in 1949.

The Redlich–Kwong equation of state is an empirical, algebraic equation that relates temperature, pressure, and volume of gases. It is generally more accurate than the van der Waals and the ideal gas equations of state at temperatures above the critical temperature. It was formulated by Otto Redlich and Joseph Neng Shun Kwong in 1949, who showed that a simple two-parameter

equation of state could well reflect reality in many situations. Redlich and Kwong revised the van der Waals Equation of State (Equation 1.3.1) and proposed the following expressions:

$$\left(P+\frac{a}{\sqrt{T}\bar{V}(\bar{V}+b)}\right)(\bar{V}-b)=RT \tag{1.3.2}$$

The fundamental change they introduced was to the functional form of $\partial P_{\text{attraction}}$. Additionally, they introduced the co-volume b into the denominator of this functional form. The important concept here is that the attraction parameter a of van der Waals needed to be made a function of temperature to do a better job of quantitatively matching experimental data. This was a realization that van der Waals had suggested, but no actual functional dependency had been introduced until the Redlich-Kwong equation.

We know what follows at this point. To come up with an expression for a and b of Equation 1.3.2, we apply the criticality conditions to this equation of state. As we recall, imposing the criticality conditions allows us to relate the coefficients a and b to the critical properties (P_c, T_c) of the substance. Once we have done that, we obtain the definition of a and b for the Redlich-Kwong equation of state:

$$a=0.42780\frac{R^2T_c^{2.5}}{P_c} \tag{1.3.3}$$

$$b=0.086640\frac{RT_c}{P_c} \tag{1.3.4}$$

The Redlich-Kwong equation of state radically improved, in a quantitative sense, the predictions of the van der Waals equation of state. We now recall that van der Waals-type equations are cubic because they are cubic polynomials in molar volume and compressibility factor. It comes as no surprise then, that we can transform Equation 1.3.2 into:

$$\bar{v}^3-\left(\frac{RT}{P}\right)\bar{v}^2+\frac{1}{P}\left(\frac{1}{T^{0.5}}-bRT-Pb^2\right)\bar{v}-\frac{ab}{PT^{0.5}}=0 \tag{1.3.5}$$

and, by defining the following parameters:

$$A=\frac{aP}{R^2T^{2.5}} \tag{1.3.6}$$

$$B=\frac{bP}{RT} \tag{1.3.7}$$

and introducing the compressibility factor definition:

$$Z=\frac{P\bar{v}}{RT}$$

we get:

$$Z^3-Z^2+(A-B-B^2)Z-AB=0 \tag{1.3.8}$$

We may also verify the two-parameter corresponding state theory by introducing Equations 1.3.3, 1.3.4, and 1.3.5 into Equation 1.3.8:

$$Z^3-Z^2+\frac{P_r}{T_r}\left(\frac{0.42748}{T_r^{1.5}}-0.08664-0.007506\frac{P_r}{T_r}\right)Z-0.03704\frac{P_r^2}{T_r^{3.5}}=0 \tag{1.3.9}$$

Where:

$$P_r=\frac{P}{P_c}$$

$$T_r=\frac{T}{T_c}$$

P_r and T_r are the pressure and temperature at the reduced state. See Section 16.4 for more information on reduced states. In Equation 1.3.9, we can observe the same thing that we saw with the van der Waals equation of state: gases at corresponding states

have the same properties. Equation 1.3.9 is particularly clear about it: any two different gases at the same P_r, T_r condition have the same compressibility factor.

Just as any other cubic equation of state, Equations 1.3.2 through 1.3.9, as they stand, are to be applied to pure substances. For mixtures, however, we apply *the same equation*, but we impose certain mixing rules to obtain a and b, which are functions of the properties of the pure components. Strictly speaking, we create a new "pseudo" pure substance that has the average properties of the mixture. Redlich-Kwong preserved the same mixing rules that van der Waals proposed for his eqution of state:

$$a_m = \sum_i \sum_j y_i y_j a_{ij}$$

with

$$a_{ij} = \sqrt{a_i a_j}$$

and

$$b_m = \sum_i y_i b_i$$

Naturally, Redlich and Kwong did not have the last word on possible improvements to the van der Waals equation of state. The Redlich-Kwong equation of state, as shown here, is no longer used in practical applications. Research continued and brought with it new attempts to improve the Redlich-Kwong equation of state. After more than two decades, a modified Redlich-Kwong equation of state with very good potential was developed.

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1.4: A Cubic Equation of State

1.4.1: Isotherms

Isotherms are plots of the pressure of a gas as a function of volume at a fixed constant temperature. The isotherms for an ideal gas are hypberbolas:

$$P = \frac{RT}{\bar{V}}$$

where $\bar{V}$ is the molar volume V/n. We know that at sufficiently low temperatures, any real gas, when compressed, must undergo a transition from gas to liquid. The signature of such a transition is a discontinuous change in the volume, signifying the condensation of the gas into a liquid that occupies a significantly lower volume.

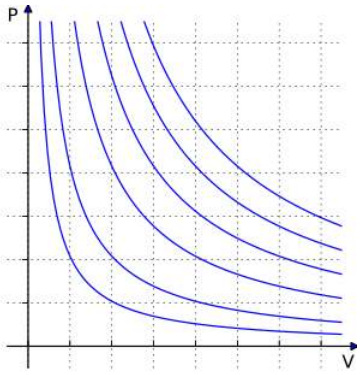


Figure 16.3.1 : Ideal gas isotherms for one mole of the gas and at select temperatures. (public domain).

CO_2 isotherms for the van der Waals Equation of state are shown in Figure 16.3.2 . At sufficiently high temperatures, the isotherms approach those of an ideal gas. At lower temperatures, the fluid obeys approximately the ideal gas law $PV = nRT$ at large volumes when the pressures are low. If we decrease the volume (go to the left in the figure along an isotherm), the pressure rises. Consider the (blue) isotherm of 10 °C, which is below the critical temperature. Decrease the volume until we reach the point B, where condensation (formation of liquid CO_2) starts. At this point the van der Waals curve is no longer physical (excluding the possibility of the occurrence of an oversaturated, metastable gas) because P and V increase together. It should be clear that many approximations and assumptions go into the derivation of the van der Waals equation so that some of the important physics is missing from the model. Hence, we should not be surprised if the van der Waals equation has some unphysical behavior buried in it. In reality, the pressure stays constant between the region A and B and the real physical behavior is given by the dashed blue line, called the *tie line*. This lines represents the gas-liquid coexistence and the pressure is equal to the vapor pressure of the liquid.

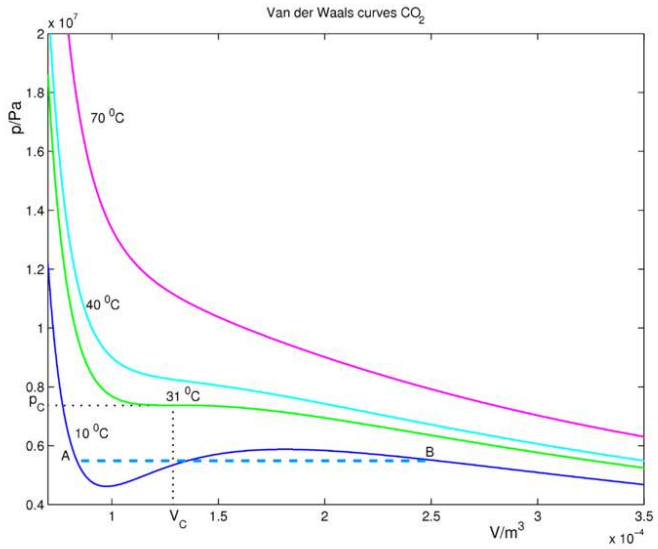


Figure 16.3.2 : Different isotherms (curves of constant temperature) of the van der Waals equation of state using parameters a and b computed for carbon dioxide. The dashed line from A to B is drawn in accordance with Maxwell's equal area rule. The carbon dioxide molecule (CO_2) has p_C = 7.37 MPa and T_C = 304.1 K = 31 ˚C , which gives a = 0.366 m^6 Pa and b = 42.9 10^{-6} m^3. The critical pressure is at 73.7 bar = 7370 kPa.

The tie line must be added in *ad hoc* by drawing a horizontal line through the isotherm (Figure 16.3.2). The vertical position of the line is chosen so that the area above the line (between the line and the isotherm) and below the line (again between the line and the isotherm) is exactly the same. This is known as *Maxwell's construction*. In this way, we entirely remove the artifact of the unphysical increase of P with V when we compute the compressional work on the gas from $\int P(V)\, dV$, to be discussed in our section on thermodynamics. Although the van der Waals curves have regions where they are not physical, the equation for these curves, derived by van der Waals in 1873, was a great scientific achievement.

Note

Even today it is not possible to give a *single* equation that describes correctly the gas-liquid phase transition.

1.4.2: Critical Point

Looking to the left of point A on the 10 °C isotherm (blue curve), the system is in the liquid state. Increasing the volume to point A leads to a rapid drop in the pressure of the system because the compressibility of a liquid is considerable smaller than that of a gas. The system is still in the liquid state at point A, but as we increase the volume further, we enter the gas-liquid coexistence line and the liquid begins to transition to gas. As we move along this line to the right, there is less liquid and more gas in the system until we reach point B, at which point the system will be completely in the gas phase. The areas, bounded by the 10 °C isotherm (blue curve) below and above the coexistence line are equal. Any further increase in the volume will lead to an expansion of the gas.There is exactly one isotherm along which the van der Waals equation correctly predicts the gas-to-liquid phase transition. If one follows the 31 °C isotherm (green curve in Figure 16.3.2) of critical temperature, the volume discontinuity captured by the tie line is shrunken down to a single point (so that there is no possibility of an increase of P with V!). This point is called the critical point and it exists at only one temperature, called the **critical temperature**, denoted T_c. The critical isotherm at the critical temperature corresponds to the highest possible temperature at which a gas-liquid transition can occur. Isotherms at higher temperatures have no liquid-gas phase transitions. Along those isotherms, the higher pressure fluid, called a supercritical fluid, resembles a liquid, while at lower pressures the fluid is more gas-like.

The critical point exists at an inflection where the first and second derivatives of P with respect to V are zero:

$$\left(\frac{\partial P}{\partial V}\right)_{T_c} = 0$$

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_{T_c} = 0$$

Substituting the van der Waals equation into these two conditions, we find the following:

$$-\frac{nRT_c}{(V_c - nb)^2} + \frac{2an^2}{V_c^3} = 0$$
$$\frac{2nRT_c}{(V_c - nb)^3} - \frac{6an^2}{V_c^4} = 0$$

Hence, we have two equations in two unknowns V_c and T_c for the critical temperature and critical volume. Once these are determined, the van der Waals equation, itself, allows us to determine the critical pressure, P_c. To solve the equations, first divide one by the other. This gives us a simple condition for the volume:

$$\frac{V_c - nb}{2} = \frac{V_c}{3}$$
$$3V_c - 3nb = 2V_c$$
$$V_c = 3nb$$

This is the **critical volume**. Now use either of the two conditions to obtain the critical temperature, T_c. If we use the first one, we find:

$$\frac{nRT_c}{(V_c - nb)^2} = \frac{2an^2}{V_c^3}$$
$$\frac{nRT_c}{(3nb - nb)^2} = \frac{2an^2}{(3nb)^3}$$
$$\frac{nRT_c}{4n^2b^2} = \frac{2an^2}{27n^3b^3}$$
$$RT_c = \frac{8a}{27b}$$

Finally, plugging the critical temperature and volume into the van der Waals equation, we obtain the critical pressure:

$$P_c = \frac{nRT_c}{V_c - nb} - \frac{an^2}{V_c^2}$$
$$= \frac{8an/27b}{3nb - nb} - \frac{an^2}{(3nb)^2}$$
$$= \frac{a}{27b^2}$$

It comes as no surprise that cubic equations of state like the van der Waals (and Redlich-Kwong) equations of state yield three different roots for volume and compressibility factor. This is simply because they are algebraic equations, and any nth order algebraic equation will always yield “n” roots. However, those “n” roots are not required to be distinct, and that is not all: they are not required be real numbers, either. A quadratic expression (n = 2) may have zero real roots (e.g., $x^2 + 1 = 0$); this is because those roots are complex numbers. In the case of cubic expressions (n = 3), we will either have one or three real roots; this is because complex roots always show up in pairs (i.e., once you have a complex root, its conjugate must also be a solution). In our case, and because we are dealing with physical quantities (densities, volumes, compressibility factors), only real roots are of interest. More specifically, we look for real, positive roots such that $\bar{V} > b$ in the case of molar volume and $Z > \frac{Pb}{RT}$ in the case of compressibility factor.

In a cubic equation of state, the possibility of three real roots is restricted to the case of sub-critical conditions ($T < T_c$), because the S-shaped behavior, which represents the vapor-liquid transition, takes place only at temperatures below critical. This restriction is mathematically imposed by the criticality conditions. Anywhere else, beyond the S-shaped curve, we will only get one real root of the type $\bar{V} > b$. Figure 16.3.3 illustrates this point.

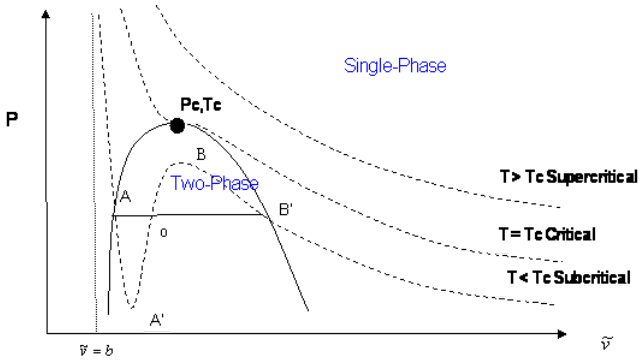


Figure 16.3.3 : Multiple Roots in Cubic EOS

The shape of the critical isotherm at the critical point allows us to determine the exact temperature, pressure, and volume at which the phase transitions from gas to liquid will occur. If we draw a curve through the isotherms joining all points of these isotherms at which the tie lines begin, continue the curve up to the critical isotherm, and down the other side where the tie lines end, this curve reaches a maximum at the critical point. The region inside this curve is when the gas and liquid phases coexist.

Let us summarize the three cases presented in Figure 16.3.3 :

1. Supercritical isotherms ($T > T_c$: At temperatures beyond critical, the cubic equation will have only one real root (the other two are imaginary complex conjugates). In this case, there is no ambiguity in the assignment of the volume root since we have single-phase conditions. The occurrence of a unique real root remains valid at any pressure: any horizontal (isobaric) line cuts the supercritical isotherm just once in Figure 16.3.3 .
2. Critical isotherm ($T = T_c$): At the critical point ($P = P_c$), vapor and liquid properties are the same. Consequently, the cubic equation predicts three real and equal roots at this special and particular point. However, for any other pressure along the critical isotherm ($P < P_c$ or $P > P_c$,) the cubic equation gives a unique real root with two complex conjugates.
3. Subcritical isotherm ($T < T_c$): Predictions for pressures within the pressure range for metastability ($P'_A < P < P'_B$) or for the saturation condition ($P = P^{sat}$) will always yield three real, different roots. In fact, this is the only region where an isobar cuts the same isotherm more than once. The smallest root is taken as the specific volume of the liquid phase; the largest is the specific volume of the vapor phase; the intermediate root is not computed as it is physically meaningless. However, do not get carried away. Subcritical conditions will not always yield three real roots of the type $\bar{v} > b$. If the pressure is higher than the maximum of the S-shaped curve, P_B, we will only have one (liquid) real root that satisfies $\bar{v} > b$. By the same token, pressures between $0 < P < P'_A$ yield only one (vapor) root. In the case of P'_A being a negative number, three real roots are to be found even for very low pressures when the ideal gas law applies. The largest root is always the correct choice for the gas phase molar volume of pure components.

Most of these considerations apply to the cubic equation of state in Z (compressibility factor). The most common graphical representation of compressibility factor is the well-known chart of Standing and Katz, where compressibility, Z, is plotted against pressure (Figure 16.3.4). Standing and Katz presented their chart for the compressibility factor of sweet natural gases in 1942. This chart was based on experimental data. Graphical determination of properties was widespread until the advent of computers, and thus the Standing and Katz Z-chart became very popular in the natural gas industry. Typical Standing and Katz charts are given for high temperature conditions ($T > T_c$ or $T_r > 1$).

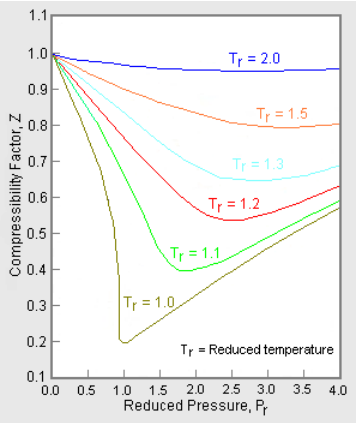


Figure 16.3.4 : Compressibility Factor versus Pressure

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1.5: The Law of Corresponding States

Johannes Diderik van der Waals modified the ideal gas law to better describe the behavior of real gases by introducing corrections to account for the finite size of molecules and the intermolecular forces between them, leading to the well-known van der Waals equation.

$$\left(P + \frac{a}{V_m^2}\right)(V_m - b) = RT \tag{1.5.1}$$

This expression for the van der Waal gas involves two phenomenological constants, a and b. Van der Waals postulated that all real gases at corresponding states should behave similarly and he focused on applying Equation 1.5.1 at the critical point of difference gases—the unique temperature, pressure, and volume at which the distinction between liquid and gas disappears.

The corresponding state that van der Waals chose to use is called the **reduced state**, which is based on the deviation of the conditions of a substance from its own critical conditions. We can define reduced quantities:

$$P_r = \frac{P}{P_c}$$
$$V_r = \frac{V}{V_c}$$
$$T_r = \frac{T}{T_c}$$

By substitution into Equation 1.5.1, the Van der Waal equations can be expressed differently

$$\left(P_r + \frac{3}{\bar{V}_r^2}\right)\left(\bar{V}_r - \frac{1}{3}\right) = \frac{8}{3}T_r \tag{1.5.2}$$

Equation 1.5.2 means the critical parameters for a gas can be expressed in terms of a and b parameters:

$$V_c = 3b$$
$$P_c = \frac{a}{27b^2}$$
$$T_c = \frac{8a}{27bR}$$

Hence, when gases are expressed in terms of their **reduced variables**, the van der Waals equation takes on a universal form (Equation 1.5.2) that applies to all gases, regardless of their chemical identity. This discovery led van der Waals to formulate the **Law of Corresponding State**s, which states that different gases at the same reduced temperature and reduced pressure will exhibit similar thermodynamic behavior. This principle provided a unifying framework for understanding real-gas behavior and laid the foundation for generalized equations of state and compressibility charts used in modern thermodynamics.

Although the actual pressures and volumes may differ, two gases are said to be in corresponding states if their reduced pressure, volume, and temperature are the same. What it says is that the behavior of all gases (and liquids!!) is pretty much the same, except for a scaling factor that is related to the critical point of the substance. The compressibility value (Z) of 3/8 at the critical point for the van der Waals equation is actually not in such good agreement with measurement. This is why the more complicated Redlich-Kwong and Peng-Robertson expressions are better, although the idea is the same. Hence, all one needs to know to describe any fluid's behavior is its critical point. For example, argon behaves much the same at 300 K as ethane does at 600 K because these temperatures correspond to twice their respective critical temperatures (150.72 K and 305.4 K, respectively) so $T_r = 2.0$.

1.5.1: Compressibility

The Compressibility provides a useful way to compare the behavior of real gases with that predicted by the ideal gas law, and it connects directly to the critical ratios first introduced by van der Waals.

$$Z = \frac{PV}{RT}$$

Over the past 150 years, researchers have collected extensive experimental data on a wide variety of fluids, allowing the Law of Corresponding States to be tested and validated. When the pressure, temperature, and volume of different fluids are expressed in terms of their reduced values, their measurements can be superimposed on the same compressibility chart (Figure **1.5.1**). This overlap shows that most “normal” fluids, despite having different molecular structures, follow a common pattern of behavior when scaled by their critical properties.

We can rewrite the universal expression for compressibility Z using reduced variables and plot measured values of Z versus the reduced pressure, P_r (Figure **1.5.1**). As you can see, very different gases/liquids like nitrogen and water can be made to coincide if their properties are plotted relative to there critical points rather than in absolute terms. The compressibility factor Z can also be cast into the form of corresponding states showing that Z also can be expressed as a universal function of V_r and T_r or any other two reduced quantities:

$$Z = \frac{\bar{V}_r}{\bar{V}_r - \frac{1}{3}} - \frac{9}{8\bar{V}_r T_r}$$

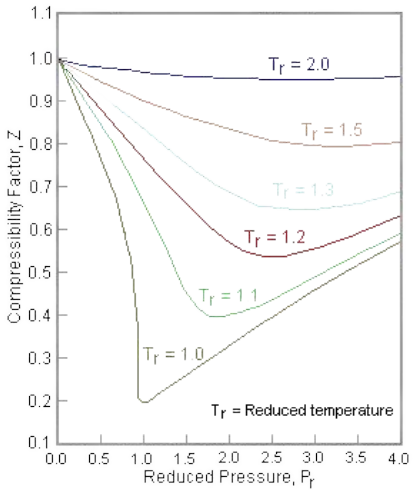


Figure **1.5.1**: Example of a generalized compressibility factor graph (Public domain; Milton Beychok)

These charts show that most “normal” fluids, such as simple hydrocarbons, noble gases, and diatomic molecules, conform closely to the predictions of the Law of Corresponding States. Deviations occur mainly in more complex or strongly associating fluids—such as water, ammonia, or hydrogen fluoride—where strong polarity or hydrogen bonding introduces additional interactions not accounted for by van der Waals’ simple model. Nevertheless, the overall success of the law demonstrates its power: by scaling thermodynamic variables to the critical constants, we can describe the behavior of a wide variety of substances with a single framework. This insight not only validated van der Waals’ pioneering theory but also provided a foundation for modern equations of state and practical tools in chemical engineering and physical chemistry.

Van der Waals did not stop here. He went on to describe the root cause of condensation of gases into liquids at lower temperatures: the attractive interactions between the molecules.

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1.6: The Second Virial Coefficient

The second virial coefficient describes the contribution of the pair-wise potential to the pressure of the gas. The third virial coefficient depends on interactions between three molecules, and so on and so forth.

1.6.1: Introduction

As the density is increased the interactions between gas molecules become non-negligible. Deviations from the ideal gas law have been described in a large number of equations of state. The *virial equation of state* expresses the deviation from ideality in terms of a power series in the density:

$$\frac{P}{kT} = \rho + B_2(T)\rho^2 + B_3(T)\rho^3 + ...$$

- $B_2(T)$ is the second virial coefficient,
- $B_3(T)$ is called the third virial coefficient, etc.

The j[th] virial coefficient can be calculated in terms of the interaction of j molecules in a volume V. The second and third virial coefficients give most of the deviation from ideal (P/rkT) up to 100 atm.

The **second virial coefficient** is usually written as B or as B_2. The second virial coefficient represents the initial departure from ideal-gas behavior. The second virial coefficient, in three dimensions, is given by:

$$B_2(T) = -\frac{1}{2}\int \left(\exp\left(-\frac{\Phi_{12}(\mathbf{r})}{k_B T}\right) - 1\right) 4\pi r^2 dr$$

where $\Phi_{12}(\mathbf{r})$ is the intermolecular pair potential, T is the temperature, and k_B is the Boltzmann constant. Notice that the expression within the parenthesis of the integral is the *Mayer f-function*. In practice, the integral is often *very hard* to integrate analytically for anything other than, say, the hard sphere model, thus one numerically evaluates:

$$B_2(T) = -\frac{1}{2}\int \left(\left\langle \exp\left(-\frac{\Phi_{12}(\mathbf{r})}{k_B T}\right)\right\rangle - 1\right) 4\pi r^2 dr$$

calculating:

$$\left\langle \exp\left(-\frac{\Phi_{12}(\mathbf{r})}{k_B T}\right)\right\rangle$$

for each r using the numerical integration scheme proposed by Harold Conroy [1][2].

1.6.2: Calculation of virial coefficients

The configuration integrals for Z_1, Z_2, and Z_3 are:

- $Z_1 = \int dr_1 = V$
- $Z_2 = \int e^{-U_2/kT} dr_1\ dr_2$
- $Z_3 = \int e^{-U_3/kT} dr_1\ dr_2\ dr_3$

The series method allows the calculation of a number of virial coefficients. Recall that the second and third virial coefficient can account for the properties of gases up to hundreds of atmospheres. We will discuss the calculation of the second virial coefficient for a monatomic gas to illustrate the procedure. To calculate $B_2(T)$ we need U_2. For monatomic particles it is reasonable to assume that the potential depends only on the separation of the two particles so $U_2 = u(r_{12})$, where $r_{12} = |r_2 - r_1|$. Using a change of variables we can write this integral $r_{12} = r_2 - r_1$ and after integration over r_1 we can transform variables from dr_{12} to $4\pi r^2 dr$. The result is:

$$B_2(T) = -2\pi \int [e^{-\beta u(r)} - 1] r^2\ dr$$

This expression can be used to obtain parameters from experiment. The second virial coefficient is tabulated for a number of gases. For a hard-sphere potential there is an infinite repulsive wall at a particle radius σ. There is no attractive part.

$$B_2(T) = -2\pi \int_0^\sigma [-1] r^2 \, dr$$
$$= \frac{2\pi\sigma^3}{3}$$

The Lennard-Jones potential cannot be calculated analytically, but the integral can be computed numerically. The second virial coefficient was a useful starting point for obtaining Lennard-Jones parameters that were used in simulations.

1.6.3: Isihara-Hadwiger Formula

The Isihara-Hadwiger formula was discovered simultaneously and independently by Isihara and the Swiss mathematician Hadwiger in 1950. The second virial coefficient for any hard convex body is given by the exact relation:

$$B_2 = RS + V$$

or:

$$\frac{B_2}{V} = 1 + 3\alpha$$

where:

$$\alpha = \frac{RS}{3V}$$

where V is the volume, S, the surface area, and R the mean radius of curvature.

1.6.4: Hard spheres

For the hard sphere model one has:[9]

$$B_2(T) = -\frac{1}{2} \int_0^\sigma (\langle 0 \rangle - 1) \, 4\pi r^2 dr$$

leading to

$$B_2 = \frac{2\pi\sigma^3}{3}$$

Note that B_2 for the hard sphere is independent of temperature.

1.6.5: Van der Waals equation of state

For the Van der Waals equation of state one has:

$$B_2(T) = b - \frac{a}{RT}$$

1.6.6: Excluded volume

The second virial coefficient can be computed from the expression:

$$B_2 = \frac{1}{2} \iint v_{\text{excluded}}(\Omega, \Omega') f(\Omega) f(\Omega') \, \mathrm{d}\Omega \mathrm{d}\Omega'$$

where v_{excluded} is the excluded volume.

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1.6.8: **Related reading**

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- G. A. Vliegenthart and H. N. W. Lekkerkerker "Predicting the gas–liquid critical point from the second virial coefficient", Journal of Chemical Physics **112** pp. 5364-5369 (2000)

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1.7: The Repulsive Term in the Lennard-Jones Potential

Proposed by Sir John Edward Lennard-Jones, the Lennard-Jones potential describes the potential energy of interaction between two non-bonding atoms or molecules based on their distance of separation. The potential equation accounts for the difference between attractive forces (dipole-dipole, dipole-induced dipole, and London interactions) and repulsive forces.

1.7.1: Introduction

Imagine two rubber balls separated by a large distance. Both objects are far enough apart that they are not interacting. The two balls can be brought closer together with minimal energy, allowing interaction. The balls can continuously be brought closer together until they are touching. At this point, it becomes difficult to further decrease the distance between the two balls. To bring the balls any closer together, increasing amounts of energy must be added. This is because eventually, as the balls begin to invade each other's space, they repel each other; the force of repulsion is far greater than the force of attraction.

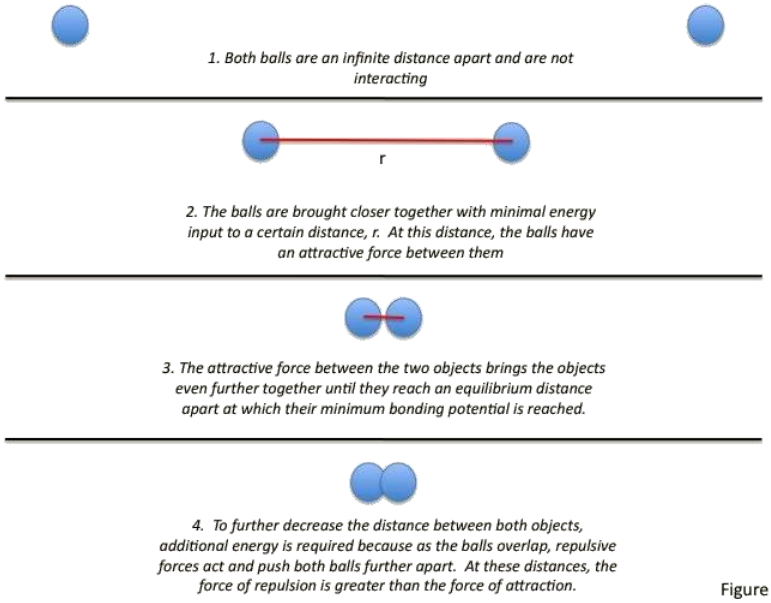


Figure A

This scenario is similar to that which takes place in neutral atoms and molecules and is often described by the **Lennard-Jones potential**.

1.7.2: The Lennard-Jones Potential

The Lennard-Jones model consists of two 'parts'; a steep repulsive term, and smoother attractive term, representing the London dispersion forces. Apart from being an important model in itself, the Lennard-Jones potential frequently forms one of 'building blocks' of many force fields. It is worth mentioning that the 12-6 Lennard-Jones model is not the most faithful representation of the potential energy surface, but rather its use is widespread due to its computational expediency. The Lennard-Jones Potential is given by the following equation:

$$V(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right] \tag{1.7.1}$$

or is sometimes expressed as:

$$V(r) = \frac{A}{r^{12}} - \frac{B}{r^{6}} \tag{1.7.2}$$

where

- V is the intermolecular potential between the two atoms or molecules.
- ϵ is the well depth and a measure of how strongly the two particles attract each other.

- σ is the distance at which the intermolecular potential between the two particles is zero (Figure **1.7.1**). σ gives a measurement of how close two nonbonding particles can get and is thus referred to as the *van der Waals radius*. It is equal to one-half of the internuclear distance between nonbonding particles.
- r is the distance of separation between both particles (measured from the center of one particle to the center of the other particle).
- $A = 4\epsilon\sigma^{12}$, $B = 4\epsilon\sigma^{6}$
- Minimum value of $\Phi_{12}(r)$ at $r = r_{min}$.

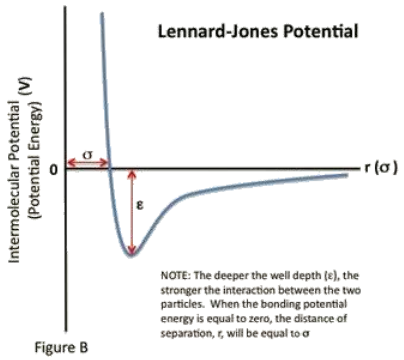


Figure **1.7.1**: The Lennard-Jones potential describes both the attraction and repulsion between nonionic particles. The first part of the equation, the short-ranged $\sigma/r)^{12}$ term describes the repulsive forces between particles while the latter part of the equation and the longer-ranged σ/r^{6} term denotes the attraction.

Example 1.7.1: The van der Waals Radius

The ϵ and σ values for Xenon (**Xe**) are found to be 1.77 kJ/mol and 4.10 Angstroms, respectively. Determine the van der Waals radius for the Xenon atom.

Solution

Recall that the van der Waals radius is equal to one-half of the internuclear distance between nonbonding particles. Because σ gives a measure of how close two non-bonding particles can be, the van der Waals radius for Xenon (Xe) is given by:

$$r = \sigma/2 = 4.10 \text{ Angstroms}/2 = 2.05 \text{ Angstroms}$$

1.7.2.1: Bonding Potential

The Lennard-Jones potential is a function of the distance between the centers of two particles. When two non-bonding particles are an infinite distance apart, the possibility of them coming together and interacting is minimal. For simplicity's sake, their bonding potential energy is considered zero. However, as the distance of separation decreases, the probability of interaction increases. The particles come closer together until they reach a region of separation where the two particles become bound; their bonding potential energy decreases from zero to a negative quantity. While the particles are bound, the distance between their centers continue to decrease until the particles reach an equilibrium, specified by the separation distance at which the minimum potential energy is reached.

If the two bound particles are further pressed together, past their equilibrium distance, repulsion begins to occur: the particles are so close together that their electrons are forced to occupy each other's orbitals. Repulsion occurs as each particle attempts to retain the space in their respective orbitals. Despite the repulsive force between both particles, their bonding potential energy increases rapidly as the distance of separation decreases.

Example 1.7.2

Calculate the intermolecular potential between two Argon (Ar) atoms separated by a distance of 4.0 Angstroms (use ϵ=0.997 kJ/mol and σ=3.40 Angstroms).

Solution

To solve for the intermolecular potential between the two Argon atoms, we use equation 2.1 where V is the intermolecular potential between two non-bonding particles.

$$V = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

The data given are:

- $\epsilon = 0.997\ \text{kJ/mol}$,
- $\sigma = 3.40\ \text{Angstroms}$, and
- the distance of separation, $r = 4.0\ \text{Angstroms}$.

We plug these values into Equation 1.7.1 and solve as follows:

$$\begin{aligned} V &= 4(0.997\ \text{kJ/mol})\left[\left(\frac{3.40\ \text{Angstroms}}{4.0\ \text{Angstroms}}\right)^{12} - \left(\frac{3.40\ \text{Angstroms}}{4.0\ \text{Angstroms}}\right)^{6}\right] \\ &= 3.988(0.14 - 0.38) \\ &= 3.988(-0.24) \\ &= -0.96 kJ/mol \end{aligned}$$

1.7.2.2: Stability and Force of Interactions

Like the bonding potential energy, the stability of an arrangement of atoms is a function of the Lennard-Jones separation distance. As the separation distance decreases below equilibrium, the potential energy becomes increasingly positive (indicating a repulsive force). Such a large potential energy is energetically unfavorable, as it indicates an overlapping of atomic orbitals. However, at long separation distances, the potential energy is negative and approaches zero as the separation distance increases to infinity (indicating an attractive force). This indicates that at long-range distances, the pair of atoms or molecules experiences a small stabilizing force. Lastly, as the separation between the two particles reaches a distance slightly greater than σ, the potential energy reaches a minimum value (indicating zero force). At this point, the pair of particles is most stable and will remain in that orientation until an external force is exerted upon it.

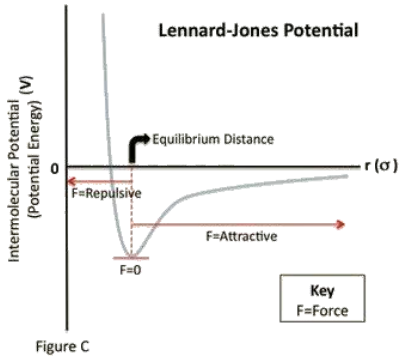


Figure C

Example 1.7.3

Two molecules, separated by a distance of 3.0 angstroms, are found to have a σ value of 4.10 angstroms. By decreasing the separation distance between both molecules to 2.0 angstroms, the intermolecular potential between the molecules becomes more negative. Do these molecules follow the Lennard-Jones potential? Why or why not?

Solution

Recall that σ is the distance at which the bonding potential between two particles is zero. On a graph of the Lennard-Jones potential, then, this value gives the x-intersection of the graph. According to the Lennard-Jones potential, any value of r greater than σ should yield a negative bonding potential and any value of r smaller than σ should yield a positive bonding potential. In this scenario, as the separation between the two molecules decreases from 3.0 angstroms to 2.0 angstroms, the bonding potential is becomes more negative. In essence however, because the starting separation (3.0 angstroms) is already less than σ

(4.0 angstroms), decreasing the separation even further (2.0 angstroms) should result in a more positive bonding potential. Therefore, these molecules do not follow the Lennard-Jones potential.

? Exercise 1.7.1

The second part of the Lennard-Jones equation is $(\sigma/r)^6$ and denotes attraction. Name at least three types of intermolecular interactions that represent attraction.

Answer

From section 2.1, dipole-dipole, dipole-induced dipole, and London interactions are all attractive forces.

? Exercise 1.7.2

At what separation distance in the Lennard-Jones potential does a species have a repulsive force acting on it? An attractive force? No force?

Answer

See Figure C. A species will have a repulsive force acting on it when r is less than the equilibrium distance between the particles. A species will have an attractive force acting on it when r is greater than the equilibrium distance between the particles. Lastly, when r is equal to t↑he equilibrium distance between both particles, the species will have no force acting upon it.

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1.8: Van der Waals Constants in Terms of Molecular Parameters

The van der Waals equation can be written as:

$$P = \frac{RT}{\bar{V} - b} - \frac{a}{\bar{V}^2}$$

Using the binomial expansion:

$$\frac{1}{1-x} = 1 + x + x^2 + \cdots$$

We can write the van der Waals equation of state as:

$$\begin{aligned} P &= \frac{RT}{\bar{V}}\left[1 + \frac{b}{\bar{V}} + \frac{b^2}{\bar{V}^2} + \cdots\right] - \frac{a}{\bar{V}^2} \\ &= \frac{RT}{\bar{V}} + (RTb - a)\frac{1}{\bar{V}^2} + \frac{RTb^2}{\bar{V}^3} + \cdot \end{aligned}$$

Rearranging in terms of compressibility, Z:

$$Z = \frac{P\bar{V}}{RT} = 1 + \left(b - \frac{a}{RT}\right)\frac{1}{\bar{V}} + \frac{b^2}{\bar{V}^2} + \cdots$$

Comparing to the Viral equation of state, we can see that the second Viral coefficient is related to the van der Waals coefficients:

$$B_{2V}(T) = b - \frac{a}{RT}$$

Using a combination of the hard sphere model and the Lennard-Jones potential, we obtain:

$$u(r) = \begin{cases} \infty & r \le \sigma \\ -\dfrac{C_6}{r^6} & r > \sigma \end{cases} \tag{1.8.1}$$

We can write the second Virial coefficient as

$$B_2(T) = \frac{2}{3}\pi N_0 \sigma^3 \left[1 - \frac{C_6}{3k_B T \sigma^6}\right] \tag{1.8.2}$$

Let us introduce to simplifying variables

$$b = \frac{2}{3}\pi N_0 \sigma^3 \tag{1.8.3}$$

$$a = \frac{2\pi N_0^2 C_6}{9\sigma^3} \tag{1.8.4}$$

In which the second Virial coefficient becomes:

$$B_2(T) = b - \frac{a}{RT} \tag{1.8.5}$$

From these equations, we can see that a is directly proportional to c_6, the intermolecular attraction between particles with a force proportional to r^{-6}. Likewise, b is equivalent to four times the volume of the particle. In other words, the van der Waals equations assumes the hard sphere model at small distances and weak interactions (attractive forces) at larger distances.

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1.E: The Properties of Gases (Exercises)

A Libretexts Textmap organized around McQuarrie and Simon's textbook

Physical Chemistry: A Molecular Approach

Template:HideTOC

These are homework exercises to accompany Chapter 16 of McQuarrie and Simon's "Physical Chemistry: A Molecular Approach" Textmap.

1.E.0.1: Q16.10

One liter of N_2 (g) at 2.1 bar and two liters of Ar(g) at 3.4 bar are mixed in a 4.0-L flask to form an ideal-gas mixture. Calculate the value of the final pressure of the mixture if the initial and final temperature of the gases are the same. Then, repeat this calculation if the initial temperatures of the N_2 (g) and Ar(g) are 304 K and 402 K, respectively, and the final temperature of the mixture is 377 K. (Assume ideal-gas behavior.)

1.E.0.1: S16.10

Using the ideal gas law, we can find the number of moles of each gas.

$$n_{N_2} = \frac{P_{N_2}V_{N_2}}{RT} = \frac{(2.1x10^5 Pa) * (1x10^{-3}m^3)}{RT} = \frac{210Pa * m^3}{RT}$$

$$n_{Ar} = \frac{P_{Ar}V_{Ar}}{RT} = \frac{(3.4x10^5 Pa) * (2x10^{-3}m^3)}{RT} = \frac{680Pa * m^3}{RT}$$

The total moles of gas in the final mixture is the sum of the moles of each gas in the mixture, which is

$$\frac{210Pa * m^3}{RT} + \frac{680Pa * m^3}{RT} = \frac{890Pa * m^3}{RT}$$

Therefore,

$$P = \frac{nRT}{V} = \frac{890Pa * m^3}{0.0040m^3} = 2.2x10^5 Pa = 2.2bar$$

Now, considering the initial temperatures of the gases are different from each other and from the final temperature of the mixture, we calculate the total number of moles to be

$$n_{total} = n_{N_2} + n_{Ar} = \frac{210Pa * m^3}{R * (304K)} + \frac{680Pa * m^3}{R * (402K)}$$

Substituting this into the ideal gas law, we get the final pressure to be

$$P = [\frac{210Pa * m^3}{R * (304K)} + \frac{680Pa * m^3}{R * (402K)}] * \frac{R * (377K)}{0.0040m^3} = 2.2x10^5 Pa = 2.2bar$$

1.E.1: Q16.12

What is the molar Gas Constant in units of cm^3 torr K^{-1} mol^{-1}.

1.E.1.1: S16.12

We know $R = 0.082058L \cdot atm \cdot mol^{-1}K^{-1}$

using dimensional analysis:

$$R = 0.082058L \cdot atm \cdot mol^{-1}K^{-1} \times \frac{760torr}{1atm} \times \frac{1dm^3}{1L} \times \frac{1dm^3}{1000cm^3} \tag{1.E.1}$$

$$R = 0.0623639cm^3 \cdot atm \cdot mol^{-1}K^{-1} \tag{1.E.2}$$

1.E.1.2: Q16.13

Use the van der Waals equation to plot the compressibility factor, Z, against P for methane for T = 180 K, 189 K, 190 K, 200 K, and 250 K.

1.E.1.3: S16.13

First, calculate Z as a function of $\bar{V}$ and P as a function of $\bar{V}$ and plot Z versus P

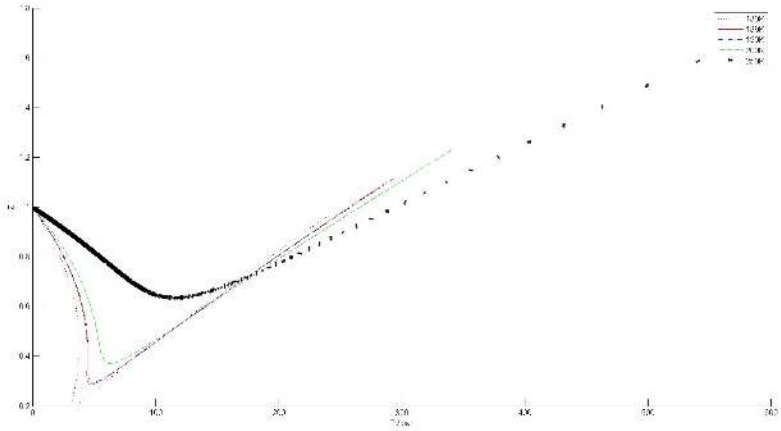
For methane, a = 2.3026 $dm^6 \cdot bar \cdot mol^{-2}$ and b = 0.043067 $dm^3 \cdot mol^{-1}$

$$Z = \frac{P\bar{V}}{RT} \tag{1.E.3}$$

and the van der Waals equation of state is:

$$P = \frac{RT}{\bar{V} - b} - \frac{a}{\bar{V}^2} \tag{1.E.4}$$

Then create a parametric plot of Z versus P for the suggested temperatures as shown below.



1.E.1.4: Q16-15

Define the equation that could be solved by using the Netwon-Raphson method to find the molar volume of O2 at 300K and 200atm. Use the van der Waals anf Redlich-Kwong equations.

Constants:

- van der Waals:

$$a = 1.3820 dm^6 * bar * mol, b = 0.031860 dm^3 * mol^{-1} \tag{1.E.5}$$

- Redlich-Kwong:

$$A = 17.411 dm^6 * bar * mol^{-2} * K^{1/2}, B = 0.022082 dm^3 * mol^{-1} \tag{1.E.6}$$

1.E.1.5: S16.15

Solving van der Waals equation for volume produces:

$$\bar{V}^{3} - (b + \dfrac{RT}{P})\bar{V}^{2} + \dfrac{a}{P}\bar{V} - \dfrac{ab}{P}=0$$

Plugging in constants gives:

$$\bar{V}^{3} - 0.15486\bar{V}^{2} + 0.00691\bar{V} - 0.00022015=0$$

which can be solved numerically to find molar volume.

The Redlich-Kwong equation can be written as a cubic in volume:

$$\bar{V}^{3} - \dfrac{RT}{P}\bar{V}^{2} - \left(B^{2} + \dfrac{BRT}{P} - \dfrac{A}{T^{1/2}P}\right)\bar{V} - \dfrac{AB}{T^{1/2}P} = 0\]

Plugging in constants gives:

$$\bar{V}^{3} - 0.123\bar{V}^{2} + 0.001822\bar{V} - 0.00011099 = 0\]

which can be solved numerically to find molar volume.

1.E.1.6: Q16.16

Compare the Redlich-Kwong and the van der Waals equations for ethane. Take the molar volume to be 0.09416 .

1.E.1.7: S16.16

van der Waals:

$$P = \dfrac{RT}{\bar{V}-b}-\dfrac{a}{(\bar{V})^2}\]

Reference Table 16.3 for a, b

$$P = \dfrac{0.083145*400}{.09416-0.065144}-\dfrac{5.5818}{(0.09416)^2}\]

Redlich-Kwong equation of state improved the accuracy of the van der Waals equation by adding a temperature dependence for the attractive term:

$$P = \dfrac{RT}{\bar{V}-B} - \dfrac{A}{T^(\dfrac{1}{2})\bar{V}(\bar{V}+B)}\]

Reference Table 16.4 for A, B

$$P = \dfrac{0.083145*400}{0.09416-0.045153} - \dfrac{98.831}{400^(\dfrac{1}{2})0.09416*(0.09416+0.62723)}\]

1.E.1.8: Q16.17

$$p = \frac{RT}{\frac{V}{n} - b} - \frac{a}{\sqrt{T}\frac{V}{n}\left(\frac{V}{n} + b\right)} \tag{1.E.7}$$

$$\left(p + \frac{n^2 a}{V^2}\right)(V - nb) = nRT \tag{1.E.8}$$

Use the equations above to calculate the temperature of a system with $1.5\ mol$ of methane at $300\ K$ confined to a volume of $100\ cm^3$. Compare the two calculated pressures.

1.E.1.9: S16.17

$R = 82.057338 \frac{cm^2\ atm}{K\ mol}$

Redlich-Kwong constants: $a = 31.59 \times 10^6\ (atm)(K^{\frac{1}{2}})\left(\frac{cm^3}{mol}\right)^2$ and $b = 29.6\ \frac{cm^3}{mol}$

Van der Waals constants: $a = 2.25 \times 10^6\ (atm)\left(\frac{cm^3}{mol}\right)^2$ and $b = 42.8\ \frac{cm^3}{mol}$

Redlich-Kwong equation: $p = \frac{82.057338 \frac{cm^2\ atm}{K\ mol}\ 300\ K}{\frac{100\ cm^3}{1.5\ mol} - 29.6\ \frac{cm^3}{mol}} - \frac{31.59 \times 10^6\ (atm)(K^{\frac{1}{2}})\left(\frac{cm^3}{mol}\right)^2}{\sqrt{300\ K}\frac{100\ cm^3}{1.5\ mol}\left(\frac{100\ cm^3}{1.5\ mol} + 29.6\ \frac{cm^3}{mol}\right)} = 379.95\ atm$

Van der Waals equation: $p = \frac{(1.5\ mol)(82.057338 \frac{cm^2\ atm}{K\ mol})(300\ K)}{(100\ cm^3) - (1.5\ mol)(42.8\ \frac{cm^3}{mol})} - \frac{(1.5\ mol)^2(2.25 \times 10^6\ (atm)\left(\frac{cm^3}{mol}\right)^2)}{(100\ cm^3)^2} = 525.2\ atm$

There is a $145.25\ atm$ difference in the calculated pressures.

1.E.1.10: Q16.20

The following equation can be used to relate the pressure of propane to its density at temperatures below 400 K:

$$P = 33.258\rho - 7.5884\rho^2 + 1.0306\rho^3 - 0.058757\rho^4 - 0.0033566\rho^5 + 0.00060696\rho^6 \quad (1.E.9)$$

where the pressure (P) is in bar and the density (ρ) is in $\frac{mol}{L}$ and ranges from $0\frac{mol}{L} \leq \rho \leq 12.3\frac{mol}{L}$.

Calculate and plot the pressure for the given density range using:

a. the equation given above
b. the Van der Waals equation of state
c. the Redlich-Kwong equation of state

Compare your results from the above parts.

1.E.1.11: S16.20

a.) Straight forward to calculate.

Even though straight forward, should still put solution for students.



graph plotted using matlab.

b.) The following constants were used in the equation below:

$$a = 9.3919\frac{L^2 bar}{mol^2} \text{ and } b = 0.09049\frac{L}{mol}$$

$$P_{VDW} = \frac{RT}{\overline{V} - b} - \frac{a}{\overline{V}^2} \quad (1.E.10)$$

c.) The following constants were used in the equation below:

$$a = 183.01\frac{L^2 bar}{mol^2} \text{ and } b = 0.06272\frac{L}{mol}$$

$$P_{RK} = \frac{RT}{\overline{V} - b} - \frac{a}{\sqrt{T}\overline{V}(\overline{V} + b)} \quad (1.E.11)$$



As can be seen by the plot, the Van der Waals equation of state deviates greatly from the empirical fit at higher densities. The Redlich-Kwong equation provides a reasonable approximation to the empirical data. (All calculations were done in MATLAB, and the above plot was produced by me)

1.E.1.12: Q16.21

Use the data below to evaluate the van der waals and Redlich Kwong constants for benzene.

Species	T_c/K	P_c/bar	P_c/atm	V_{nc}/L mol^{-1}*	P_cV_{nc}/RT_c
Benzene	561.75	48.758	48.120	0.256	0.26724

*n to indicate molar volume

Van Der Waals

$$a = \frac{27(RT_c)^2}{64P_c} \; and \; b = \frac{RT_c}{8P_c}$$

Redlich-Kwong

$$A = 0.42748\frac{R^2T_c^{\frac{5}{2}}}{P_c} \; and \; B = 0.08664\frac{RT_c}{P_c}$$

1.E.1.13: S16.21

Van Der Waals

$$\text{a} = \frac{27 * (0.083145 dm^3 \cdot bar \cdot mol^{-1}K^{-1})^2 * (561.75K)^2}{64 * 48.758 bar} = \mathbf{18.8754\,dm^6 \cdot atm \cdot mol^{-2}}$$

$$\text{b} = \frac{(0.083145 dm^3 \cdot bar \cdot mol^{-1}K^{-1})^2 * (561.75K)^2}{8 * 48.758 bar} = \mathbf{5.5927\,dm^3 \cdot mol^{-1}}$$

Redlich-Kwong

$$A = 0.42748 * \frac{(0.083145 dm^3 \cdot bar \cdot mol^{-1}K^{-1})^2 * (561.75K)^{\frac{5}{2}}}{48.758 bar} = \mathbf{453.315\,dm^6 \cdot atm \cdot mol^{-2} \cdot K^{\frac{1}{2}}}$$

$$B = 0.42748 * \frac{(0.083145 dm^3 \cdot bar \cdot mol^{-1}K^{-1})^2 * (561.75K)^2}{48.758 bar} = \mathbf{19.126\,dm^3 \cdot mol^{-1}}$$

1.E.1.14: Q16.22

Show that the van der Waals equation for argon at T = 142.69 K and P = 35.00 atm can be written as

$$\overline{V}^3 - 0.3664\overline{V}^2 + 0.001210 = 0 \qquad (1.E.12)$$

where, for convenience, we have suppressed the units in the coefficients. Use the Newton-Raphson method (MathChapter G) to find the three roots to this equation, and calculate the values of the density of liquid and vapor in equilibrium with each other under

these conditions.

1.E.1.15: S16.22

Using Table 16.3, we can get the values of a and b for argon to use in Van der Waals equation of state.

By doing this, you can isolate $\overline{V}$ in van der Waals equation of state. Next, by applying the Newton-Raphson method to the function given by van der Waals equation (which is only dependent on $\overline{V}$), and the derivative of the function, we find the roots to the equation. On the case here, the smallest root represents the molar volume of liquid argon, and the largest root represents the molar volume of vapor argon.

1.E.1.16: Q16.23

Calculate the Volume occupied by $50\ kg$ of propane at $50°C$ and $35\ bar$, using the Redlich-Kwong equation of state and the Peng-Robinson equation of state.

1.E.1.17: S16.23

Redlich-Kwong equation of state:

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b)} \tag{1.E.13}$$

v is volume of gas per mole.

we have $T = 50°C = 323\ K$, $P = 35\ bar = 35 \times (10^5) Pa$

For propane, we have $P_c = 42.4924\ bar = 42.4924 \times 10^5 Pa$ and $T_c = 369.522\ K$

so we have $a = \frac{0.42748 R^2 T_c^{2.5}}{P_c T^{0.5}}$;

$b = \frac{0.08664 * R * T_c}{P_c}$

so, $a = \frac{0.42748(8.314^2)369.522^{2.5}}{42.4924\times10^5(323^{0.5})} = 1.015603$

$b = \frac{(0.08664)(8.314)(369.522)}{42.4924\times10^5} = 6.2640829 \times 10^{-5}$

so, $P = \frac{RT}{v-b} - \frac{a}{v(v+b)}$

$(35 * (10^5)) = \frac{(8.314)(323)}{v-(6.2640829\times10^{-5})} - \frac{1.015603}{v(v+6.2640829\times10^{-5})}$

The only real solution is

$v = 0.00010933 \frac{m^3}{mol}$

so In $50\ Kg$ propane, number of moles = $\frac{50*1000}{44.10} = 1133.78684$

total volume occupied by $50\ Kg$ propane at the specified conditions = $(1133.78684)(0.00010933) = 0.1239569 m^3 = 123.9569$ Liters is the answer.

Peng - Robinson's equation of state:

$P = \frac{RT}{v-b} - \frac{a}{v(v+b)+b(v-b)}$

$a = 0.45724 R^2 * T_c^2 * \frac{\alpha}{P_c}$

$b = 0.0778 R \frac{T_c}{P_c}$

$\alpha = 1 + S(1 - \sqrt{T_r})$

$S = 0.37464 + 1.54226w - 0.26992w^2$

$T_r = \frac{T}{T_c}$

we have $P = 35 \times 10^5 Pa$ and $T = 323\ K$

$P_c = 42.4924\ bar = 42.4924 \times 10^5 Pa$ and $T_c = 369.522\ K$

we have accentric factor = $w = 0.152$.

$T_r = \frac{T}{T_c} = \frac{323}{369.522} = 0.87410$

$S = 0.37464 + (1.54226)(0.152) - (0.26992)(0.152^2) = 0.602827$

$\alpha = 1 + 0.602827 * (1 - \sqrt{0.87410}) = 1.0392240523$

$a = (0.45724)(8.314^2)(369.522^2)\frac{1.0392240523}{42.4924 \times 10^5} = 1.055462444$

$b = (0.0778)(8.314)\frac{369.522}{42.4924 \times 10^5} = 0.0000562494$

so, by the equation of state:

$(35 \times 10^5) = \frac{(8.314)(323)}{v - 0.0000562494} - \frac{1.055462444}{v(v + 0.0000562494 + 0.0000562494(v - 0.0000562494)}$

$v = 0.0000988504 \frac{m^3}{mol}$

so In $50\ Kg$ propane, number of moles = $\frac{(50)(1000)}{44.10} = 1133.78684$

total volume occupied by $50\ Kg$ propane at the specified conditions = $(1133.78684)(0.0000988504) = 0.1120752 m^3 = 112.0752$ Liters is the answer.

1.E.1.18: Q16.25

A way to obtain the expressions for the van der Waals constants is to make $(\frac{\partial P}{\partial \bar{V}})_T$ and $(\frac{\partial^2 P}{\partial \bar{V}^2})_T$ zero at the critical point, but why do they equal to zero at critical point? Obtain the equation $\bar{V}_c = 3b$from this procedure.

1.E.1.19: S16.25

$$(\frac{\partial P}{\partial \bar{V}})_T = 0$$

$$(\frac{\partial^2 P}{\partial \bar{V}^2})_T = 0$$

$$(\frac{\partial P}{\partial \bar{V}})_T = \frac{\partial}{\partial \bar{V}} (\frac{RT}{\bar{V} - b} - \frac{a}{T^2})_T$$

$$= RT (-\frac{1}{(\bar{V} - b)^2}) - a (\frac{-2}{\bar{V}^3})$$

$$= -\frac{RT}{(\bar{V} - b)^2} + \frac{2a}{\bar{V}^3}$$

At critical point,

$$\frac{RT_c}{(\bar{V}_c - b)^2} = \frac{2a}{\bar{V}_c^3}$$ by equating $(\frac{\partial P}{\partial \bar{V}})_T = 0$.

By differentiating the equation $RT (-\frac{1}{(\bar{V} - b)^2}) - a (\frac{-2}{\bar{V}^3})$ with respect to $\bar{V}$,

$$(\frac{\partial^2 P}{\partial \bar{V}^2})_T = \frac{\partial}{\partial \bar{V}} (-\frac{RT}{(\bar{V} - b)^2} + \frac{2a}{\bar{V}^3})_T$$

$$= RT (-\frac{2}{(\bar{V} - b)^3}) + 2a (\frac{-3}{\bar{V}^4})$$

$$= \frac{2RT}{(\bar{V} - b)^3} - \frac{6a}{\bar{V}^4}$$

At critical point,

$$\frac{2RT_c}{(\bar{V}_c - b)^3} = \frac{6a}{\bar{V}_c^4}$$ by equating $(\frac{\partial^2 P}{\partial \bar{V}^2})_T = 0$.

Now,

$$\frac{\frac{2a}{\bar{V}_c^3}}{\frac{6a}{\bar{V}_c^4}} = \frac{\frac{RT_c}{(\bar{V}_c - b)^2}}{\frac{2RT_c}{(\bar{V}_c - b)^3}}$$

$$\frac{\bar{V}_c}{3} = \frac{(\bar{V}_c - b)}{2}$$

$$\bar{V}_c = 3b$$

1.E.2: Q16.26

Show that the Redlich-Kwong equation can be rewritten in the following form:

$$\bar{(V)}^3 - \frac{RT}{P}\bar{V}^2 - (B^2 + \frac{BRT}{P} - \frac{A}{PT^{1/2}})\bar{V} - \frac{AB}{PT^{1/2}} = 0 \qquad (1.E.14)$$

1.E.3: S16.26

Starting with the Redlich-Kwong equation and manipulating it we get the following:

$$P = \frac{RT}{\bar{V} - B} - \frac{A}{T^{1/2}\bar{V}(\bar{V} + B)} \tag{1.E.15}$$

$$P(\bar{V} - B)T^{1/2}\bar{V}(\bar{V} + B) = RT^{3/2}\bar{V}(\bar{V} + B) - A(\bar{V} - B) \tag{1.E.16}$$

$$PT^{1/2}\bar{V}(\bar{V}^2 - B^2) = RT^{3/2}\bar{V}^2 + RT^{3/2}\bar{V}B - A\bar{V} + AB \tag{1.E.17}$$

$$\bar{(V)}^3 - \frac{RT}{P}\bar{V}^2 - (B^2 + \frac{BRT}{P} - \frac{A}{PT^{1/2}})\bar{V} - \frac{AB}{PT^{1/2}} = 0 \tag{1.E.18}$$

1.E.4: Q16.27

Use the results of the previous question, Q16.26, to derive Equations 16.14.

$(a)\bar{V}_c = 3.8473B$, $(b)P_c = .029894\frac{A^{2/3}R^{1/3}}{B^{5/3}}$, and $(c)T_c = .34504\left(\frac{A}{BR}\right)^{2/3}$

The following are solved from Q16.26 and are necessary to solve for Equation 16.14:

$$1)B = .25992\bar{V}_c \tag{1.E.19}$$

$$2)A = 0.42748\frac{R^2T_c^{5/2}}{P_c} \tag{1.E.20}$$

$$3)\frac{P_c\bar{V}_C}{RT_c} = \frac{1}{3} \tag{1.E.21}$$

1.E.5: S16.27

From equation (1) we see that solving for $\bar{V}_c$ yields the first equation

$$\bar{V}_c = 3.8473B \tag{1.E.22}$$

.

From equation (2) we can rewrite the expression with some manipulation as

$$A = .42748RT_c^{3/2}\left(\frac{RT_c}{P_c\bar{V}_c}\right)\bar{V}_c \tag{1.E.23}$$

Substituting equation (3) and 16.14a into the previous equation gives the expression

$$A = 3(.42748)RT_c^{3/2}(3.8473B) \tag{1.E.24}$$

Lastly, solving for T_c gives the equation for 16.14c

$$T_c = .34504\left(\frac{A}{BR}\right)^{2/3} \tag{1.E.25}$$

Finally, solving for equation 16.14b we must substitute the previously solved 16.14c into equation (2),solving for P_c

$$P_c = 0.42748\frac{R^2T_c^{5/2}}{A} = \left(\frac{.42748}{A}\right)R^2\left[.34504\left(\frac{A}{BR}\right)^{2/3}\right]^{5/2} = .029894\frac{A^{2/3}R^{1/3}}{B^{5/3}} \tag{1.E.26}$$

which is equation 16.14b.

1.E.6: Q16.28

Derive the Van der Waals cubic equation of state from

$$\left(P + \frac{a}{\bar{V}^2}\right)\left(\bar{V} - b\right) = RT \tag{1.E.27}$$

1.E.7: S16.28

The Van der Waal equation can be rewritten in terms of Z:

$$Z = \frac{P\bar{V}}{RT} = \frac{\bar{V}}{\bar{V} - b} - \frac{a}{RT\bar{V}} \tag{1.E.28}$$

solving for $\bar{V}$

$$\bar{V}^3 - \left(b + \frac{RT}{P}\right)\bar{V}^2 + \frac{a}{P}\bar{V} - \frac{ab}{P} = 0 \tag{1.E.29}$$

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CHAPTER OVERVIEW

2: The Kinetic Theory of Gases

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2.2: Common Ideal Gas Difficulties
2.3: Connecting Gas Properties to Kinetic Theory of Gases
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2.1: Basics of Kinetic Molecular Theory

Learning Objectives

- To understand the five fundamentals of Kinetic Molecular Theory.
- To use Kinetic Molecular Theory to describe the behavior of the macroscopic gas laws.

The ideal gas equation

$$PV = nRT \tag{2.1.1}$$

describes ***how*** gases behave, e.g.:

- A gas expands when heated at constant pressure
- The pressure increases when a gas is compressed at constant temperature

However, the ideal gas law (nor any of the constituent gas laws) does not explain ***why*** gases behave this way? What happens to gas particles when conditions such as pressure and temperature change? This is addressed via Kinetic Molecule Theory.

The Fundamentals of Kinetic Molecular Theory (KMT)

The molecules of a gas are in a state of perpetual motion in which the velocity (that is, the speed and direction) of each molecule is completely random and independent of that of the other molecules. This fundamental assumption of the kinetic-molecular model helps us understand a wide range of commonly-observed phenomena. According to this model, most of the volume occupied by a gas is *empty space*; this is the main feature that distinguishes gases from *condensed* states of matter (liquids and solids) in which neighboring molecules are constantly in contact. Gas molecules are in rapid and continuous motion; at ordinary temperatures and pressures their velocities are of the order of 0.1-1 km/sec and each molecule experiences approximately 10^{10}collisions with other molecules every second.

The five basic tenets of the kinetic-molecular theory are as follows:

1. A gas is composed of molecules that are separated by average distances that are much greater than the sizes of the molecules themselves. ***The volume occupied by the molecules of the gas is negligible compared to the volume of the gas itself.***
2. The molecules of an ideal gas exert **no attractive forces** on each other, or on the walls of the container.
3. The molecules are in **constant random motion**, and as material bodies, they obey Newton's laws of motion. This means that the molecules move in **straight lines** (see demo illustration at the left) until they collide with each other or with the walls of the container.
4. Collisions are perfectly *elastic*; when two molecules collide, they change their directions and kinetic energies, but the total **kinetic energy is conserved**. *Collisions are not "sticky".*
5. **The average kinetic energy of the gas molecules is directly proportional to the absolute temperature**. Notice that the term "average" is very important here; the velocities and kinetic energies of individual molecules will span a wide range of values, and some will even have zero velocity at a given instant. This implies that all molecular motion would cease if the temperature were reduced to absolute zero.

Note

The Kinetic-Molecular Theory is "the theory of moving molecules." -Rudolf Clausius, 1857

Pressure

If gases do in fact consist of widely-separated particles, then the observable properties of gases must be explainable in terms of the simple mechanics that govern the motions of the individual molecules. The kinetic molecular theory makes it easy to see why a gas should exert a pressure on the walls of a container. Any surface in contact with the gas is constantly bombarded by the molecules.

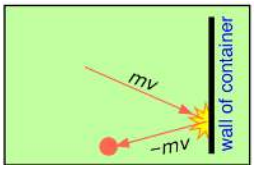


Figure 5.6.1: Pressure arises from the force due to the acceleration of molecules as they bound off a container's walls

At each collision, a molecule moving with momentum *mv* strikes the surface. Since the collisions are elastic, the molecule bounces back with the same velocity in the opposite direction. This change in velocity ΔV is equivalent to a*n acceleratio*n a; according to Newton's second law,

$$F = ma \tag{2.1.2}$$

with a force, F, that is exerted on the surface of area A exerting a pressure

$$P = \frac{f}{A} \tag{2.1.3}$$

- The pressure of a gas is causes by collisions of the molecules with the walls of the container.
- The magnitude of the pressure is related to how hard and how often the molecules strike the wall
- The "hardness" of the impact of the molecules with the wall will be related to the velocity of the molecules times the mass of the molecules

Kinetic Interpretation of Absolute Temperature

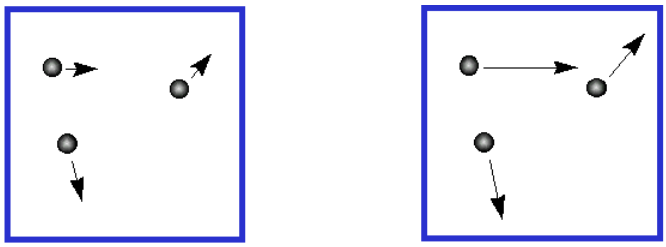
According to the kinetic molecular theory, the average kinetic energy of an ideal gas is directly proportional to the absolute temperature. Kinetic energy is the energy a body has by virtue of its motion:

$$KE = \frac{1}{2}mv^2 \tag{2.1.4}$$

with

- KE is the kinetic energy of a molecule,
- m is the mass of the molecule, and
- v is the magnitude of the velocity of a molecule.

As the temperature of a gas rises, the average velocity of the molecules will increase; a doubling of the temperature will increase this velocity by a factor of four. Collisions with the walls of the container will transfer more momentum, and thus more kinetic energy, to the walls.



Lower average kinetic energy
Lower absolute temperature

Higher average kinetic energy
Higher absolute temperature

Figure 5.6.2: A microscopic picture of the molecules in a gas (balls) as a specific time. The magnitude of the velocity of each molecule is indicated by the length of the arrow.

If the walls are cooler than the gas, they will get warmer, returning less kinetic energy to the gas, and causing it to cool until thermal equilibrium is reached. Because temperature depends on the *average* kinetic energy, the concept of temperature only applies to a statistically meaningful sample of molecules. We will have more to say about molecular velocities and kinetic energies farther on.

Molecular Speed

Although the molecules in a sample of gas have an average kinetic energy (and therefore an average speed) the individual molecules move at various speeds. Some are moving fast, others relatively slowly

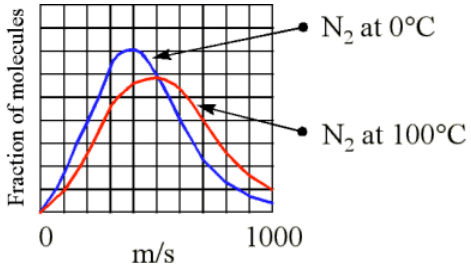


Figure 5.6.3: The distribution of speeds of nitrogen molecules at 0 °C and 100 °C.

At higher temperatures at greater fraction of the molecules are moving at higher speeds (Figure 3). What is the speed (velocity) of a molecule possessing average kinetic energy? KMT theory shows the the average kinetic energy (KE) is related to the ***root mean square*** (rms) speed u

$$KE = \frac{1}{2}mu^2 \tag{2.1.5}$$

This is different from the typical definition of an average speed $\langle v \rangle$ as demonstrated in Example 5.6.1.

Example 5.6.1

Suppose a gas consists of four molecules with speeds of 3.0, 4.5, 5.2 and 8.3 m/s. What is the difference between the average speed and root mean square speed of this gas?

Solution

The *average* speed is:

$$\langle v \rangle = \frac{3.0 + 4.5 + 5.2 + 8.3}{4} = 5.25\ m/s \tag{2.1.6}$$

The *root mean square speed* is:

$$u = \sqrt{\frac{3.0^2 + 4.5^2 + 5.2^2 + 8.3^2}{4}} = 5.59\ m/s \tag{2.1.7}$$

The Gas Laws Explained from a KMT Perspective

- **Kinetic explanation of Boyle's law**: Boyle's law is easily explained by the kinetic molecular theory. The pressure of a gas depends on the number of times per second that the molecules strike the surface of the container. If we compress the gas to a smaller volume, the same number of molecules are now acting against a smaller surface area, so the number striking per unit of area, and thus the pressure, is now greater.
- **Kinetic explanation of Charles' law:** Kinetic molecular theory states that an increase in temperature raises the average kinetic energy of the molecules. If the molecules are moving more rapidly but the pressure remains the same, then the molecules must stay farther apart, so that the increase in the rate at which molecules collide with the surface of the container is compensated for by a corresponding increase in the area of this surface as the gas expands.
- **Kinetic explanation of Avogadro's law**: If we increase the number of gas molecules in a closed container, more of them will collide with the walls per unit time. If the pressure is to remain constant, the volume must increase in proportion, so that the molecules strike the walls less frequently, and over a larger surface area.
- **Kinetic explanation of Dalton's law**: "Every gas is a vacuum to every other gas". This is the way Dalton stated what we now know as his law of partial pressures. It simply means that each gas present in a mixture of gases acts independently of the others. This makes sense because of first fundamental tenet of KMT theory is that gas molecules have negligible volumes. So

Gas A in mixture of A and B acts as if Gas B were not there at all. Each contributes its own pressure to the total pressure within the container, in proportion to the fraction of the molecules it represents

Note

- The absolute temperature is a measure of the ***average kinetic energy*** of its molecules
- If two different gases are at the same temperature, their molecules have the same average kinetic energy
- If the temperature of a gas is ***doubled***, the average kinetic energy of its molecules is ***doubled***

Contributors and Attributions

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2.2: Common Ideal Gas Difficulties

This page looks at the assumptions which are made in the Kinetic Theory about ideal gases, and takes an introductory look at the Ideal Gas Law: pV = nRT.

Kinetic Theory assumptions about ideal gases

There is no such thing as an ideal gas, of course, but many gases behave approximately as if they were ideal at ordinary working temperatures and pressures. Real gases are dealt with in more detail on another page. The assumptions are:

- Gases are made up of molecules which are in constant random motion in straight lines.
- The molecules behave as rigid spheres.
- Pressure is due to collisions between the molecules and the walls of the container.
- All collisions, both between the molecules themselves, and between the molecules and the walls of the container, are perfectly elastic. (That means that there is no loss of kinetic energy during the collision.)
- The temperature of the gas is proportional to the average kinetic energy of the molecules.

And then two absolutely key assumptions, because these are the two most important ways in which real gases differ from ideal gases:

- There are no (or entirely negligible) intermolecular forces between the gas molecules.
- The volume occupied by the molecules themselves is entirely negligible relative to the volume of the container.

The Ideal Gas Equation

The ideal gas equation is:

$$pV = nRT \tag{2.2.1}$$

On the whole, this is an easy equation to remember and use. The problems lie almost entirely in the units, which should be in strict SI units

Pressure, p

Pressure is measured in Pascals, Pa - sometimes expressed as newtons per square meter, N m^{-2}. These mean exactly the same thing. Be careful if you are given pressures in kPa (kilopascals). For example, 150 kPa is 150,000 Pa. You must make that conversion before you use the ideal gas equation.

Should you want to convert from other pressure measurements:

- 1 atmosphere = 101,325 Pa
- 1 bar = 100 kPa = 100,000 Pa

Volume, V

This is the most likely place for you to go wrong when you use this equation. That's because the SI unit of volume is the cubic metre, m^3 - not cm^3 or dm^3 with 1 m^3 = 1000 dm^3 = 1,000,000 cm^3. So if you are inserting values of volume into the equation, you first have to convert them into cubic metres.

You would have to divide a volume in dm^3 by 1000, or in cm^3 by a million.

Similarly, if you are working out a volume using the equation, remember to covert the answer in cubic metres into dm^3 or cm^3 if you need to - this time by multiplying by a 1000 or a million. If you get this wrong, you are going to end up with a silly answer, out by a factor of a thousand or a million. So it is usually fairly obvious if you have done something wrong, and you can check back again.

Number of moles, n

This is easy, of course - it is just a number. You already know that you work it out by dividing the mass in grams by the mass of one mole in grams. You will most often use the ideal gas equation by first making the substitution to give:

$$pV = \frac{\text{mass (g)}}{\text{mass of 1 mole (g)}} \times RT$$

The gas constant, R

A value for R will be given you if you need it, or you can look it up in a data source. The SI value for R is 8.31441 J K^{-1} mol^{-1}.

The temperature, T

The temperature has to be in Kelvin. Don't forget to add 273 if you are given a temperature in degrees Celsius.

Using the ideal gas equation

Calculations using the ideal gas equation are included in my calculations book (see the link at the very bottom of the page), and I can't repeat them here. There are, however, a couple of calculations that I haven't done in the book which give a reasonable idea of how the ideal gas equation works.

The molar volume at stp

If you have done simple calculations from equations, you have probably used the molar volume of a gas.

1 mole of any gas occupies 22.4 dm^3 at stp (standard temperature and pressure, taken as 0°C and 1 atmosphere pressure). You may also have used a value of 24.0 dm^3 at room temperature and pressure (taken as about 20°C and 1 atmosphere).

These figures are actually only true for an ideal gas, and we'll have a look at where they come from.

We can use the ideal gas equation to calculate the volume of 1 mole of an ideal gas at 0°C and 1 atmosphere pressure.

First, we have to get the units right.

0°C is 273 K. T = 273 K

1 atmosphere = 101325 Pa. p = 101325 Pa

We know that n = 1, because we are trying to calculate the volume of 1 mole of gas.

And, finally, R = 8.31441 J K^{-1} mol^{-1}.

Slotting all of this into the ideal gas equation and then rearranging it gives:

$$101325 \times V = 1 \times 8.31441 \times 273$$

$$V = \frac{1 \times 8.31441 \times 273}{101325} \ m^3$$

$$= 0.0224 \ m^3 \text{ to 3 sig figs}$$

And finally, because we are interested in the volume in cubic decimetres, you have to remember to multiply this by 1000 to convert from cubic metres into cubic decimetres.

The molar volume of an ideal gas is therefore 22.4 dm^3 at stp.

And, of course, you could redo this calculation to find the volume of 1 mole of an ideal gas at room temperature and pressure - or any other temperature and pressure.

Finding the relative formula mass of a gas from its density

This is about as tricky as it gets using the ideal gas equation.

The density of ethane is 1.264 g dm^{-3} at 20°C and 1 atmosphere. Calculate the relative formula mass of ethane.

The density value means that 1 dm^3 of ethane weighs 1.264 g.

Again, before we do anything else, get the awkward units sorted out.

A pressure of 1 atmosphere is 101325 Pa.

The volume of 1 dm^3 has to be converted to cubic metres, by dividing by 1000. We have a volume of 0.001 m^3.

The temperature is 293 K.

Now put all the numbers into the form of the ideal gas equation which lets you work with masses, and rearrange it to work out the mass of 1 mole.

$$pV = \frac{\text{mass (g)}}{\text{mass of 1 mole (g)}} \times RT$$

$$101325 \times 0.001 = \frac{1.264}{\text{mass of 1 mole (g)}} \times 8.31441 \times 293$$

$$\text{mass of 1 mole (g)} = \frac{1.264 \times 8.31441 \times 293}{101325 \times 0.001}$$

$$= 30.4 \text{ g}$$

The mass of 1 mole of anything is simply the relative formula mass in grams.So the relative formula mass of ethane is 30.4, to 3 sig figs. Now, if you add up the relative formula mass of ethane, C_2H_6 using accurate values of relative atomic masses, you get an answer of 30.07 to 4 significant figures. Which is different from our answer - so what's wrong?

There are two possibilities.

- The density value I have used may not be correct. I did the sum again using a slightly different value quoted at a different temperature from another source. This time I got an answer of 30.3. So the density values may not be entirely accurate, but they are both giving much the same sort of answer.
- Ethane isn't an ideal gas. Well, of course it isn't an ideal gas - there's no such thing! However, assuming that the density values are close to correct, the error is within 1% of what you would expect. So although ethane isn't exactly behaving like an ideal gas, it isn't far off.

If you need to know about real gases, now is a good time to read about them.

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2.3: Connecting Gas Properties to Kinetic Theory of Gases

When examining the ideal gas laws in conjunction with the kinetic theory of gases, we gain insights into the behavior of ideal gas. We can then predict how gas particles behaviors such as gas molecular speed, effusion rates, distances traveled by gas molecules. Graham's Law, which was formulated by the Scottish physical chemist Thomas Graham, is an important law that connects gas properties to the kinetic theory of gases.

Introduction

The Kinetic Molecular Theory states that the average energy of molecules is proportional to absolute temperature as illustrated by the following equation:

$$e_K = \frac{3}{2}\frac{R}{N_A}T \tag{2.3.1}$$

where

- $\mathbf{e_k}$ is the average translation kinetic energy,
- **R** is the gas constant,
- $\mathbf{N_A}$ is Avogadro's number, and
- **T** is temperature in Kelvins.

Since R and N_A are constants, this means that the Kelvin temperature (T) of a gas is directly proportional to the average kinetic energy of its molecules. This means that at a given temperature, different gases (for example He or O_2) will the same average kinetic energy.

Graham's Law

Gas molecules move constantly and randomly throughout the volume of the container they occupy. When examining the gas molecules individually, we see that not all of the molecules of a particular gas at a given temperature move at exactly the same speed. This means that each molecule of a gas have slightly different kinetic energy. To calculate the average kinetic energy (e_K) of a sample of a gas, we use an average speed of the gas, called the root mean square speed (u_{rms}).

$$e_K = \frac{1}{2}mu_{rms}^2 \tag{2.3.2}$$

with

- $\mathbf{e_K}$ is the kinetic energy measures in Joules
- **m** is mass of a molecule of gas (kg)
- $\mathbf{u_{rms}}$ is the root mean square speed (m/s)

The root mean square speed, u_{rms}, can be determined from the temperature and molar mass of a gas.

$$u_{rms} = \sqrt{\frac{3RT}{M}} \tag{2.3.3}$$

with

- **R** the ideal gas constant (8.314 kg*m^2/s^2*mol*K)
- **T** temperature (Kelvin)
- **M** molar mass (kg/mol)

When examining the root mean square speed equation, we can see that the changes in temperature (T) and molar mass (M) affect the speed of the gas molecules. The speed of the molecules in a gas is proportional to the temperature and is inversely proportional to molar mass of the gas. In other words, as the temperature of a sample of gas is increased, the molecules speed up and the root mean square molecular speed increases as a result.

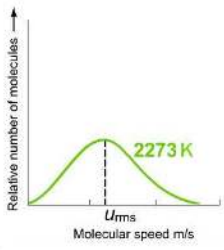


Figure **2.3.1**: As the temperature of a gas sample increases from left to right, the molecular speed distribution increases indicate by the shift of the peaks form left to right from each graph.

Graham's Law states that the rate of effusion of two different gases at the same conditions are inversely proportional to the square roots of their molar masses as given by the following equation:

$$\frac{Rate\ of\ effusion\ of\ A}{Rate\ of\ effusion\ of\ B} = \frac{(u_rms)_A}{(u_rms)_B} = \frac{\sqrt{3RT/M_A}}{\sqrt{3RT/M_B}} = \frac{\sqrt{M_B}}{\sqrt{M_A}} \tag{2.3.4}$$

In according with the Kinetic Molecular Theory, each gas molecule moves independently. However, the net rate at which gas molecules move depend on their average speed. By examining the equation above, we can conclude that the heavier the molar mass of the gas molecules slower the gas molecules move. And conversely, lighter the molar mass of the gas molecules the faster the gas molecules move.

Limitations of Graham's Law

Graham's Law can only be applied to gases at low pressures so that gas molecules escape through the tiny pinhole slowly. In addition, the pinhole must be tiny so that no collisions occur as the gas molecules pass through. Since Graham's Law is an extension of the Ideal Gas Law, gases that follows Graham's Law also follows the Ideal Gas Law.

Molecular Effusion

The random and rapid motion of tiny gas molecules results in effusion. **Effusion** is the escape of gas molecules through a tiny hole or pinhole.

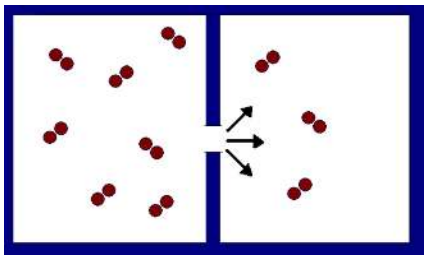


Figure **2.3.1**: Illustration of gas molecules escaping through a small opening. This is a phenomenon called effusion.

The behavior of helium gas in balloons is an example of effusion. The balloons are made of latex which is porous material that the small helium atom can effuse through. The helium inside a newly inflated balloon will eventually effuse out. This is the reason why balloons will deflate after a period of time. Molecular speeds are also used to explain why small molecules (such as He) diffuse more rapidly than larger molecules (O_2). That is the reason why a balloon filled with helium gas will deflate faster than a balloon filled with oxygen gas.

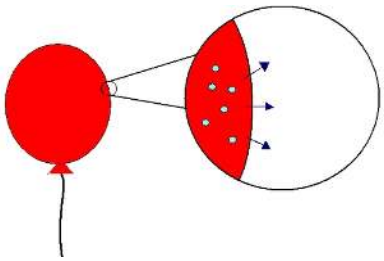


Figure **2.3.1**: Example of effusion. The escaping of helium molecules from an inflated balloon causes the deflation of the balloon after a period of time.

The effusion rate, r, is inversely proportional to the square root of its molar mass, M.

$$r \propto \sqrt{\frac{1}{M}} \tag{2.3.5}$$

When there are two different gases the equation for effusion becomes

$$\frac{Rate\ of\ effusion\ of\ A}{Rate\ of\ effusion\ of\ B} = \frac{\sqrt{3RT/M_A}}{\sqrt{3RT/M_B}} \tag{2.3.6}$$

M_A is the molar mass of gas A, M_B is the molar mass of gas B, T Temperature in Kelvin, R is the ideal gas constant.

From the equation above,

Rates of effusion of two gases

The relative rates of effusion of two gases at the same temperature is given as:

$$\frac{Rate\ of\ effusion\ of\ gas\ 1}{Rate\ of\ effusion\ of\ gas\ 2} = \frac{\sqrt{M_2}}{\sqrt{M_1}} \tag{2.3.7}$$

Units used to express rate of effusion includes: moles/seconds, moles/minutes, grams/seconds, grams/minutes.

Relative distances of two gases

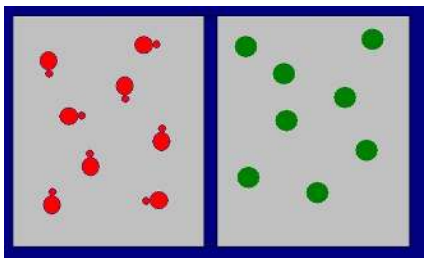
The relative distances traveled by the two gases is given as:

$$\frac{Distance\ traveled\ by\ gas\ 1}{Distance\ traveled\ by\ gas\ 2} = \frac{\sqrt{M_2}}{\sqrt{M_1}} \tag{2.3.8}$$

By examine the Graham's law as stated above, we can conclude that a lighter gas will effuse or travel more rapidly than a heavier gas. Mathematically speaking, a gas with smaller molar mass will effuse faster than a gas with larger molar mass under the same condition.

Molecular Diffusion

Similar to effusion, the process of **diffusion** is the spread of gas molecules through space or through a second substance such as the atmosphere.



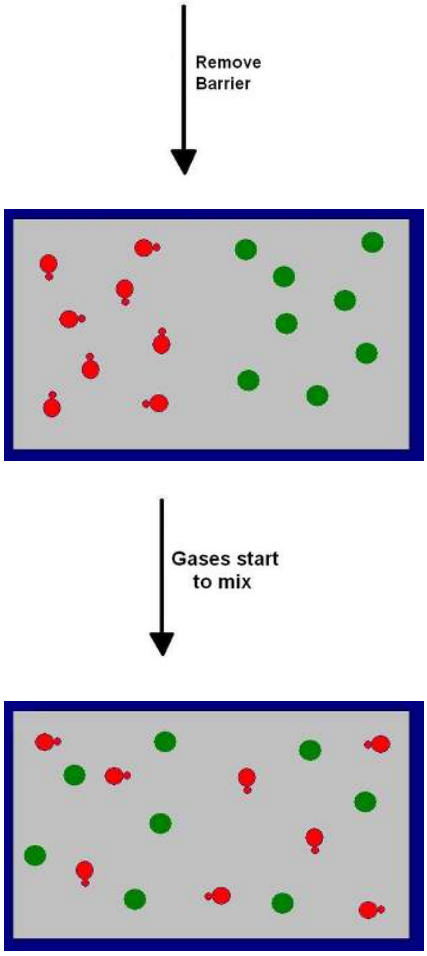
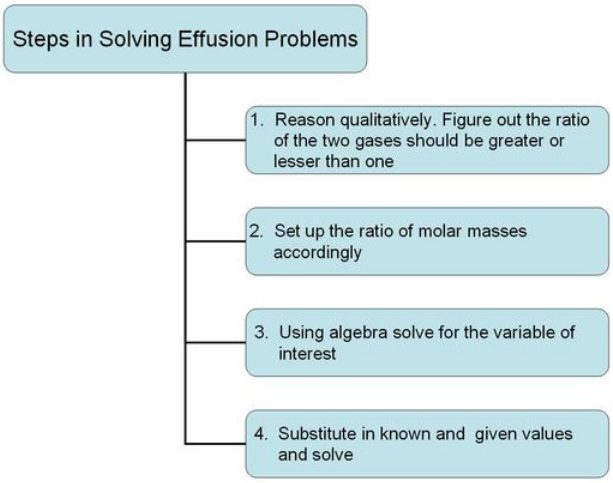


Figure **2.3.4**. The passage of one gas through another substance. In this example, the other substance is another gas.

Diffusion has many useful applications. Here is an example of diffusion that is use in everyday households. Natural gas is odorless and used commercially daily. An undetected leakage can be very dangerous as it is highly flammable and can cause an explosion when it comes in contact with an ignition source. In addition, the long term breathing of natural gas can lead to asphyxiation. Fortunately, chemists have discovered a way to easily detect natural gas occur leak by adding a small quantity of a gaseous organic sulfur compound named methyl mercaptan, CH_3SH, to the natural gas. When a leak happens, the diffusion of the odorous methyl mercaptan in the natural gas will serve as a sign of warning.

General guideline in solving effusion problems

The following flowchart outlines the steps in solving quantitative problems involving Graham's Law. It can be used as a general guideline.



Example 2.3.1

Calculate the root mean square speed, u_{rms}, in m/s of helium at 30^oC.

Solution

Start by converting the molar mass for helium from g/mol to kg/mol.

$$M = (4.00\ g/mol) \times \frac{1\ kg}{1000\ g}$$

$$M = 4.00 \times 10^{-3}\ kg/mol$$

Now, using the equation for u_{rms} substitute in the proper values for each variable and perform the calculation.

$$u_{rms} = \sqrt{\frac{3RT}{M}} \tag{2.3.9}$$

$$u_{rms} = \sqrt{\frac{3 \times (8.314\ kg\ m^2/s^2 * mol * K)(303K)}{4.00 \times 10^{-3} kg/mol}} \tag{2.3.10}$$

$$u_{rms} = 1.37 \times 10^3\ m/s \tag{2.3.11}$$

Example 2.3.2

What is the ratio of u_{rms} values for helium vs. xenon at 30^oC. Which is higher and why?

Solution

There are two approaches to solve this problem: the hard way and the easy way

Hard way:

The u_{rms} speed of helium is calculated from the above example.

First convert the molar mass of xenon from g/mol to kg/mol as we did for helium in example 1

$$M_{Xe} = (131.3\ g/mol) \times \frac{1\ kg}{1000\ g}$$

$$M = 0.1313\ kg/mol$$

Now, using the equation for the u_{rms}, insert the given and known values and solve for the variable of interest.

$$u_{rms} = \sqrt{\frac{3(8.314\ kg\ m^2/s^2 * mol * K)(303\ K)}{0.1313\ kg/mol}} \tag{2.3.12}$$

$$u_{rms} = 2.40 \times 10^2\ m/s \tag{2.3.13}$$

Compare the two values for xenon and helium and decide which is greater.

- $u_{Xe} = 2.4 \times 10^2\ m/s$
- $u_{He} = 1.37 \times 10^3\ m/s$

So the ratio of RMS speeds is

$$\frac{u_{Xe}}{u_{He}} \approx 0.18 \tag{2.3.14}$$

Helium has the higher u_{rms} speed. This is in according with Graham's Law, because helium atoms are much lighter than xenon atoms.

Easy Way:

Since the temperature is the same for both gases, only the square root of the ratio of molar mass is needed to be calculated.

$$\sqrt{\frac{M_{He}}{M_{Xe}}} = \sqrt{\frac{4.00\ g/mol}{131.3\ g/mol}} \approx 0.18 \tag{2.3.15}$$

In either approach, helium has a faster RMS speed than xenon and this is due exclusively to its smaller mass.

Example 2.3.3

If oxygen effuses from a container in 5.00 minutes, what is the molecular weight of a gas with the same given quantity of molecules effusing from the same container in 4.00 min?

Solution

Let oxygen be gas A and its rate is 1/5.00 minutes because it takes that much time for a certain quantity of oxygen to effuse and its molecular weight is 32 grams/mole (O_2 (g)). Let the unknown gas be B and its rate is 1/4.00 minutes and M_b be the molecular weight of the unknown gas.

First, choose the appropriate equation,

$$\frac{Rate\ effusion\ of\ gas\ A}{Rate\ effusion\ of\ gas\ B} = \frac{\sqrt{M_B}}{\sqrt{M_A}}$$

Second, using algebra, solve for the variable of interest on one side of the equation and plug in known and given values from the problem.

$$\sqrt{M_B} = \frac{(Rate\ effusion\ of\ gas\ A)(\sqrt{M_A})}{Rate\ effusion\ of\ gas\ B}$$

$$\sqrt{M_B} = \frac{(1/5.00\ minutes)(\sqrt{32\ grams/mole})}{1/4.00\ minutes}$$

$$\sqrt{M_B} = 4.525$$

$$M_B = (4.525)^2 = 20.5\ grams/mole$$

Example 2.3.4

Oxygen, O_2 (g), effuses from a container at the rate of 3.64 mL/sec, what is the molecular weight of a gas effusing from the same container under identical conditions at 4.48 mL/sec?

Solution

Let label oxygen as gas A. Therefore, rate of effusion of gas A is equaled to 3.64 mL/sec and the molecular weight is 32 grams/mole. The unknown gas is B and its rate of effusion is 4.48 mL/sec. We are solving for the molecular weight of gas B which is labeled as M_B.

First, choose the appropriate equation,

$$\frac{Rate\ effusion\ of\ gas\ A}{Rate\ effusion\ of\ gas\ B} = \frac{\sqrt{M_B}}{\sqrt{M_A}}$$

$$\sqrt{M_B} = \frac{(Rate\ effusion\ of\ gas\ A)(\sqrt{M_A})}{Rate\ effusion\ of\ gas\ B}$$

Second, using algebra, solve for the variable of interest on one side of the equation and plug in known and given values from the problem.

$$\sqrt{M_B} = \frac{(Rate\ effusion\ of\ gas\ A)(\sqrt{M_A})}{Rate\ effusion\ of\ gas\ B}$$

$$\sqrt{M_B} = \frac{(3.64\ mL/sec)(\sqrt{32\ grams/mole})}{4.48\ mL/sec}$$

$$\sqrt{M_B} = 4.50$$

$$M_B = (4.50)^2 = 20.2\ grams/mole$$

Example 2.3.5

Which answer(s) are true when comparing 1.0 mol O_2 (g) at STP (Standard Temperature and Pressure) and 0.50 mole of S_2 (g) at STP?

The two gases have equal through the same orifice, a tiny opening:

a. average molecular kinetic energies
b. root-mean-square speeds
c. masses
d. volumes
e. densities
f. effusion rates

Solution

The average kinetic energy of gas molecules depends on only the Temperature as exemplifies in this equation:

$$e_K = \frac{3}{2}\frac{R}{N_A}T$$

In addition, the mass of 0.50 mole of S_2 is the same as that of 1.0 mole of O_2. The rest of the choices are false.

Therefore, the correct answers are (a) and (c).

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2.4: Kinetic Molecular Theory of Gases

To better understand the molecular origins of the ideal gas law,

$$PV = nRT \tag{2.4.1}$$

the basics of the **Kinetic Molecular Theory of Gases** (**KMT**) should be understood. This model is used to describe the behavior of gases. More specifically, it is used to explain macroscopic properties of a gas, such as pressure and temperature, in terms of its microscopic components, such as atoms. Like the ideal gas law, this theory was developed in reference to ideal gases, although it can be applied reasonably well to real gases.

In order to apply the kinetic model of gases, five assumptions are made:

1. Gases are made up of particles with no defined volume but with a defined mass. In other words their volume is miniscule compared to the distance between themselves and other molecules.
2. Gas particles undergo no intermolecular attractions or repulsions. This assumption implies that the particles possess no potential energy and thus their total energy is simply equal to their kinetic energies.
3. Gas particles are in continuous, random motion.
4. Collisions between gas particles are completely elastic. In other words, there is no net loss or gain of kinetic energy when particles collide.
5. The average kinetic energy is the same for all gases at a given temperature, regardless of the identity of the gas. Furthermore, this kinetic energy is proportional to the absolute temperature of the gas.

Temperature and KMT

The last assumption can be written in equation form as:

$$KE = \frac{1}{2}mv^2 = \frac{3}{2}k_BT \tag{2.4.2}$$

where

- k_B is Boltzmann's constant ($k_B = 1.381\times10^{-23}$ m^2 kg s^{-2} K^{-1}) and
- T is the absolution temperature (in Kelvin)

This equation says that the speed of gas particles is related to their absolute temperature. In other words, as their temperature increases, their speed increases, and finally their total energy increases as well. However, it is impossible to define the speed of any *one* gas particle. As such, the speeds of gases are defined in terms of their root-mean-square speed.

Pressure and KMT

The macroscopic phenomena of pressure can be explained in terms of the kinetic molecular theory of gases. Assume the case in which a gas molecule (represented by a sphere) is in a box, length *L* (Figure 1). Through using the assumptions laid out above, and considering the sphere is only moving in the x-direction, we can examine the instance of the sphere colliding elastically with one of the walls of the box.

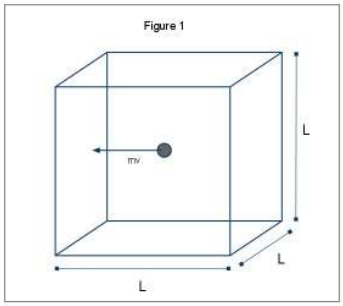


Figure 1

The momentum of this collision is given by $p=mv$, in this case $p=mv_x$, since we are only considering the x dimension. The total momentum change for this collision is then given by

$$mv_x - m(-v_x) = 2mv_x \tag{2.4.3}$$

Given that the amount of time it takes between collisions of the molecule with the wall is L/v_x we can give the frequency of collisions of the molecule against a given wall of the box per unit time as $v_x/2L$. One can now solve for the change in momentum per unit of time:

$$(2mv_x)(v_x/2L) = mv_x^2/L \tag{2.4.4}$$

Solving for momentum per unit of time gives the force exerted by an object ($F=ma=p/time$). With the expression that $F=mv_x^2/L$ one can now solve for the pressure exerted by the molecular collision, where area is given as the area of one wall of the box, $A=L^2$:

$$P = \frac{F}{A} \tag{2.4.5}$$

$$P = \frac{mv_x^2}{[L(L^2)} \tag{2.4.6}$$

The expression can now be written in terms of the pressure associated with collisions from N number of molecules:

$$P = \frac{Nmv_x^2}{V} \tag{2.4.7}$$

This expression can now be adjusted to account for movement in the x, y and z directions by using mean-square velocity for three dimensions and a large value of N. The expression now is written as:

$$P = \frac{Nm\bar{v}^2}{3V} \tag{2.4.8}$$

This expression now gives pressure, a macroscopic quality, in terms of atomic motion. The significance of the above relationship is that pressure is proportional to the mean-square velocity of molecules in a given container. Therefore, as molecular velocity increases so does the pressure exerted on the container.

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2. Chang, Raymond. *Physical Chemistry for the Biosciences*. California: University Science Books. 2005.

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2.5: Real Gases

Gases that deviate from ideality are known as Real Gases, which originate from two factors: (1) First, the theory assumes that as pressure increases, the volume of a gas becomes very small and approaches zero. While it does approach a small number, it will not be zero because molecules do occupy space (i.e. have volume) and cannot be compressed. (2) Intermolecular forces do exist in gases. These become increasingly important in low temperatures, when translational (definition of translational, please) molecular motion slows down, almost to a halt. However, at high temperatures, or even normal, every day temperatures, the intermolecular forces are very small and tend to be considered negligible.

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2.6: The Average Translational Kinetic Energy of a Gas

The laws that describe the behavior of gases were well established long before anyone had developed a coherent model of the properties of gases. In this section, we introduce a theory that describes why gases behave the way they do. The theory we introduce can also be used to derive laws such as the ideal gas law from fundamental principles and the properties of individual particles.

One key property of the individual particles is their velocity. However, in a sample of many gas particles, the particles will likely have various velocities. Rather than list the velocity of each individual gas molecule, we can combine these individual velocities in several ways to obtain "collective" velocities that describe the sample as a whole.

Table 27.1.1: Kinetic Properties of a Thermalized Ensemble (i.e., follows Maxwell-Boltzmann Distribution)

Property	Speed	Kinetic Energy
Most probable	$\sqrt{\frac{2k_bT}{m}}$	k_BT
Average	$\sqrt{\frac{8k_bT}{\pi m}}$	$\frac{4k_BT}{\pi}$
Root-mean-square	$\sqrt{\frac{3k_bT}{m}}$	$\frac{3}{2}k_BT$

In the following example, these three collective velocities are defined and calculated for a sample of gas consisting of only eight molecules.

Example 27.1.1 : A Gas Sample with Few Molecules

The speeds of eight molecules were found to be 1.0, 4.0, 4.0, 6.0, 6.0, 6.0, 8.0, and 10.0 m/s. Calculate their average speed (v_{avg}) root mean square speed (v_{rms}), and most probable speed (v_{mp}).

Solution

Start with definitions:

- **average speed** (v_{avg}) = the sum of all the speeds divided by the number of molecules
- **root-mean square speed** (v_{rms}) = the square root of the sum of the squared speeds divided by the number of molecules
- **most probable speed** (v_{mp}) = the speed at which the greatest number of molecules is moving

The average speed:

$$v_{\text{avg}} = \frac{(1.0 + 4.0 + 4.0 + 6.0 + 6.0 + 6.0 + 8.0 + 10.0)\ \text{m/s}}{8}$$
$$= 5.6\ m/s$$

The root-mean square speed:

$$v_{\text{rms}} = \sqrt{\frac{(1.0^2 + 4.0^2 + 4.0^2 + 6.0^2 + 6.0^2 + 6.0^2 + 8.0^2 + 10.0^2)\ \text{m}^2/\text{s}^2}{8}}$$
$$= 6.2\ m/s$$

The most probable speed:

Of the eight molecules, three have speeds of 6.0 m/s, two have speeds of 4.0 m/s, and the other three molecules have different speeds. Hence

$$v_{\text{mp}} = 6.0\,m/s.$$

Using expressions for v_{mp}, v_{ave}, or v_{rms}, it is fairly simple to derive expressions for kinetic energy from the expression

$$E_{kin} = \frac{1}{2}mv^2$$

It is important to remember that there will be a full distribution of molecular speeds in a thermalized sample of gas. Some molecules will be traveling faster and some more slowly. It is also important to recognize that the most probable, average, and RMS kinetic energy terms that can be derived from the kinetic molecular theory do not depend on the mass of the molecules (Table 27.1.1). As such, it can be concluded that the average kinetic energy of the molecules in a thermalized sample of gas depends only on the temperature. However, the average speed depends on the molecular mass. So, for a given temperature, light molecules will travel faster on average than heavier molecules.

The calculations carried out in Example 27.1.1 become cumbersome as the number of molecules in the sample of gas increases. Thus, a more efficient way to determine the various collective velocities for a gas sample containing a large number of molecules is required.

2.6.1: A Molecular Description of Pressure and Molecular Speed

The kinetic molecular theory of gases explains the laws that describe the behavior of gases. Developed during the mid-19th century by several physicists, including the Austrian Ludwig Boltzmann (1844–1906), the German Rudolf Clausius (1822–1888), and the Scotsman James Clerk Maxwell (1831–1879), this theory is based on the properties of individual particles as defined for an ideal gas and the fundamental concepts of physics. Thus the kinetic molecular theory of gases provides a molecular explanation for observations that led to the development of the ideal gas law. The kinetic molecular theory of gases is based on the following five postulates:

1. A gas is composed of a large number of particles called molecules (whether monatomic or polyatomic) that are in constant random motion.
2. Because the distance between gas molecules is much greater than the size of the molecules, the volume of the molecules is negligible.
3. Intermolecular interactions, whether repulsive or attractive, are so weak that they are also negligible.
4. Gas molecules collide with one another and with the walls of the container, but these collisions are perfectly elastic; that is, they do not change the average kinetic energy of the molecules.
5. The average kinetic energy of the molecules of any gas depends on only the temperature, and at a given temperature, all gaseous molecules have exactly the same average kinetic energy.

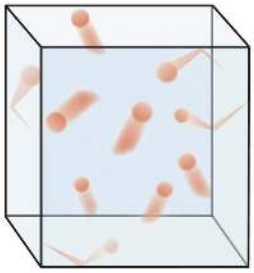


Figure 27.1.1 : Visualizing molecular motion. Molecules of a gas are in constant motion and collide with one another and with the container wall.

Although the molecules of real gases have nonzero volumes and exert both attractive and repulsive forces on one another, for the moment we will focus on how the kinetic molecular theory of gases relates to the properties of gases we have been discussing. In Topic 1C, we explain how this theory must be modified to account for the behavior of real gases.

Postulates 1 and 4 state that gas molecules are in constant motion and collide frequently with the walls of their containers. The collision of molecules with their container walls results in a **momentum transfer** (impulse) from molecules to the walls (Figure 27.1.2).

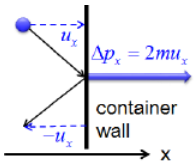


Figure 27.1.2 : Note: In this figure, the symbol u is used to represent velocity. In the rest of this text, velocity will be represented with the symbol v. Momentum transfer (Impulse) from a molecule to the container wall as it bounces off the wall. Momentum transfer ($\Delta\rho_x$) for an elastic collision is equal to mΔv_x, where m is the mass of the molecule and Δv_x is the change in the x component of the molecular velocity ($v_{x_{final}} - v_{x_{initial}}$).The wall is perpendicular to x axis. Since the collisions are elastic, the molecule bounces back with the same velocity in the opposite direction, and Δv_x equals $2v_x$.

The **momentum transfer** to the wall perpendicular to x axis as a molecule with an initial velocity v_x in the x direction hits is expressed as:

$$\text{momentum transfer}_x = \Delta\rho_x = m\Delta v_x = 2mv_x \tag{2.6.1}$$

The **collision frequency**, a number of collisions of the molecules to the wall per unit area and per second, increases with the molecular speed and the number of molecules per unit volume.

$$f \propto (v_x) \times \left(\frac{N}{V}\right) \tag{2.6.2}$$

The pressure the gas exerts on the wall is expressed as the product of impulse and the collision frequency.

$$P \propto (2mv_x) \times (v_x) \times \left(\frac{N}{V}\right) \propto \left(\frac{N}{V}\right) mv_x^2 \tag{2.6.3}$$

At any instant, however, the molecules in a gas sample are traveling at different speed. Therefore, we must replace v_x^2 in the expression above with the average value of v_x^2, which is denoted by $\bar{v_x^2}$. The overbar designates the average value over all molecules.

The exact expression for pressure is given as :

$$P = \frac{N}{V} m\bar{v_x^2} \tag{2.6.4}$$

Finally, we must consider that there is nothing special about x direction. We should expect that $\bar{v_x^2} = \bar{v_y^2} = \bar{v_z^2} = \frac{1}{3}\bar{v^2}$. Here the quantity $\bar{v^2}$ is called the **mean-square speed** defined as the average value of square-speed (v^2) over all molecules. Since $v^2 = v_x^2 + v_y^2 + v_z^2$ for each molecule, $\bar{v^2} = \bar{v_x^2} + \bar{v_y^2} + \bar{v_z^2}$. By substituting $\frac{1}{3}\bar{v^2}$ for $\bar{v_x^2}$ in the expression above, we can get the final expression for the pressure:

$$P = \frac{1}{3}\frac{N}{V} m\bar{v^2} \tag{2.6.5}$$

Because volumes and intermolecular interactions are negligible, postulates 2 and 3 state that all gaseous particles behave identically, regardless of the chemical nature of their component molecules. This is the essence of the ideal gas law, which treats all gases as collections of particles that are identical in all respects except mass. Postulate 2 also explains why it is relatively easy to compress a gas; you simply decrease the distance between the gas molecules.

Postulate 5 provides a molecular explanation for the temperature of a gas. Postulate 5 refers to the *average translational* kinetic energy of the molecules of a gas,

$$\epsilon = m\bar{v^2}/2 \tag{2.6.6}$$

By rearranging equation 2.6.5 and substituting in equation 2.6.6, we obtain

$$PV = \frac{1}{3}Nm\bar{v^2} = \frac{2}{3}N\epsilon \tag{2.6.7}$$

The 2/3 factor in the proportionality reflects the fact that velocity components in each of the three directions contributes ½ *kT* to the kinetic energy of the particle. The average translational kinetic energy is directly proportional to temperature:

$$\epsilon = \frac{3}{2}kT \tag{2.6.8}$$

in which the proportionality constant k is known as the *Boltzmann constant*. Substituting Equation 2.6.8 into Equation 2.6.7 yields

$$PV = \left(\frac{2}{3}N\right)\left(\frac{3}{2}kT\right) = NkT \tag{2.6.9}$$

The Boltzmann constant k is just the gas constant per molecule, so if N is chosen as Avogadro's number, N_A, then N_Ak is R, the gas constant per mole. Thus, for *n* moles of particles, the Equation 2.6.9 becomes

$$PV = nRT \tag{2.6.10}$$

which is the ideal gas law.

As noted in Example 27.1.1 , the root-mean square speed (v_{rms}) is the square root of the sum of the squared speeds divided by the number of particles:

$$v_{rms} = \sqrt{\bar{v^2}} = \sqrt{\frac{v_1^2 + v_2^2 + \cdots v_N^2}{N}} \tag{2.6.11}$$

where N is the number of particles and v_i is the speed of particle i.

The v_{rms} for a sample containing a large number of molecules can be obtained by combining equations 2.6.7 and 2.6.8 in a slightly different fashion than that used to obtain equation 2.6.10:

$$PV = \frac{1}{3}Nm\bar{v^2} = \frac{2}{3}N\epsilon \tag{27.1.10}$$

$$\epsilon = \frac{3}{2}kT \tag{27.1.11}$$

$$\frac{1}{3}Nm\bar{v^2} = \left(\frac{2}{3}\right)\left(\frac{3}{2}\right)NkT \tag{2.6.12}$$

$$\frac{1}{3}Nm\bar{v^2} = NkT \tag{2.6.13}$$

$$Nm\bar{v^2} = 3NkT \tag{2.6.14}$$

If N is chosen to be Avogadro's number, N_A, then $N_Am = M$, the molar mass, and $N_Ak = R$, the gas constant per mole,

$$\bar{v^2} = \frac{3RT}{M} \tag{2.6.15}$$

$$v_{rms} = \sqrt{\bar{v^2}} = \sqrt{\frac{3RT}{M}} \tag{2.6.16}$$

In Equation 2.6.16, v_{rms} has units of meters per second; consequently, the units of molar mass M are kilograms per mole, temperature T is expressed in kelvins, and the ideal gas constant R has the value 8.3145 J/(K•mol). Equation 2.6.16 shows that v_{rms} of a gas is proportional to the square root of its Kelvin temperature and inversely proportional to the square root of its molar mass. The root mean-square speed of a gas increase with increasing temperature. At a given temperature, heavier gas molecules have slower speeds than do lighter ones.

✔ Example 27.1.2 :

What is the root mean-square speed for O_2 molecules at 25ºC?

Given: Temperature in ºC, type of molecules, ideal gas gas constant

Asked for: v_{rms}, the root mean-square speed

Strategy:

Convert temperature to kelvins:

$$\text{T (in kelvin)} = (25^{\circ}\text{C} + 273^{\circ}\text{C})\frac{1\text{ K}}{1\ ^{\circ}\text{C}} = 298\text{ K}$$

Convert molar mass of O_2 molecules to kg per mole:

$$\text{M (in } \frac{\text{kg}}{\text{mole}}) = 32.00\frac{\text{g}}{\text{mole}}\text{x}\frac{1\text{ kg}}{1000\text{ g}} = 0.03200\frac{\text{kg}}{\text{mole}}$$

Use equation 2.6.16 to calculate the rms speed.

Solution

$$v_{\text{rms}_{O_2}} = \sqrt{\frac{3(8.3145\frac{\text{J}}{\text{K}\cdot\text{mole}})(298.15\text{ K})}{0.03200\frac{\text{kg}}{\text{mole}}}} = 482\frac{m}{s}$$

? Exercise 27.1.2

What is the root mean-square speed for Cl_2 molecules at 25°C?

$v_{\text{rms}_{Cl_2}} = 324\frac{m}{s}$

2.6.2: Many molecules, many velocities

At temperatures above absolute zero, all molecules are in motion. In the case of a gas, this motion consists of straight-line jumps whose lengths are quite great compared to the dimensions of the molecule. Although we can never predict the velocity of a particular *individual* molecule, the fact that we are usually dealing with a huge number of them allows us to know what fraction of the molecules have kinetic energies (and hence velocities) that lie within any given range.

The trajectory of an individual gas molecule consists of a series of straight-line paths interrupted by collisions. What happens when two molecules collide depends on their relative kinetic energies; in general, a faster or heavier molecule will impart some of its kinetic energy to a slower or lighter one. Two molecules having identical masses and moving in opposite directions at the same speed will momentarily remain motionless after their collision.

If we could measure the instantaneous velocities of all the molecules in a sample of a gas at some fixed temperature, we would obtain a wide range of values. A few would be zero, and a few would be very high velocities, but the majority would fall into a more or less well-defined range. We might be tempted to define an average velocity for a collection of molecules, but here we would need to be careful: molecules moving in opposite directions have velocities of opposite signs. Because the molecules are in a gas are in random thermal motion, there will be just about as many molecules moving in one direction as in the opposite direction, so the velocity vectors of opposite signs would all cancel and the average velocity would come out to zero. Since this answer is not very useful, we need to do our averaging in a slightly different way.

The proper treatment is to average the *squares* of the velocities, and then take the square root of this value to obtain the root-mean-square velocity (v_{rms}), which is what we developed above. This velocity describes the gas sample as a whole, but it does not tell us about the range of velocities possible, nor does it tell us the distribution of velocities. To obtain a more complete description of how many gas molecules are likely to be traveling at a given velocity range we need to make use of the Maxwell-Boltzmann distribution law.

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2.7: The Gaussian Distribution of One Component of the Molecular Velocity

As was shown in section 27.1, the pressure of an ideal gas is given as the total force exerted per unit area

$$P = \frac{F_{tot}}{A} = N_{tot}\left(\frac{mv_x^2}{V}\right) = \frac{N_{tot}m}{V}v_x^2$$

The question then becomes how to deal with the velocity term. Initially, it was assumed that all of the molecules had the same velocity, and so the magnitude of the velocity in the x-direction was merely a function of the trajectory. However, real samples of gases comprise molecules with an entire distribution of molecular speeds and trajectories. To deal with this distribution of values, we replaced (v_x^2) with the squared average of velocity in the x direction $\langle v_x \rangle^2$.

$$P = \frac{N_{tot}m}{V}\langle v_x \rangle^2$$

The distribution function for velocities in the x direction, known as the **Maxwell-Boltzmann distribution**, is given by:

$$f(v_x) = \underbrace{\sqrt{\frac{m}{2\pi k_B T}}}_{\text{normalization term}} \underbrace{\exp\left(\frac{-mv_x^2}{2k_B T}\right)}_{\text{exponential term}} \tag{2.7.1}$$

This function has two parts: a **normalization constant** and an exponential term. The normalization constant is derived by noting that

$$\int_{-\infty}^{\infty} f(v_x)dv_x = 1 \tag{2.7.2}$$

Normalizing the Maxwell-Boltzmann Distribution

The Maxwell-Boltzmann distribution has to be normalized because it is a continuous probability distribution. As such, the sum of the probabilities for all possible values of v_x **must** be unity. And since v_x can take any value between -∞ and ∞, then Equation 2.7.2 must be true. So if the form of $f(v_x)$ is assumed to be

$$f(v_x) = N\exp\left(\frac{-mv_x^2}{2k_B T}\right)$$

The normalization constant N can be found from

$$\int_{-\infty}^{\infty} f(v_x)dv_x = \int_{-\infty}^{\infty} N\exp\left(\frac{-mv_x^2}{2k_B T}\right)dv_x = 1$$

The expression can be simplified by letting $\alpha = m/2k_B T$:

$$N\int_{-\infty}^{\infty} \exp\left(-\alpha v_x^2\right)dv_x = 1$$

A table of definite integrals says that

$$\int_{-\infty}^{\infty} e^{-ax^2}dx = \sqrt{\frac{\pi}{a}}$$

So

$$N\sqrt{\frac{\pi}{\alpha}} = 1$$

Thus,

$$N = \sqrt{\frac{\alpha}{\pi}} = \left(\frac{m}{2\pi k_B T}\right)^{1/2}$$

And thus the normalized distribution function is given by

$$f(v_x) = \left(\frac{m}{2\pi k_B T}\right)^{1/2} \exp\left(-\frac{mv_x^2}{2k_B T}\right) \tag{2.7.3}$$

Calculating an Average from a Probability Distribution

Calculating an average for a finite set of data is fairly easy. The average is calculated by

$$\bar{x} = \frac{1}{N}\sum_{i=1}^{N} x_i$$

But how does one proceed when the set of data is infinite? Or how does one proceed when all one knows are the probabilities for each possible measured outcome? It turns out that that is fairly simple too!

$$\bar{x} = \sum_{i=1}^{N} x_i P_i$$

where P_i is the probability of measuring the value x_i. This can also be extended to problems where the measurable properties are not discrete (like the numbers that result from rolling a pair of dice) but rather come from a continuous parent population. In this case, if the probability is of measuring a specific outcome, the average value can then be determined by

$$\bar{x} = \int xP(x)dx$$

where $P(x)$ is the function describing the probability distribution, and with the integration taking place across all possible values that x can take.

Calculating the average velocity in the x direction

A value that is useful (and will be used in further developments) is the average velocity in the x direction. This can be derived using the probability distribution, as shown in the mathematical development box above. The average value of v_x is given by

$$\langle v_x \rangle = \int_{-\infty}^{\infty} v_x f(v_x) dx$$

This integral will, by necessity, be zero. This must be the case as the distribution is symmetric, so that half of the molecules are traveling in the +x direction, and half in the –x direction. These motions will have to cancel. So, a more satisfying result will be given by considering the magnitude of v_x, which gives the speed in the x direction. Since this cannot be negative, and given the symmetry of the distribution, the problem becomes

$$\langle |v_x| \rangle = 2\int_{0}^{\infty} v_x f(v_x) dx$$

In other words, we will consider only half of the distribution, and then double the result to account for the half we ignored.

For simplicity, we will write the distribution function as

$$f(v_x) = N\exp(-\alpha v_x^2)$$

where

$$N = \left(\frac{m}{2\pi k_B T}\right)^{1/2}$$

and

$$\alpha = \frac{m}{2k_B T}.$$

A table of definite integrals shows

$$\int_0^\infty x e^{-ax^2} dx = \frac{1}{2a}$$

so

$$\langle v_x \rangle = 2N\left(\frac{1}{2\alpha}\right) = \frac{N}{\alpha}$$

Substituting our definitions for N and α produces

$$\langle v_x \rangle = \left(\frac{m}{2\pi k_B T}\right)^{1/2}\left(\frac{2k_B T}{m}\right) = \left(\frac{2k_B T}{\pi m}\right)^{1/2}$$

This expression indicates the average speed for motion in one direction.

It is important to note that equation 2.7.1 describes the distribution function for one component of the molecular ***velocity***. Because a molecule is able to move in a positive or a negative direction, the range of one component of the molecular velocity (v_x in this case) is $-\infty$ to ∞. This distribution of velocities is a Gaussian distribution of velocities, as shown in Figure 27.2.1 .

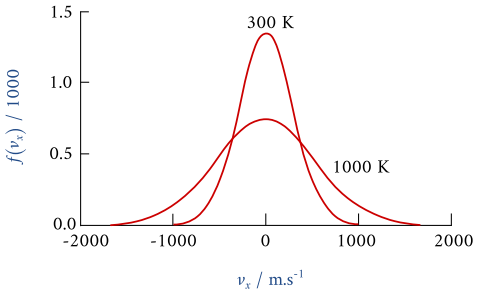


Figure 27.2.1 : Distribution of the x component of the velocity of a nitrogen molecule at 300 K and 1000 K. (CC BY-NC; Ümit Kaya via LibreTexts)

We will find in section 27.3 that the distribution of molecular ***speeds*** is not a Gaussian distribution.

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2.8: The Distribution of Molecular Speeds is Given by the Maxwell-Boltzmann Distribution

2.8.1: The Boltzmann Distribution

If we were to plot the number of molecules whose velocities fall within a series of narrow ranges, we would obtain a slightly asymmetric curve known as a *velocity distribution*. The peak of this curve would correspond to the *most probable* velocity. This velocity distribution curve is known as the *Maxwell-Boltzmann distribution*, but is frequently referred to only by Boltzmann's name. The **Maxwell-Boltzmann distribution law** was first worked out around 1860 by the great Scottish physicist, **James Clerk Maxwell** (1831-1879), who is better known for discovering the laws of electromagnetic radiation. Later, the Austrian physicist **Ludwig Boltzmann** (1844-1906) put the relation on a sounder theoretical basis and simplified the mathematics somewhat. Boltzmann pioneered the application of statistics to the physics and thermodynamics of matter and was an ardent supporter of the atomic theory of matter at a time when it was still not accepted by many of his contemporaries.

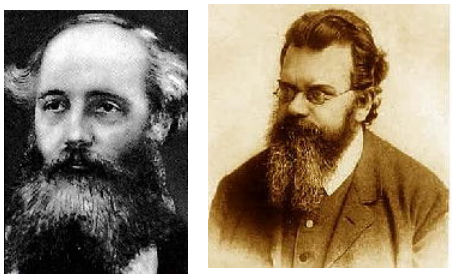


Figure 27.3.1 : Maxwell (left) and Boltzmann (right) are responsible for describing the velocity distribution of gas molecules

In section 27.2 we saw that the distribution function for molecular speeds in the x direction is given by:

$$f(v_x) = \underbrace{\sqrt{\frac{m}{2\pi k_B T}}}_{\text{normalization term}} \underbrace{\exp\left(\frac{-mv_x^2}{2k_B T}\right)}_{\text{exponential term}}$$

However, real gas samples have molecules not only with a distribution of molecular speeds and but also a random distribution of directions. Using normal vector magnitude properties (or simply using the Pythagorean Theorem), it can be seen that

$$\langle v \rangle^2 = \langle v_x \rangle^2 + \langle v_y \rangle^2 + \langle v_z \rangle^2$$

Since the direction of travel is random, the velocity can have any component in x, y, or z directions with equal probability. As such, the average value of the x, y, or z components of velocity should be the same. And so

$$\langle v \rangle^2 = 3\langle v_x \rangle^2$$

Substituting this into the expression for pressure yields

$$p = \frac{N_{tot} m}{3V} \langle v \rangle^2$$

All that remains is to determine the form of the distribution of velocity magnitudes the gas molecules can take. In his 1860 paper (Illustrations of the dynamical theory of gases. Part 1. On the motions and collisions of perfectly elastic spheres, 1860), Maxwell proposed a form for this distribution of speeds which proved to be consistent with observed properties of gases (such as their viscosities). He derived this expression based on a transformation of coordinate system from Cartesian coordinates (x, y, z) to spherical polar coordinates (v, θ, ϕ). In this new coordinate system, v represents the magnitude of the velocity (or the speed) and all of the directional data is carried in the angles θ and ϕ. The infinitesimal volume unit becomes

$$dx\, dy\, dz = v^2 \sin(\theta)\, dv\, d\theta\, d\phi$$

Applying this transformation of coordinates **Maxwell's distribution** took the following form

$$f(v) = 4\pi v^2 \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(\frac{-mv^2}{2k_B T}\right) \tag{2.8.1}$$

The Distribution of Speed over all Directions

The Distribution of Kinetic Energy in Three Dimensions

As noted above, the distribution function of molecular energies for one dimension is

$$f(v_x) = \sqrt{\frac{m}{2\pi k_B T}} \exp\left(\frac{-mv_x^2}{2k_B T}\right)$$

To obtain a three-dimensional probability distribution, you multiply the distribution function for each of the three dimensions so that

$$f(v_x, v_y, v_z) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(\frac{-mv^2}{2k_B T}\right)$$

given

$$\langle v \rangle^2 = \langle v_x \rangle^2 + \langle v_y \rangle^2 + \langle v_z \rangle^2$$

The Conversion of Energy Distribution to Speed Distribution

To convert the three-dimensional energy distribution to a speed distribution over all space, the energy distribution must be summed over all directions. This sum is usually described by imagining a "velocity space" in spherical polar coordinates. As noted above, in this new coordinate system, v represents the magnitude of the velocity (or the speed) and all of the directional data is carried in the angles θ and ϕ. The infinitesimal volume unit becomes

$$dx\, dy\, dz = v^2 \sin(\theta)\, dv\, d\theta\, d\phi$$

You integrate over θ and ϕ to sum over all space, thus

$$f(v) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(\frac{-mv^2}{2k_B T}\right) \underbrace{\int_0^{\pi} \int_0^{2\pi} v^2 \sin\theta d\phi d\theta}_{=4\pi v^2}$$

This equation is rearranged to give

$$f(v) = 4\pi v^2 \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(\frac{-mv^2}{2k_B T}\right)$$

This function can be thought of as having three basic parts to it: **a normalization constant** (N), a velocity dependence (v^2), and an exponential term that contains the kinetic energy ($\frac{1}{2}mv^2$).

Because the function represents the fraction of molecules with the speed v, the sum of the fractions for all possible velocities must be unity. This sum can be calculated as an integral. The normalization constant ensures that

$$\int_0^{\infty} f(v) dv = 1$$

Thus the normalization constant is

$$N = 4\pi \sqrt{\left(\frac{m}{2\pi k_B T}\right)^3}$$

2.8.2: Velocity distributions depend on temperature and mass

Higher temperatures allow a larger fraction of molecules to acquire greater amounts of kinetic energy, causing the Boltzmann plots to spread out. Figure 27.3.2 shows how the Maxwell-Boltzmann distribution is affected by temperature. At lower temperatures, the molecules have less energy. Therefore, the speeds of the molecules are lower and the distribution has a smaller range. As the temperature of the molecules increases, the distribution flattens out. Because the molecules have greater energy at higher temperature, the molecules are moving faster.

Notice how the left ends of the plots are anchored at zero velocity (there will always be a few molecules that happen to be at rest.) As a consequence, the curves flatten out as the higher temperatures make additional higher-velocity states of motion more accessible. The area under each plot is the same for a constant number of molecules.

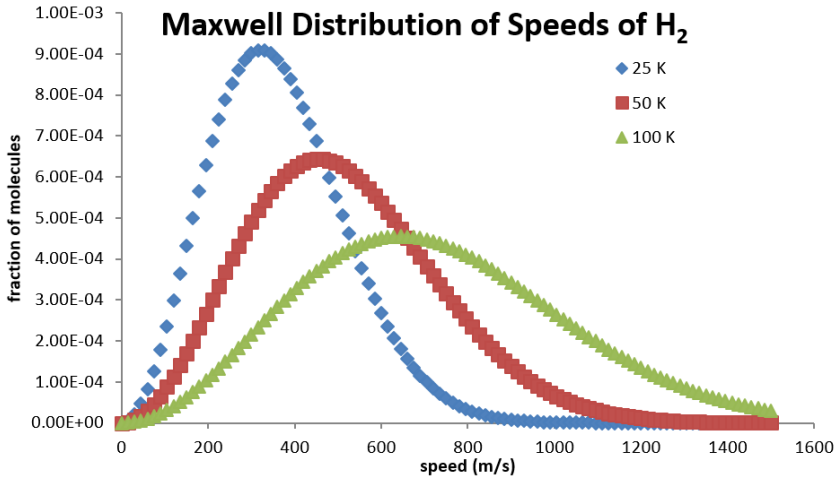


Figure 27.3.2: Maxwell Distribution of speeds for hydrogen molecules at differing temperatures.

Calculating the Average Speed

Using the Maxwell distribution as a distribution of probabilities, the average molecular speed in a sample of gas molecules can be determined.

$$\begin{aligned}\langle v\rangle &= \int_{-\infty}^{\infty} v\, f(v) dv \\ &= \int_{-\infty}^{\infty} v\, 4\pi \sqrt{\left(\frac{m}{2\pi k_B T}\right)^3} v^2 \exp\left(\frac{-mv^2}{2k_B T}\right)\, dv \\ &= 4\pi \sqrt{\left(\frac{m}{2\pi k_B T}\right)^3} \int_{-\infty}^{\infty} v^3 \exp\left(\frac{-mv^2}{2k_B T}\right)\, dv\end{aligned}$$

The following can be found in a table of integrals:

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

So

$$\langle v\rangle = 4\pi \sqrt{\left(\frac{m}{2\pi k_B T}\right)^3} \left[\frac{1}{2\left(\frac{m}{2k_B T}\right)^2}\right]$$

Which simplifies to

$$\langle v\rangle = \left(\frac{8k_B T}{\pi m}\right)^{1/2}$$

Note: the value of $\langle v\rangle$ is twice that of $\langle v_x\rangle$ which was derived in an earlier example!

$$\langle v\rangle = 2\langle v_x\rangle$$

Example 27.3.1 :

What is the average value of the squared speed according to the Maxwell distribution law?

Solution:

$$\begin{aligned}\langle v^2\rangle &= \int_{-\infty}^{\infty} v^2\, f(v) dv \\ &= \int_{-\infty}^{\infty} v^2\, 4\pi \sqrt{\left(\frac{m}{2\pi k_B T}\right)^3}\, v^2 \exp\left(\frac{-mv^2}{2k_B T}\right)\, dv \\ &= 4\pi \sqrt{\left(\frac{m}{2\pi k_B T}\right)^3} \int_{-\infty}^{\infty} v^4 \exp\left(\frac{-mv^2}{2k_B T}\right)\, dv\end{aligned}$$

A table of integrals indicates that

$$\int_0^{\infty} x^{2n} e^{-ax^2} dx = \frac{1 \cdot 3 \cdot 5 \ldots (2n-1)}{2^{n+1} a^n} \sqrt{\frac{\pi}{a}}$$

Substitution (noting that $n = 2$) yields

$$\langle v^2\rangle = 4\pi \sqrt{\left(\frac{m}{2\pi k_B T}\right)^3} \left[\frac{1 \cdot 3}{2^3 \left(\frac{m}{2k_B T}\right)^2} \sqrt{\frac{\pi}{\left(\frac{m}{2k_B T}\right)}}\right]$$

which simplifies to

$$\langle v^2\rangle = \frac{3k_B T}{m}$$

Note: The square root of this average squared speed is called the **root mean square** (RMS) speed, and has the value

$$v_{rms} = \sqrt{\langle v^2\rangle} = \left(\frac{3k_B T}{m}\right)^{1/2}$$

All molecules have the same kinetic energy ($\frac{1}{2}mv^2$) at the same temperature, so the fraction of molecules with higher velocities will increase as m, and thus the molecular weight, decreases. Figure 27.3.3 shows the dependence of the Maxwell-Boltzmann distribution on molecule mass. On average, heavier molecules move more slowly than lighter molecules. Therefore, heavier molecules will have a smaller speed distribution, while lighter molecules will have a speed distribution that is more spread out.

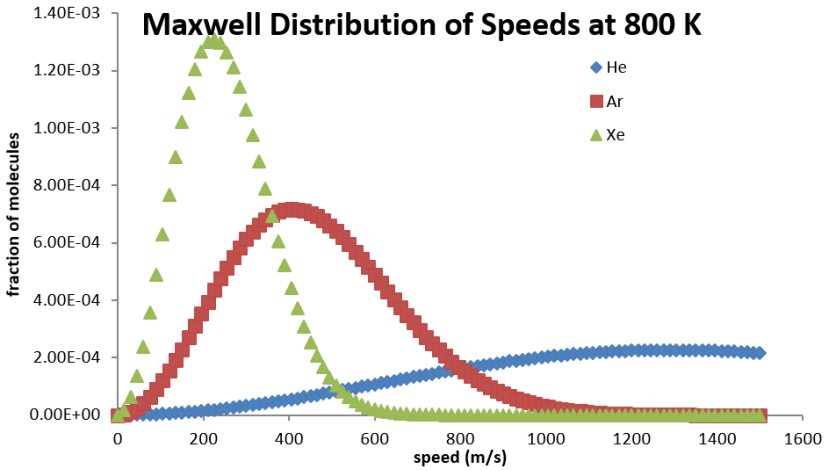


Figure 27.3.3: Maxwell Distribution of speeds at 800 K for different gasses of differing molecular masses.

2.8.3: Related Speed Expressions

Usually, we are more interested in the speeds of molecules rather than their component velocities. The Maxwell–Boltzmann distribution for the speed follows immediately from the distribution of the velocity vector, above. Note that the speed of an individual gas particle is:

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

Three speed expressions can be derived from the Maxwell-Boltzmann distribution:

- the most probable speed,
- the average speed, and
- the root-mean-square speed.

The **most probable speed** is the maximum value on the distribution plot (Figure 27.3.4). This is established by finding the velocity when the derivative of Equation 2.8.1 is zero

$$\frac{df(v)}{dv} = 0$$

which is

$$v_{mp} = \sqrt{\frac{2RT}{M}} \tag{2.8.2}$$

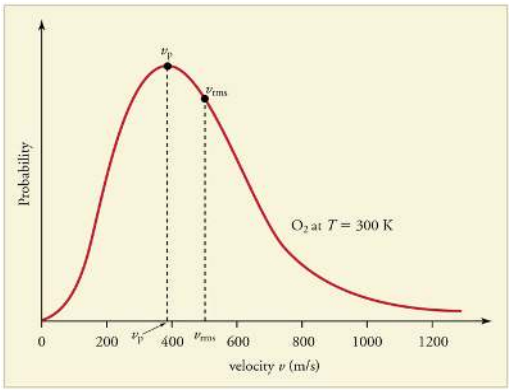


Figure 27.3.4 : The Maxwell-Boltzmann distribution is shifted to higher speeds and is broadened at higher temperatures. from OpenStax. The speed at the top of the curve is called the most probable speed because the largest number of molecules have that speed.

The **average speed** is the sum of the speeds of all the molecules divided by the number of molecules.

$$v_{avg} = \bar{v} = \int_0^\infty vf(v)dv = \sqrt{\frac{8RT}{\pi M}}$$

The **root-mean-square speed** is square root of the average speed-squared.

$$v_{rms} = \bar{v^2} = \sqrt{\frac{3RT}{M}}$$

where

- R is the gas constant,
- T is the absolute temperature and
- M is the molar mass of the gas.

It *always* follows that for gases that follow the Maxwell-Boltzmann distribution:

$$v_{mp} < v_{avg} < v_{rms}$$

2.8.4: Problems

1. Using the Maxwell-Boltzman function, calculate the fraction of argon gas molecules with a speed of 305 m/s at 500 K.
2. If the system in problem 1 has 0.46 moles of argon gas, how many molecules have the speed of 305 m/s?
3. Calculate the values of C_{mp}, C_{avg}, and C_{rms} for xenon gas at 298 K.
4. From the values calculated above, label the Boltzmann distribution plot with the approximate locations of (C_{mp}\), C_{avg}, and C_{rms}.

5. What will have a larger speed distribution, helium at 500 K or argon at 300 K? Helium at 300 K or argon at 500 K? Argon at 400 K or argon at 1000 K?

2.8.4.1: Answers

1. 0.00141
2. 3.92×10^{20} argon molecules
3. c_{mp} = 194.27 m/s, c_{avg} = 219.21 m/s, c_{rms} = 237.93 m/s
4. As stated above, C_{mp} is the most probable speed, thus it will be at the top of the distribution curve. To the right of the most probable speed will be the average speed, followed by the root-mean-square speed.
5. Hint: Use the related speed expressions to determine the distribution of the gas molecules: helium at 500 K. helium at at 300 K. argon at 1000 K.

2.8.5: Sources

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2.9: The Frequency of Collisions with a Wall

In the derivation of an expression for the pressure of a gas, it is useful to consider the frequency with which gas molecules collide with the walls of the container. To derive this expression, consider the expression for the "collision volume".

$$V_{col} = v_x \Delta t \cdot A$$

in which the product of the velocity v_x and a time interval Δt is multiplied by A, the area of the wall with which the molecules collide.

All of the molecules within this volume, and with a velocity such that the x-component exceeds v_x (and is positive) will collide with the wall. That fraction of molecules is given by

$$N_{col} = \frac{N}{V} \frac{\langle v_x \rangle \Delta t \cdot A}{2}$$

and the frequency of collisions with the wall per unit area per unit time is given by

$$z_w = \frac{N}{V} \frac{\langle v_x \rangle}{2}$$

In order to expand this model into a more useful form, one must consider motion in all three dimensions. Considering that

$$\langle v \rangle = \sqrt{\langle v_x \rangle + \langle v_y \rangle + \langle v_z \rangle}$$

and that

$$\langle v_x \rangle = \langle v_y \rangle = \langle v_z \rangle$$

it can be shown that

$$\langle v \rangle = 2 \langle v_x \rangle$$

or

$$\langle v_x \rangle = \frac{1}{2} \langle v \rangle$$

and so

$$z_w = \frac{1}{4} \frac{N}{V} \langle v \rangle$$

A different approach to determining z_w is to consider a collision cylinder that will enclose all of the molecules that will strike an area of the wall at an angle θ and with a speed v in the time interval dt. The volume of this collision cylinder is the product of its base area (A) times its vertical height ($v \cos\theta dt$), as shown in figure **2.9.1**.

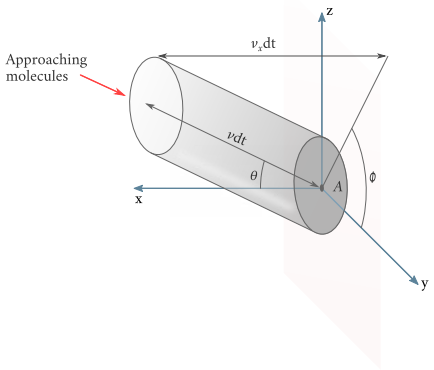


Figure **2.9.1**: The collision cylinder for determining the number of collisions of gas molecules with a wall. (CC BY-NC; Ümit Kaya)

The number of molecules in this cylinder is $\rho \cdot A \cdot v \cdot \cos\theta dt$, where ρ is the number density $\frac{N}{V}$. The fraction of molecules that are traveling at a speed between v and $v + dv$ is $F(v)dv$. The fraction of molecules traveling within the solid angle bounded by θ and $\theta + d\theta$ and between ϕ and $\phi + d\phi$ is $\frac{\sin\theta d\theta d\phi}{4\pi}$. Multiplying these three terms together results in the number of molecules colliding with the area A from the specified direction during the time interval dt

$$dN_w = \rho \cdot A \cdot v \cdot \cos\theta\, dt \cdot F(v)dv \cdot \frac{\sin\theta d\theta d\phi}{4\pi}$$

This equation can be rearranged to obtain

$$\frac{1}{A}\frac{dN_w}{dt} = \frac{\rho}{4\pi} vF(v)dv \cdot \cos\theta \sin\theta\, d\theta d\phi = dz_w$$

Integrating this equation over all possible speeds and directions (on the front side of the wall only), we get

$$z_w = \frac{\rho}{4\pi}\int_0^\infty vF(v)dv \cdot \int_0^{\pi/2} \cos\theta \sin\theta\, d\theta \int_0^{2\pi} d\phi$$

The result is that

$$z_w = \frac{1}{A}\frac{dN_w}{dt} = \frac{1}{4}\frac{N}{V}\langle v\rangle = \rho\frac{\langle v\rangle}{4} \tag{2.9.1}$$

Example 27.4.1

Calculate the collision frequency per unit area (Z_w) for oxygen at 25.0°C and 1.00 bar using equation 2.9.1:

$$z_w = \frac{1}{4}\frac{N}{V}\langle v\rangle$$

Solution

N molecules = N_A x n, so that

$$\frac{N}{V} = \frac{(N_A)\cdot n}{V} = \frac{(N_A)\cdot P}{R\cdot T}$$

$$\frac{(6.022x10^{23}\, mole^{-1})(1.00\, bar)}{(0.08319\, L\cdot bar\cdot mole^{-1}\cdot K^{-1})(298\, K)} = 2.43\times 10^{22}\, L^{-1} = 2.43\times 10^{25}\, m^{-3}$$

and

$$\langle v\rangle = \left(\frac{8RT}{\pi M}\right)^{\frac{1}{2}} = \left(\frac{8(8.314 J\cdot K^{-1}\cdot mol^{-1})(298K)}{\pi\cdot(0.031999\, kg)}\right)^{\frac{1}{2}} = 444\, m\cdot s^{-1}$$

Thus

$$z_w = \frac{1}{4}(2.43\times 10^{25} m^{-3})(444\, m\cdot s^{-1})\left(\frac{1\, m}{100\, cm}\right)^2 = 2.70\times 10^{23} s^{-1}\cdot cm^{-2}$$

The factor of N/V is often referred to as the "number density" as it gives the number of molecules per unit volume. At 1 atm pressure and 298 K, the number density for an ideal gas is approximately 2.43 x 10^{19} molecule/cm^3. (This value is easily calculated using the ideal gas law.) By comparison, the average number density for the universe is approximately 1 molecule/cm^3.

Exercise 27.4.1

Calculate the collision frequency per unit area (Z_w) for hydrogen at 25.0°C and 1.00 bar using equation 2.9.1:

$$z_w = \frac{1}{4}\frac{N}{V}\langle v\rangle$$

Answer

$$\langle v \rangle = 1770\, m \cdot s^{-1}$$

and

$$Z_w = 1.08 \times 10^{24} s^{-1} \cdot cm^{-2}$$

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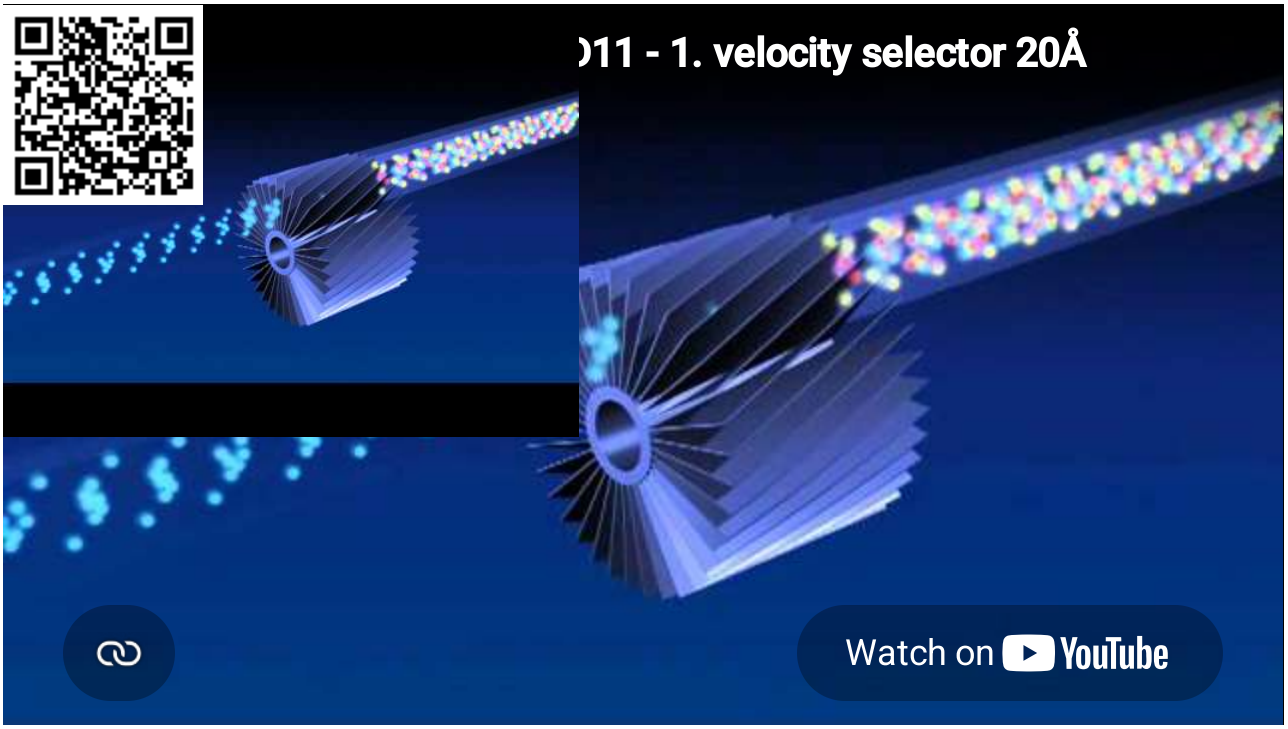
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2.10: The Maxwell-Boltzmann Distribution Has Been Verified Experimentally

The Maxwell-Boltzman distruction distribution has been verified experimentally by a device called a velocity selector, which is essentially a series of spinning wheels with a hole through which the gas is effused. This ensures that only gas particles with a certain velocity will pass through all the holes as the wheels are spun at various rates. Thus it is possible to count the number of particles with various velocities and show that, indeed they do satisfy the Maxwell-Boltzmann distribution.



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2.11: Mean Free Path

2.11.1: Collision energy

Consider two particles A and B in a system. The kinetic energy of these two particles is

$$K_{AB} = \frac{\mathbf{p}_A^2}{2m_A} + \frac{\mathbf{p}_B^2}{2m_B} \tag{2.11.1}$$

We can describe kinetic energy in terms of center-of-mass ($\mathbf{P}$) and relative momentum ($\mathbf{p}$), which are given by

$$\mathbf{P} = \mathbf{p}_A + \mathbf{p}_B$$

and

$$\begin{aligned} \mathbf{p} &= \text{relative velocity} \times \mu \\ &= (\mathbf{v}_A - \mathbf{v}_B) \times \left(\frac{m_A m_B}{m_A + m_B}\right) \\ &= \frac{m_B \mathbf{p}_A - m_A \mathbf{p}_B}{M} \end{aligned}$$

where

$$M = m_A + m_B$$

is the total mass of the two particles, and

$$\mu = \frac{m_A m_B}{M}$$

is the **reduced mass** of the two particles.

Substituting these terms into equation 2.11.1, we find

$$K_{AB} = \frac{\mathbf{p}_A^2}{2m_A} + \frac{\mathbf{p}_B^2}{2m_B} = \frac{\mathbf{P}^2}{2M} + \frac{\mathbf{p}^2}{2\mu}$$

Note that the kinetic energy separates into a sum of a center-of-mass term and a relative momentum term.

Now the relative position of the two particles is $\mathbf{r} = \mathbf{r}_A - \mathbf{r}_B$ so that the relative velocity is $\dot{\mathbf{r}} = \dot{\mathbf{r}}_A - \dot{\mathbf{r}}_B$ or $\mathbf{v} = \mathbf{v}_A - \mathbf{v}_B$. Thus, if the two particles are approaching each other such that $\mathbf{v}_A = -\mathbf{v}_B$, then $\mathbf{v} = 2\mathbf{v}_A$. However, by equipartitioning the relative kinetic energy, which is mass independent, we get

$$\left\langle \frac{\mathbf{p}^2}{2\mu} \right\rangle = \frac{3}{2} k_B T$$

which is called the *collision energy*

2.11.2: Collision cross-section

Consider two molecules in a system. The probability that they will collide increases with the effective “size” of each particle. However, the size measure that is relevant is the apparent cross-section area of each particle. For simplicity, suppose the particles are spherical, which is not a bad approximation for small molecules. If we are looking at a sphere, what we perceive as the size of the sphere is the cross section area of a great circle. Recall that each spherical particle has an associated “collision sphere” that just encloses two particles at closest contact, i.e., at the moment of a collision, and that this sphere is a radius d, where d is the diameter of each spherical particle. The cross-section of this collision sphere represents an effective cross section for each particle inside which a collision is imminent. The cross-section of the collision sphere is the area of a great circle, which is πd^2. We denote this apparent cross section area σ. Thus, for spherical particles A and B with diameters d_A and d_B, the individual cross sections are

$$\sigma_A = \pi d_A^2, \quad \sigma_B = \pi d_B^2$$

The *collision cross section*, σ_{AB} is determined by an effective diameter d_{AB} characteristic of both particles. The collision probability increases of both particles have large diameters and decreases if one of them has a smaller diameter than the other. Hence, a simple

measure sensitive to this is the arithmetic average

$$d_{AB} = \frac{1}{2}(d_A + d_B)$$

and the resulting collision cross section becomes

$$\begin{aligned}\sigma_{AB} &= \pi d_{AB}^2 \\ &= \pi\left(\frac{d_A + d_B}{2}\right)^2 \\ &= \frac{\pi}{4}(d_A^2 + 2d_A d_B + d_B^2) \\ &= \frac{1}{4}(\sigma_A + 2\sqrt{\sigma_A\sigma_B} + \sigma_B) \\ &= \frac{1}{2}\left[\left(\frac{\sigma_A + \sigma_B}{2}\right) + \sqrt{\sigma_A\sigma_B}\right]\end{aligned}$$

which, interestingly, is an average of the two types of averages of the two individual cross sections, the arithmetic and geometric averages!

2.11.3: Average collision Frequency

Consider a system of particles with individual cross sections σ. A particle of cross section σ that moves a distance l in a time Δt will sweep out a cylindrical volume (ignoring the spherical caps) of volume σl (Figure 27.6.1). If the system has a number density ρ, then the number of collisions that will occur is

$$N_{\text{coll}} = \rho\sigma l$$

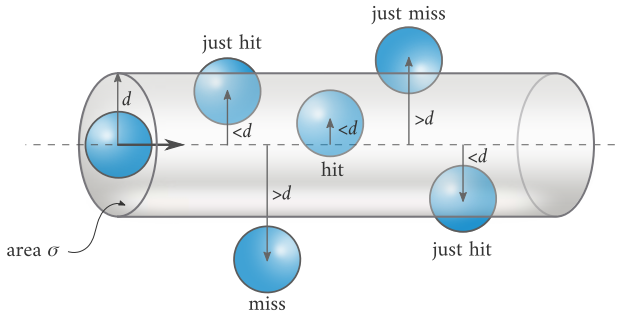


Figure 27.6.1 : Collision cylinder. Any particle that partially overlaps with this volume will experience a collision with a test particle tracing out this volume. (CC BY-NC; Ümit Kaya)

We define the collision frequency for a single molecule, z_A, also known as the average collision rate as $N_{\text{coll}}/\Delta t$, i.e.,

$$z_A = \frac{N_{\text{coll}}}{\Delta t} = \frac{\rho\sigma l}{\Delta t} = \rho\sigma\langle v\rangle \tag{2.11.2}$$

where $\langle v\rangle$ is the average speed of a particle

$$\langle v\rangle = \sqrt{\frac{8k_BT}{\pi m_A}}$$

Equation 2.11.2 is not quite correct because it is based on the assumption that only the molecule of interest is moving. If we take into account the fact that all of the particles are moving relative to one another, and assume that all of the particles are of the same type (say, type A), then performing the average over a Maxwell-Boltzmann speed distribution gives

$$\langle v_r\rangle = \sqrt{\frac{8k_BT}{\pi\mu}}$$

where $\mu = m_A/2$ is the reduced mass.

Thus,

$$\langle v_r \rangle = \sqrt{2}\langle v \rangle$$

and

$$z_A = \sqrt{2}\rho\sigma\langle v \rangle \ = \rho\sigma\langle v_r \rangle$$

The reciprocal of z_A is a measure of the average time between collisions for a single molecule.

2.11.4: Mean Free Path

The mean free path is the distance a particle will travel, on average, before experiencing a collision event. This is defined as the product of the average speed of a particle and the time between collisions. The former is $\langle v \rangle$, while the latter is $1/z_A$. Hence, we have

$$\lambda = \frac{\langle v \rangle}{\sqrt{2}\rho\sigma\langle v \rangle} = \frac{1}{\sqrt{2}\rho\sigma}$$

The mean free path can also be described using terms from the ideal gas law, because $\rho = \frac{P \cdot N_A}{R \cdot T}$:

$$\lambda = \frac{R \cdot T}{\sqrt{2} \cdot N_A \cdot \sigma \cdot P}$$

2.11.5: Random Walks

In any system, a particle undergoing frequent collisions will have the direction of its motion changed with each collision and will trace out a path that appears to be random. In fact, if we treat the process as statistical, then, we are, in fact, treating each collision event as a random event, and the particle will change its direction at random times in random ways! Such a path might appear as shown in Figure **2.11.2**. Such a path is often referred to as a *random walk path*.

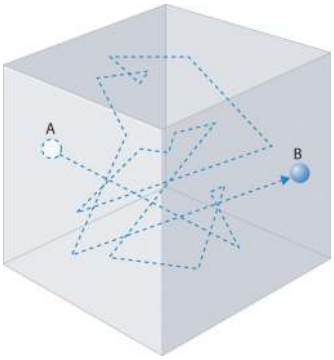


Figure **2.11.2**: Random walk path. The Path of a Single Particle in a Gas Sample. The frequent changes in direction are the result of collisions with other gas molecules and with the walls of the container.

In order to analyze such paths, let us consider a random walk in one dimension. We'll assume that the particle move a mean-free path length λ between collisions and that each collision changes the direction of the particles motion, which in one dimension, means that the particle moves either to the right or to the left after each event. This can be mapped onto a metaphoric "coin toss" that can come up heads "H" or tails "T", with "H" causing motion to the right, and "T" causing motion to the left. Let there be N such coin tosses, let i be the number of times "H" comes up and j denote the number of times "T" comes up. Thus, the progress of the particle, which we define as net motion to the right, is given by $(i-j)\lambda$. Letting $k = i - j$, this is just $k\lambda$. Thus, we need to know what the probability is for obtaining a particular value of k in a very large number N of coin tosses. Denote this $P(k)$.

In N coin tosses, the total number of possible sequences of "H" and "T" is 2^N. However, the number of ways we can obtain i heads and \)j\) tails, with $i + j = N$ is a binomial coefficient $N!/i!j!$. Now

$$j = N - i = N - (j + k) = N - j - k$$

so that $j = (N - k)/2$. Similarly,

$$i = N - j = N - (i - k) = N - i + k$$

so that $i = (N + k)/2$. Thus, the probability $P(k)$ is

$$P(k) = \frac{N!}{2^N i! j!} = \frac{1}{2^N} \frac{N!}{\left(\frac{N+k}{2}\right)! \left(\frac{N-k}{2}\right)!}$$

We now take the logarithm of both sides:

$$\ln P(k) = \ln N! - \ln 2^N - \ln \left(\frac{N+k}{2}\right)! - \ln \left(\frac{N-k}{2}\right)!$$

and use Stirling's approximation:

$$\ln N! \approx N \ln N - N$$

and write $\ln P(k)$ as

$$\begin{aligned}
\ln P(k) &\approx N \ln N - N - N \ln 2 - \frac{1}{2}(N+k) \ln \frac{1}{2}(N+k) + \frac{1}{2}(N+k) \\
&\quad - \frac{1}{2}(N-k) \ln \frac{1}{2}(N-k) + \frac{1}{2}(N-k) \\
&= N \ln N - N \ln 2 + \frac{1}{2}(N+k) \ln \frac{1}{2} - \frac{1}{2}(N+k) \ln (N+k) \\
&\quad - \frac{1}{2}(N-k) \ln \frac{1}{2} - \frac{1}{2}(N-k) \ln (N-k) \\
&= N \ln N - N \ln 2 + \frac{1}{2}(N+k) \ln 2 - \frac{1}{2}(N+k) \ln (N+k) + \frac{1}{2}(N-k) \ln 2 \\
&\quad - \frac{1}{2}(N-k) \ln (N-k) \\
&= N \ln N - \frac{1}{2} \left[(N+k) \ln (N+k) + (N-k) \ln (N-k)\right]
\end{aligned}$$

Now, write

$$\ln (N+k) = \ln N \left(1 + \frac{k}{N}\right) = \ln N + \ln \left(1 + \frac{k}{N}\right)$$

and

$$\ln (N-k) = \ln N \left(1 - \frac{k}{N}\right) = \ln N + \ln \left(1 - \frac{k}{N}\right)$$

We now use the expansions

$$\begin{aligned}
\ln \left(1 + \frac{k}{N}\right) &= \left(\frac{k}{N}\right) - \frac{1}{2}\left(\frac{k}{N}\right)^2 + \cdots \\
\ln \left(1 - \frac{k}{N}\right) &= -\left(\frac{k}{N}\right) - \frac{1}{2}\left(\frac{k}{N}\right)^2 + \cdots
\end{aligned}$$

If we stop at the second-order term, then

$$\begin{aligned}
\ln P(k) &= N \ln N - \frac{1}{2}(N+k) \left[\ln N + \left(\frac{k}{N}\right) - \frac{1}{2}\left(\frac{k}{N}\right)^2\right] \\
&\quad - \frac{1}{2}(N-k) \left[\ln N - \left(\frac{k}{N}\right) - \frac{1}{2}\left(\frac{k}{N}\right)^2\right] \\
&= -\frac{1}{2}(N+k) \left[\left(\frac{k}{N}\right) - \frac{1}{2}\left(\frac{k}{N}\right)^2\right] + \frac{1}{2}(N-k) \left[\left(\frac{k}{N}\right) + \frac{1}{2}\left(\frac{k}{N}\right)^2\right] \\
&= \frac{1}{2} N \left(\frac{k}{N}\right)^2 - k \left(\frac{k}{N}\right) \\
&= \frac{k^2}{2N} - \frac{k^2}{N} = -\frac{k^2}{2N}
\end{aligned}$$

so that

$$P(k) = e^{-k^2/2N}$$

Now, if we let $x = k\lambda$ and $L = \sqrt{N}\lambda$, and if we let x be a continuous random variable, then the corresponding probability distribution $P(x)$ becomes

$$P(x) = \frac{1}{L\sqrt{2\pi}}\, e^{-x^2/2L^2} = \frac{1}{\sqrt{2\pi N\lambda^2}}\, e^{-x^2/2N\lambda^2} \tag{2.11.3}$$

which is a simple Gaussian distribution. Now, N is the number of collisions, which is given by $z_A t$, so we can write the probability distribution for the particle to diffuse a distance x in time t as

$$P(x,t) = \frac{1}{\sqrt{2\pi z_A t\lambda^2}}\, e^{-x^2/2z_A t\lambda^2}$$

Define $D = z_A\lambda^2/2$ as the *diffusion constant*, which has units of (length)^2/time. The distribution then becomes

$$P(x,t) = \frac{1}{\sqrt{4\pi Dt}}\, e^{-x^2/4Dt}$$

Note that this distribution satisfies the following equation:

$$\frac{\partial}{\partial t}P(x,t) = D\frac{\partial^2}{\partial x^2}P(x,t)$$

which is called the diffusion equation. The diffusion equation is, in fact, more general than the Gaussian distribution in Equation 2.11.3. It is capable of predicting the distribution in any one-dimensional geometry subject to any initial distribution $P(x,0)$ and any imposed boundary conditions.

In three dimensions, we consider the three spatial directions to be independent, hence, the probability distribution for a particle to diffuse to a location $\mathbf{r} = (x,y,z)$ is just a product of the three one-dimensional distributions:

$$\mathcal{P}(\mathbf{r}) = P(x)\,P(y)\,P(z) = \frac{1}{(4\pi Dt)^{3/2}}\, e^{-(x^2+y^2+z^2)/4Dt}$$

and if we are only interested in diffusion over a distance r, we can introduce spherical coordinates, integrate over the angles, and we find that

$$P(r,t) = \frac{4\pi}{(4\pi Dt)^{3/2}}\, e^{-r^2/4Dt}$$

2.11.6: Total collision frequency per unit volume

In equation 27.6.18, z_A represents the collision frequency for one specific molecule in a gas sample. If we wish to calculate the total collision frequency per unit volume, the number density of the molecules, ρ, must be taken into account. The total collision frequency in a sample that contains only A molecules, Z_{AA}, is

$$Z_{AA} = \frac{1}{2}\rho z_A = \frac{1}{2}\sigma\langle v_r\rangle\rho^2 = \frac{\sigma\langle v\rangle\rho^2}{\sqrt{2}}$$

The factor of $\frac{1}{2}$ must be included to avoid double counting collisions between similar molecules. (This is identical reasoning to the fact that there is only one way to roll double 3 with two dice.)

If you have a gas sample that contains A molecules and B molecules, then

$$Z_{AB} = \sigma_{AB}\langle v_r\rangle\rho_A\rho_B \tag{2.11.4}$$

where

$$\sigma_{AB} = \pi\left(\frac{d_A + d_B}{2}\right)^2 \text{ and } \langle v_r\rangle = \sqrt{\frac{8k_BT}{\pi\mu}}$$

Example 2.11.1

Calculate the frequency of hydrogen-hydrogen collisions in a 1.00 cubic centimeter container at 1.00 bar and 298 K.

Solution

The collisional frquency requires knowledge of (1) the number denisty, the average speed (Equation 2.11.4).

The value of σ_{H_2} is 2.30 x 10^{-19} m^2.

The number density:

$$\rho = \left(\frac{N_A P_{H_2}}{RT}\right) = \left(\frac{(6.022x10^{23} mole^{-1})(1.00\ \text{bar})}{(0.08314 L \cdot bar \cdot mol^{-1} \cdot K^{-1})(298 K)}\right)$$
$$= 2.43 \times 10^{22} L^{-1} = 2.43 \times 10^{25} m^{-3}$$

The average speed:

$$\langle \text{v} \rangle = \sqrt{\frac{8\text{R T}}{\pi \text{M}}} = \sqrt{\left(\frac{8(8.314 J \cdot K^{-1})(298 K)}{\pi(0.002016 kg)}\right)} = 1770 \frac{m}{s}$$

These are substituted into Equation 2.11.4 to get the collisional frequency

$$Z_{H_2,H_2} = \frac{(2.30x10^{-19} m^2)(1770 \frac{m}{s})(2.43x10^{25} m^{-3})^2}{\sqrt{2}}$$
$$= 1.7x10^{35} s^{-1} m^{-3}$$
$$= 1.7 \times 10^{29} s^{-1} cm^{-3}$$

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2.12: Rates of Gas-Phase Chemical Reactions

Now that we have a description of how often gas molecules will collide with one another, we can make an initial attempt to describe how the collision of gas molecules can lead to reactions between the molecules. This topic will be covered in much more detail in Chapter 30.

2.12.1: Collision Frequency, Collision Energy, and Effective Collisions

In example 27.6.1, we calculated that the number of collision between H_2 molecules at one bar and 25ºC is around $10^8 \ \frac{\text{moles}}{\text{dm}\cdot\text{s}}$. Consider the elementary reaction

$$\text{A} + \text{B} \longrightarrow \text{C}$$

If all of the collisions between A and B resulted in a reaction, then the rate of the reaction would be about $10^8 \ \frac{\text{moles}}{\text{dm}\cdot\text{s}}$. We know from experiment that most chemical reactions do not occur this quickly. It must be true, then, that not all collisions result in a reaction. It is intuitive that molecules traveling at faster speeds should be more likely to react because they have sufficient energy to overcome electronic repulsions, and to break existing bonds.

One way to approach this estimate is to use a modified version of the equation for the collision frequency with a wall. The reason for starting with this equation is that it is reasonable to assume that the faster a molecule is traveling, the more likely it is to hit the wall. If this is so, then the faster a molecule is traveling, the more likely it is to collide with other molecules so as to react.

Recall equation 26.4.1

$$z_w = \frac{1}{4}\frac{N}{V}\langle v \rangle$$

which can be rewritten for the molecular level by substituting ρ for $\frac{N}{V}$

$$z_w = \frac{1}{4}\rho\langle v \rangle$$

This equation was obtained by carrying out the integration

$$z_w = \frac{\rho}{4\pi}\int_0^\infty vF(v)dv \int_0^{\pi/2} \cos\theta \sin\theta d\theta \int_0^{2\pi} d\phi \tag{2.12.1}$$

which takes into account the fact that molecules will only hit the wall from one direction.

Recall from equation 27.3.1, the Maxwell-Boltzmann distribution of speeds

$$f(v) = 4\pi v^2 \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(\frac{-mv^2}{2k_B T}\right)$$

that $f(v)$ has a factor of v^2. Thus, equation 2.12.1 has a factor of v^3, meaning that the molecules colliding with the wall are traveling faster than the molecule in the bulk of the sample. The assumption is that the faster molecules are more likely to hit the wall in a given amount of time.

We must modify equation 2.12.1 to take into account the collision of molecules with each other, rather than with the wall. This is done by replacing the mass of a single molecule m with the reduced mass of the two colliding molecules μ. The resulting speed is the relative average speed v_r. The result of these assumptions is that the collision frequency of molecules A and B per unit volume in which the molecules collide with a relative speed between v_r and $v_r + dv_r$ is

$$dZ_{AB} = Av_r^3 e^{-\mu v_r^2/2k_B T} dv_r \tag{2.12.2}$$

where A is a proportionality constant.

If we require the integral of this equation over all relative speeds to be equal to Z_{AB}, then

$$Z_{AB} = \sigma_{AB}\rho_A\rho_B \left(\frac{8k_B T}{\pi\mu}\right)^{1/2} = A\int_0^\infty v_r^3 e^{-\mu v_r^2/2k_B T} dv_r$$

$$Z_{AB} = \sigma_{AB}\rho_A\rho_B\left(\frac{8k_BT}{\pi\mu}\right)^{1/2} = 2A\left(\frac{k_BT}{\mu}\right)^2$$

Rearranging to solve for A gives

$$A = \sigma_{AB}\rho_A\rho_B\left(\frac{\mu}{k_BT}\right)^{3/2}\left(\frac{2}{\pi}\right)^{1/2} \tag{2.12.3}$$

Substituting equation 2.12.3 into equation 2.12.2 gives

$$dZ_{AB} = \sigma_{AB}\rho_A\rho_B\left(\frac{\mu}{k_BT}\right)^{3/2}\left(\frac{2}{\pi}\right)^{1/2} v_r^3 e^{-\mu v_r^2/2k_BT} dv_r$$

With this equation, we can describe the collision frequency per unit volume between A molecules and B molecules with relative speeds in the range of v_r and $v_r + dv_r$. In this equation, the portion

$$\left(\frac{\mu}{k_BT}\right)^{3/2}\left(\frac{2}{\pi}\right)^{1/2} v_r^3 e^{-\mu v_r^2/2k_BT} dv_r$$

which is $v_r f(v_r) dv_r$, is the probability that the relative speed of the molecules will fall between v_r and $v_r + dv_r$.

Contributors and Attributions

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2.E: The Kinetic Theory of Gases (Exercises)

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CHAPTER OVERVIEW

3: Properties of Liquids

Ensemble properties result from being or relating to the greater in number of atoms in a sample. This are in contrast to atomic or molecular properties.

3.1: Capillary Action
3.2: Cohesive and Adhesive Forces
3.3: Contact Angles
3.4: Surface Tension
3.5: Unusual Properties of Water
3.6: Vapor Pressure
3.7: Viscosity
3.8: Wetting Agents

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3.1: Capillary Action

Capillary action can be defined as the ascension of liquids through slim tube, cylinder or permeable substance due to adhesive and cohesive forces interacting between the liquid and the surface. When intermolecular bonding of a liquid itself is substantially inferior to a substances' surface it is interacting, capillarity occurs**.** Also, the diameter of the container as well as the gravitational forces will determine amount of liquid raised. While, water possesses this unique property, a liquid like mercury will not display the same attributes due to the fact that it has higher cohesive force than adhesive force.

Forces in Capillary Action

Three main variables that determine whether a liquid possesses capillary action are:

- **Cohesive force**: It is the intermolecular bonding of a substance where its mutual attractiveness forces them to maintain a certain shape of the liquid.
- **Surface tension**: This occurs as a result of like molecules, cohesive forces, banding together to form a somewhat impenetrable surface on the body of water. The surface tension is measured in Newton/meter.
- **Adhesive force**: When forces of attraction between unlike molecules occur, it is called adhesive forces.

Capillary action only occurs when the adhesive forces are stronger than the cohesive forces, which invariably becomes surface tension, in the liquid.

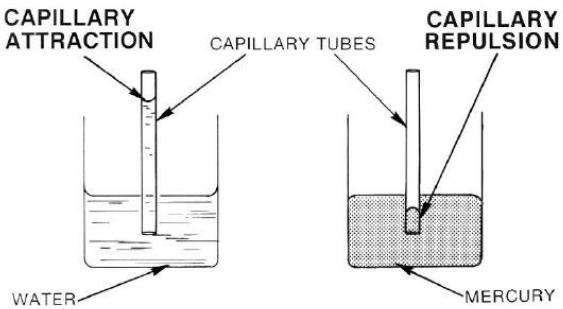


Figure **3.1.1**: It is possible to see that in water, the strength of the adhesive forces are larger than the strength of the cohesive forces. This results in the concave formation of water in the capillary tube; this is known as capillary attraction. Alternatively for mercury, the cohesive forces are stronger than the adhesive forces which allows the the meniscus to bend away from the walls of the capillary tube. This is known as capillary Repulsion. commons.wikimedia.org/wiki/Fi...(PSF)(bjl).svg

A good way to remember the difference between adhesive and cohesive forces is that with *ad*hesive forces you *add* another set of molecules, the molecules of the surface, for the liquid to bond with. With *co*hesive forces, the molecules of the liquid will only *co*operate with their own kind. Decreased surface tension also increases capillary action. This is because decreased surface tension means that the intermolecular forces are decreased, thus decreasing cohesive forces. As a result, capillary action will be even greater.

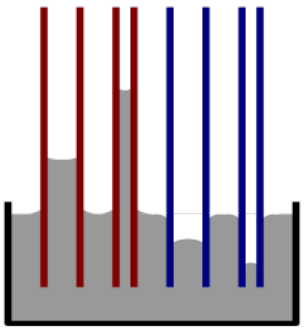


Figure **3.1.2**: Scalable illustration of capillary action for large and small bore capillaries, and for positive and negative contact angles. (Public Domain; Eduard Konečný via Wikipedia).

Applications

Practical use of capillary action is evident in all forms of our daily lives. It makes performing our tasks efficiently and effectively. Some applications of this unique property include:

- The fundamental properties are used to absorb water by using paper towels. The cohesive and adhesive properties draw the fluid into the paper towel. The liquid flows into the paper towel at a certain rate.
- A technique called thin layer chromatography uses capillary action in which a layer of liquid is used to separate mixtures from substances.
- Capillary action helps us naturally by pumping out tear fluid in the eye. This process cleanses the eye and clears all of the dust and particles that are around the ducts of the eye.
- To generate energy: A possible use for capillary action is as a source of renewable energy. By allowing water to climb through capillaries, evaporate once it reaches the top, the condensate and drop back down to the bottom spinning a turbine on its way to create the energy, capillary action can make electricity! Although this idea is still in the works, it goes to show the potential that capillary action holds and how important it is.



Figure **3.1.3**: Capillary action is evident in nature all around us. The properties allow the water to be transpired by the xylem in the plant. The water starts in the roots and proceeds upward to the highest branches of the plant. commons.wikimedia.org/wiki/File:GemeineFichte.jpg

When measuring the level of liquid of a test tube or buret, it is imperative to measure at the meniscus line for an accurate reading. It is possible to measure the height (represented by h) of a test tube, buret, or other liquid column using the formula:

$$h = \frac{2\gamma \cos\theta}{\rho\, g\, r} \tag{3.1.1}$$

In this formula,

- γ represents the surface tension in a liquid-air environment,
- θ is the angle of contact or the degree of contact,
- ρ is the density of the liquid in the representative column,
- g is the acceleration due to the force of gravity and
- r is the radius of the tube in which the liquid is presented in.

At optimum level, in which a glass tube filled with water is present in air, this formula can determine the height of a specific column of water in meters (m):

$$h \approx \frac{1.4 \times 10^{-5}}{r} \tag{3.1.2}$$

However, the following conditions must be met for this formula to occur.

- $\gamma = 0.0728$ N/m (when water is at a temperature of 20°C)
- $\theta = 20°$
- $\rho$is 1000 kg/m^3
- $g = 9.8$ m/s^2

Formula for Volume of Liquid Transport in Medium:

When certain objects that are porous encounter a liquid medium, it will begin to absorb the liquid at a rate which actually decreases over a period of time. This formula is written as:

$$V = S * A\sqrt{t} \tag{3.1.3}$$

In this specific formula,

- A is the wet area (cross-section),
- S is the sorptivity (capacity of medium to absorb using the process of capillary action),
- V is the volume of liquid absorbed in time, t.

Questions

1. Name one way to increase capillary action, and one way to decrease it.
2. If cohesion is greater than adhesion, will the meniscus be convex or concave?
3. What would be the height of a liquid in a column, on earth, with a liquid-air surface tension 0f .0973 N/m, contact angle of 30 degrees, density of 1200 kg/m^3? Note that the radius of the tube is 0.2 meters.
4. What would be the height of water in a glass tube with a radius of .6mm?

Solutions

1. Increase capillary action: Increase temperature, decrease capillary tube diameter, perform any number of actions to decrease surface tension, etc…! Decrease capillary action: The opposite of the steps you would take to increase, also, increasing the density of the liquid you're working with.
2. The meniscus will result in a convex formation.
3. Using the formula above, the height of the liquid will be 7.165* 10^{-5}m high.
4. Using the formula above, the height of the water in the glass tube would be .014m high.

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3.2: Cohesive and Adhesive Forces

Cohesive and adhesive forces are associated with bulk (or macroscopic) properties, and hence the terms are not applicable to the discussion of atomic and molecular properties. When a liquid comes into contact with a surface (such as the walls of a graduated cylinder or a tabletop), both cohesive and adhesive forces will act on it. These forces govern the shape which the liquid takes on. Due to the effects of adhesive forces, liquid on a surface can spread out to form a thin, relatively uniform film over the surface, a process known as wetting. Alternatively, in the presence of strong cohesive forces, the liquid can divide into a number of small, roughly spherical beads that stand on the surface, maintaining minimal contact with the surface.

Adhesive and Cohesive Forces

The term "cohesive forces" is a generic term for the collective intermolecular forces (e.g., hydrogen bonding and van der Waals forces) responsible for the bulk property of liquids resisting separation. Specifically, these attractive forces exist between molecules of the *same* substance. For instance, rain falls in droplets, rather than a fine mist, because water has strong cohesion, which pulls its molecules tightly together, forming droplets. This force tends to unite molecules of a liquid, gathering them into relatively large clusters due to the molecules' dislike for its surroundings.

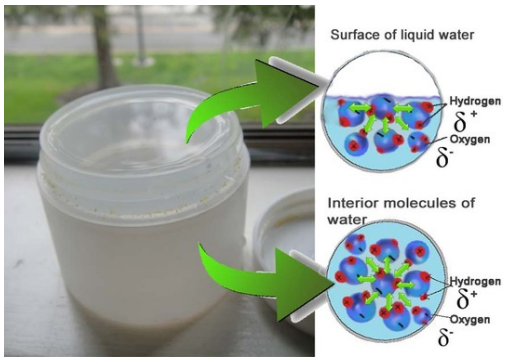
Similarly, the term "adhesive forces" refers to the attractive forces between unlike substance, such as mechanical forces (sticking together) and electrostatic forces (attraction due to opposing charges). In the case of a liquid wetting agent, adhesion causes the liquid to cling to the surface on which it rests. When water is poured on clean glass, it tends to spread, forming a thin, uniform film over the glasses surface. This is because the adhesive forces between water and glass are strong enough to pull the water molecules out of their spherical formation and hold them against the surface of the glass, thus avoiding the repulsion between like molecules.

Macroscopic Effects of Cohesive and Adhesive Forces

When a liquid is placed on a smooth surface, the relative strengths of the cohesive and adhesive forces acting on that liquid determine the shape it will take (and whether or not it will wet the surface). If the adhesive forces between a liquid and a surface are stronger, they will pull the liquid down, causing it to wet the surface. However, if the cohesive forces among the liquid itself are stronger, they will resist such adhesion and cause the liquid to retain a spherical shape and bead the surface.

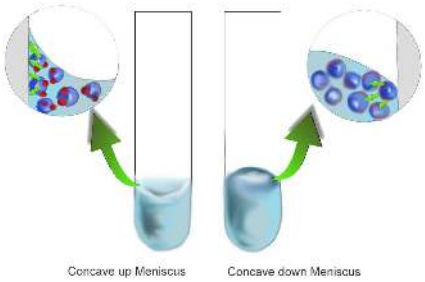
Case I: The Meniscus

The meniscus is the curvature of a liquid's surface within a container, such as a graduated cylinder. However, before we explain why some liquid have a concave up meniscus while others share a concave down meniscus, we have to understand the adhesive forces at work of surface tension. Water, for example, is a polar molecule that consists of a partial positive charge on the hydrogens and a partial negative charge on the oxygen. Thus, within liquid water, each molecule's partial positive charge is attracted to its neighbor's partial negative charge. This is the origin of the cohesive forces within the water. Water molecules buried inside the liquid is then being pulled and pushed evenly in every direction, producing no net pull. Meanwhile, the molecules on the surface of the liquid, lacking pulling forces in the upward direction, thus encompass a net downward pull.



How does this cohesive force create both a concave up and concave down surface then? The answer is in its relationship to the adhesive forces between the water molecules and the container's surface. When the cohesive force of the liquid is stronger than the adhesive force of the liquid to the wall, the liquid concaves down in order to reduce contact with the surface of the wall. When the

adhesive force of the liquid to the wall is stronger than the cohesive force of the liquid, the liquid is more attracted to the wall than its neighbors, causing the upward concavity.



Case II: Tears of Wine

In agitated glasses of wine, droplets of wine seemingly "float" above the meniscus of the liquid and form "tears." This age-old phenomenon is the result of surface tension and cohesive and adhesive forces. Alcohol is more volatile than water. As a result, "evaporation of alcohol produces a surface tension gradient driving a thin film up along the side of a wine glass" (Adamson). This process is called the "solutal Marangoni effect."[2] Due to adhesive forces, some waters clings to the walls of the glass. The "tears" form from the cohesive forces within the water holding it together. It is important to note that the surface tension gradient is "the driving force for the *motion* of the liquid" (Gugliotti), but the actual formation of the tears is a result of cohesive and adhesive forces.



The "tears of wine" are observed as a ring of clear liquid, near the top of a glass of wine, from which droplets continuously form and drop back into the wine. It is most readily observed in a wine which has a high alcohol content. (CC BY-SA-NC; Greg Emel)

Problems

1. Name two examples where the cohesive force dominates over the adhesive force and vice versa.
2. When in a glass graduated cylinder, water presents an upwardly concave meniscus. However, when water is filled to the tip of the cylinder, the water level could maintain higher than the wall of the cylinder without pouring out resembling a concave down meniscus. Use the principles of cohesive and adhesive forces to explain this situation.
3. Explain why a water strider can glide on the water with the knowledge of cohesion in water.
4. Propose different types of forces that adhesive forces can build on.

Answers

1. When cohesive force is stronger than the adhesive force: concave up meniscus, water forms droplets on the surface. When adhesive force is stronger than the cohesive force: concave down meniscus, the surfaces are covered by the wetting agent, the last drops of liquid in the bottle always refuse to come out.
2. Since water forms a concave up meniscus, the adhesion of the molecules to the glass is stronger than the cohesion among the molecules. However, in the absence of the adhesive force (when water reaches the tip of the glass), the cohesive force remains present. Thus cohesive force alone proves that it can still hold itself in place without pouring out of the cylinder. This example emphasizes the importance of that cohesive force and adhesive forces do not simply cancel each other out, yet it is the difference between the two that determines the characteristic of the liquid.

3. This problem addresses once again the concept of surface tension. Because the cohesion of the water is built on the weak intermolecular forces of the water, when a water strider stepson to the surface, an extra energy will be necessary to overcome to break those bonds to increase surface area. Moreover, since the gravitational pull down on the water strider cannot overcome the activation energy to break these intermolecular forces, the water strider is able to glide freely on the water.
4. Complementary shape, chemical bonds form, weak intermolecular forces such as H-bonding or Van der Waals forces.

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3.3: Contact Angles

Contact angle is one of the common ways to measure the wettability of a surface or material. Wetting refers to the study of how a liquid deposited on a solid (or liquid) substrate spreads out or the ability of liquids to form boundary surfaces with solid states. The wetting, as mentioned before is determined by measuring the contact angle, which the liquid forms in contact with the solids or liquids. The wetting tendency is larger, the smaller the contact angle or the surface tension is. A wetting liquid is a liquid that forms a contact angle with the solid which is smaller then 90º. A non-wetting liquid creates a contact angle between 90º and 180º with the solid.

Introduction

The contact angle is an angle that a liquid creates with a solid surface or capillary walls of a porous material when both materials come in contact together. This angle is determined by both properties of the solid and the liquid and the interaction and repulsion forces between liquid and solid and by the three phase interface properties (gas, liquid and solid). Those interactions are described by cohesion and adhesion forces which are intermolecular forces. The balance between the cohesive forces of similar molecules such as between the liquid molecules (i.e., hydrogen bonds and Van der Waals forces) and the adhesive forces between dissimilar molecules such as between the liquid and solid molecules (i.e., mechanical and electrostatic forces) will determine the contact angle created in the solid and liquid interface. The traditional definition of a contact angle is the angle a liquid creates with the solid or liquid when it is deposited on it. A less traditional definition is the angle a liquid creates with the sides of a capillary when it rises in it to create a meniscus.

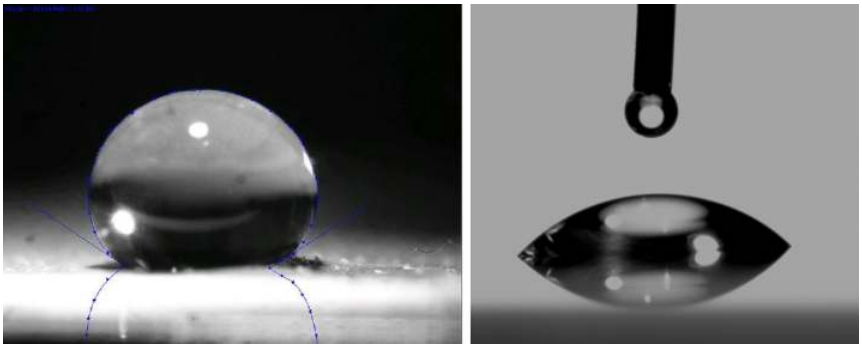


Figure **3.3.1**: Images used with permission from Wikipedia

- The smaller the contact angle - cohesive forces are weaker then adhesive forces and molecules of the liquid tend to interact more with solid molecules then liquid molecules.
- The larger the contact angle - cohesive forces are stronger then adhesive forces and the molecules of the liquid tend to interact more with each other then with the solid molecules.

Thermodynamics

Thomas Young (13 June 1773 – 10 May 1829) proposed treating the contact angle of a liquid with a surface as the mechanical equilibrium of a drop resting on a plane solid surface under the restrains of three surface tensions:

- γ_{lv} (at the interface of the liquid and vapor phases),
- γ_{sl} (at the interface of the solid and liquid phases) and
- γ_{sv} (at the interface of the solid and vapor phase). This lead to *Young's equation*:

$$\gamma_{sv} - \gamma_{sl} = \gamma_{lv} \cos\theta \tag{3.3.1}$$

This equation is deceptively simple, but there are a few difficulties with it because of the definitions of the surface tension of the solid-vapor and solid liquid phases.

Another approach avoids specifying the field of intermolecular forces between solid and liquid and instead offers a thermodynamic solution. This lead to Young and Dupre' equation which introduces the reversible work of adhesion of liquid and solid and it's relation to the surface tension between liquid and vapor phases and the contact angle:

$$W_{sl}^{adh} = \gamma_{lv}(1 + \cos\theta) \tag{3.3.2}$$

Where WA is the reversible work of adhesion of the liquid to the solid when coated with an adsorbed film of the saturated vapor.

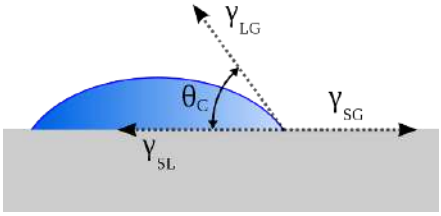


Figure **3.3.2**: Contact action for the wetting of a surface

Less Traditional Definition

Capillarity is the ability of a substance to draw another substance into it and It occurs when the adhesive intermolecular forces between the liquid and a substance are stronger than the cohesive intermolecular forces inside the liquid. The effect causes a concave meniscus to form where the substance is touching a vertical surface (Figure **3.3.3**). The same effect is what causes porous materials to soak up liquids. Capillary forces pull a wetting liquid has a low contact angle with the surface, it wets the surface. Assuming that there are no other factors involved (e.g. roughness), a low contact angle with water means that the surface is hydrophilic. A completely wetting liquid forms a zero contact angle into a capillary by creating a curved meniscus at the rising liquid front. This phenomenon can be described with the *Young-Laplace equation* and the Laplace pressure inside a capillary.

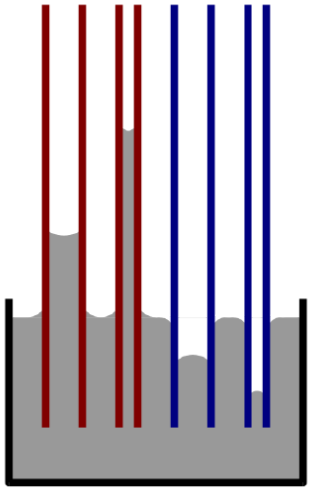


Figure **3.3.3**: Illustration of capillary rise and contact angle in a capillery. Red=contact angle less than 90°; blue=contact angle greater than 90°. (Public Domain; Eduard Konečný).

Measuring methods

Many measuring methods have been described in the literature but only a few of them have been found to be widely applicable.

The Sessile Drop Method

The most frequently used is the goniometer-telescope measurement of sessile-drop contact angles. Commercial contact angle goniometers employ a microscope objective to view the angle directly. In the static method a drop is deposited on a surface and the contact angle can be measured by looking at the drop through a goniometer (an instrument that measures contact angles). The dynamic method is similar to the static one but the drop of liquid which is deposited on a surface is modified. The droplet is being deposited via a syringe and the droplet's volume is changed dynamically without increasing its solid-liquid interface area and this maximum angle is the advancing angle. Volume is then removed to produce the smallest possible angle, which is called the receding angle. The difference between those two measured angles is called contact *angle hysteresis*.

Wilhelmy Plate Method

The capillary rise on a Wilhelmy plate is a good way to obtain the contact angle by measuring the height of the meniscus created on a partially immersed plate. The contact angle is obtained directly form the height trough:

$$\sin(\theta) = 1 - \rho g h^2 / 2\gamma \tag{3.3.3}$$

where:

- h – height of the meniscus created
- γ - surface tension of the tested liquid (N/m)
- ρ - density of the tested liquid (kg/m^3)
- θ - contact angle of the liquid on the solid (°)
- g – gravitational acceleration = 9.8 m/s^2

Capillary Rise

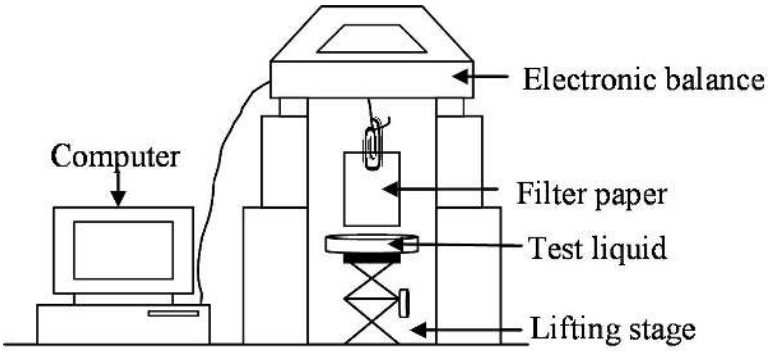
The common direct measurement of contact angles of a liquid drop on a flat and smooth solid is not applicable to powders and dry porous foods. The common method of measuring the contact angle in capillary rise in porous media is by using the Lucas-Washburn's equation which is derived from Poiseulle's law of liquid flow in capillary rise:

$$h^2 = rc\left(\frac{\gamma \cos\theta}{2\eta}\right) t \tag{3.3.4}$$

$$w^2 = c\left(\frac{\rho^2 \gamma \cos\theta}{\eta}\right) t \tag{3.3.5}$$

where:

- h – height of the rising liquid
- w – weight gain of the sample (caused by the water absorbed into it)
- γ - surface tension of the tested liquid (N/m)
- ρ - density of the tested liquid (kg/m^3)
- θ - contact angle of the liquid on the solid (°)
- r- mean static radius of the pores (m)
- η - liquid viscosity (Pa s)
- c - geometric factor (m^5)



The common method to measure the contact angles in this case is to conduct capillary rise experiments where your sample is hang bellow a balance and you dip it in the tested liquid. The main deficiency of this approach (using Washburn's equation) is its inability to separate between those two variables (r and $\cos\theta$ or c and $\cos\theta$). The common method to overcome the problem of the unknown term $r \bullet \cos(\theta)$ is by using a reference liquid that completely wets the sample (θ=0, cos(θ)=1). It was discovered however that dynamic advancing contact angle is generally larger than the static one, even for a total wetting liquid and as a result this method can be erroneous.

Seibold et al, (2000) suggested a way to overcome this problem. It was observed that this constant term varies as a function of the liquid used, in contradiction with the Washburn approach which uses Hexane as a completely wetting liquid in order to find the radius of the pores. In this study, it was proposed to get the actual constant term r in Washburn equation by plotting the measured

value r cos θ versus the rate of rise of the alkanes (the slope in Equations 3.3.4 and 3.3.5). The intercept at zero velocity gives the value of r. Siebold el al. (2000) carried out capillary rise experiments with different n-alkanes, which are all considered completely wetting, due to their low surface tension. In each case, a linear relationship was obtained between squared height of the rising liquid and time, their results of the term $r \bullet \cos(\theta)$ were calculated from the slopes of those curves. This finding was transformed into a method to calculate or measure the contact angle at zero velocity. Siebold et al. (2000) suggested that for porous media the term r•cos(θ) for each alkane (the term was calculated from Washburn equation) can be plotted against the initial front rate of each liquid. The curve that was created can be extrapolated to velocity zero (and therefore, cos(θ)=1) and this enables the determination of the representative radius r. After finding r, which is a property of the solid sample and doesn't change as a function of the liquids used, we can conduct capillary rise experiment with our test liquid and calculate the contact angles this liquid creates with the solid porous sample.

Applications

The interest in contact angles is because it plays a significant role in a number of technological, environmental and biological phenomena. Water imbibition into porous media theory has been shown to have a multidisciplinary validity in food, soil physics, geology, printings and more. Imbibition of a liquid by a porous solid is a phenomenon highly dependent on wetting. Capillary imbibition is a mechanism that plays a significant role during rehydration of dry food particles that are considered as porous media. Imbibition is highly dependent on the wettability of the porous media, which is usually determined by measuring contact angles which liquids form with the solid.

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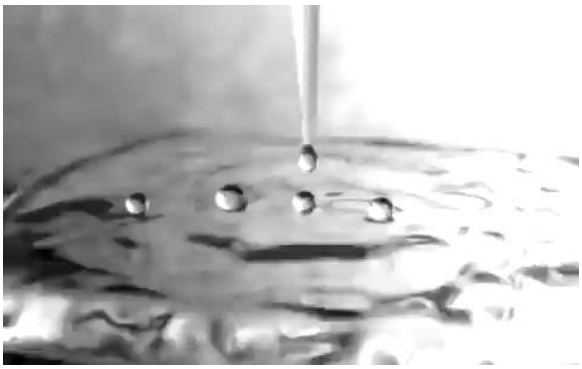
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3.4: Surface Tension

Surface tension is the energy, or work, required to increase the surface area of a liquid due to intermolecular forces. Since these intermolecular forces vary depending on the nature of the liquid (e.g. water vs. gasoline) or solutes in the liquid (e.g. surfactants like detergent), each solution exhibits differing surface tension properties. Whether you know it or not, you already have seen surface tension at work. Whenever you fill a glass of water too far, you may notice afterward that the level of the water in the glass is actually higher than the height of the glass. You may have also noticed that the water that you spilled has formed into pools that rise up off the counter. Both of these phenomena are due to surface tension.



Water droplets form on the surface of the water pool because of surface tension.

Molecular Perspective

In a sample of water, there are two types of molecules. Those that are on the outside, exterior, and those that are on the inside, interior. The interior molecules are attracted to all the molecules around them, while the exterior molecules are attracted to only the other surface molecules and to those below the surface. This makes it so that the energy state of the molecules on the interior is much lower than that of the molecules on the exterior. Because of this, the molecules try to maintain a minimum surface area, thus allowing more molecules to have a lower energy state. This is what creates what is referred to as surface tension. An illustration of this can be seen in Figure **3.4.1**.

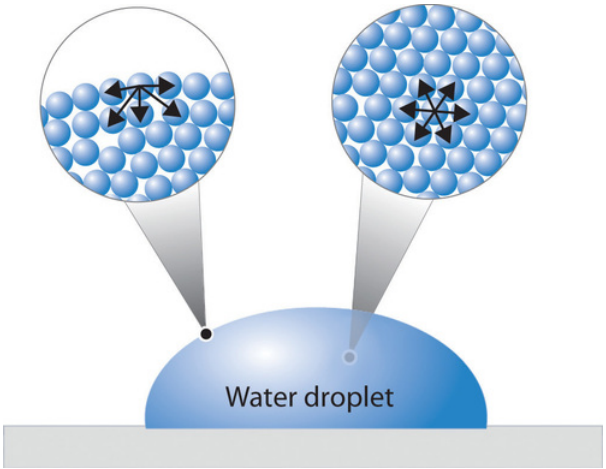


Figure **3.4.1**: Molecules at the surface of water experience a net attraction to other molecules in the liquid, which holds the surface of the bulk sample together. In contrast, those in the interior experience uniform attractive forces. (CC BY-SA-NC; anonymous by request).

The water molecules attract one another due to the water's polar property. The hydrogen ends, which are positive in comparison to the negative ends of the oxygen cause water to "stick" together. This is why there is surface tension and takes a certain amount of energy to break these intermolecular bonds. Same goes for other liquids, even hydrophobic liquids such as oil. There are forces between the liquid such as Van der Waals forces that are responsible for the intermolecular forces found within the liquid. It will then take a certain amount of energy to break these forces, and the surface tension. Water is one liquid known to have a very high surface tension value and is difficult to overcome.

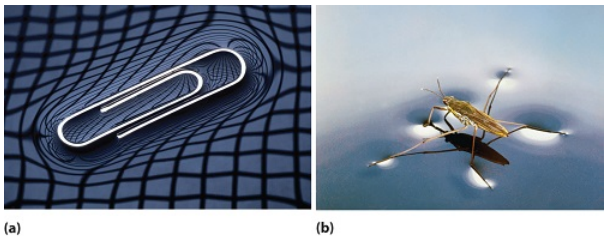


Figure **3.4.2**: (a) A paper clip can "float" on water because of surface tension. (b) Surface tension also allows insects such as this water strider to "walk on water." (CC BY-SA-NC; anonymous by request).

Surface tension of water can cause things to float which are denser than water, allowing organisms to literally walk on water (Figure **3.4.2**). An example of such an organism is the water strider, which can run across the surface of water, due to the intermolecular forces of the molecules, and the force of the strider which is distributed to its legs. Surface tension also allows for the formation of droplets that we see in nature.

Cohesive and Adhesive Forces

There are several other important concepts that are related to surface tension. The first of these is the idea of cohesive and adhesive Forces. Cohesive forces are those that hold the body of a liquid together with minimum surface area and adhesive forces are those that try to make a body of a liquid spread out. So if the cohesive forces are stronger than the adhesive forces, the body of water will maintain its shape, but if the opposite is true than the liquid will be spread out, *maximizing* its surface area. Any substance that you can add to a liquid that allows a liquid to increase its surface area is called a wetting agent.

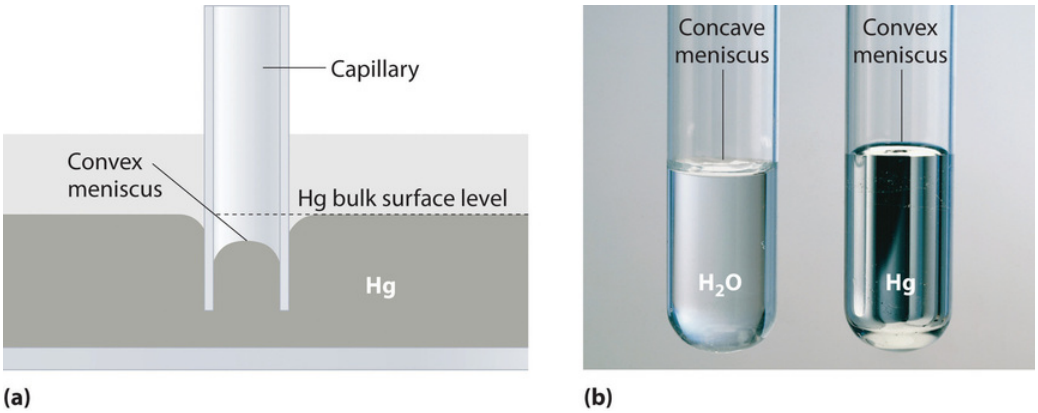


Figure **3.4.3**: (a) This drawing illustrates the shape of the meniscus and the relative height of a mercury column when a glass capillary is put into liquid mercury. The meniscus is convex and the surface of the liquid inside the tube is lower than the level of the liquid outside the tube. (b) Because water adheres strongly to the polar surface of glass, it has a concave meniscus, whereas mercury, which does not adhere to the glass, has a convex meniscus. (CC BY-SA-NC; anonymous by request).

In the lab there are also several important points to remember about surface tension. The first you've probably noticed before. This is the idea of a meniscus (Figure **3.4.3*a***). This is the concave (curved in) or convex (curved out) look that water or other liquids have when they are in test tubes. This is caused by the attraction between the glass and the liquid. With water, this causes it to climb up the sides of a test tube. This attraction is amplified as the diameter of the tubes increases; this is called capillary action. This can be seen if you take a tube with a very small diameter (a *capillary tube*) and lower it into a body of water. The liquid will climb up into the tube, even though there is no outside force. You may have also seen this when you put a straw into a drink and notice that the liquid level inside the straw is higher than it is in your drink. All of this however, requires that the adhesive forces (between the liquid and the capillary surface) be higher than the cohesive forces (between the liquid and itself), otherwise there will be no capillary action or the opposite can even happen. Mercury has higher cohesive forces than adhesive forces, so the level of the liquid will actually be lower in the capillary tubes than compared to the rest of the mercury (Figure **3.4.3*b***).

References

1. Petrucci, Ralph H., et al. General Chemistry: Principles and Modern Applications. Upper Saddle River, NJ: Prentice Hall, 2007.

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3.5: Unusual Properties of Water

With 70% of our earth being ocean water and 65% of our bodies being water, it is hard to not be aware of how important it is in our lives. There are 3 different forms of water, or H_2O: **solid** (ice), **liquid** (water), and **gas** (steam). Because water seems so ubiquitous, many people are unaware of the unusual and unique properties of water, including:

- Boiling Point and Freezing Point
- Surface Tension, Heat of Vaporization, and Vapor Pressure
- Viscosity and Cohesion
- Solid State
- Liquid State
- Gas State

Boiling Point and Freezing Point

If you look at the periodic table and locate tellurium (atomic number: 52), you find that the boiling points of hydrides decrease as molecule size decreases. So the hydride for tellurium: **H_2Te (hydrogen telluride)** has a boiling point of **-4°C**. Moving up, the next hydride would be **H_2Se (hydrogen selenide)** with a boiling point of **-42°C**. One more up and you find that **H_2S (hydrogen sulfide)** has a boiling point at **-62°C**. The next hydride would be **H_2O (WATER!)**. And we all know that the boiling point of water is **100°C**. So despite its *small* molecular weight, water has an incredibly *big* boiling point. This is because water requires more energy to break its hydrogen bonds before it can then begin to boil. The same concept is applied to freezing point as well, as seen in the table below. The boiling and freezing points of water enable the molecules to be very slow to boil or freeze, this is important to the ecosystems living in water. If water was very easy to freeze or boil, drastic changes in the environment and so in oceans or lakes would cause all the organisms living in water to die. This is also why sweat is able to cool our bodies.

COMPOUND	BOILING POINT	FREEZING POINT
Hydrogen Telluride	-4°C	-49°C
Hydrogen Selenide	-42°C	-64°C
Hydrogen Sulfide	-62°C	-84°C
Water	100°C	0 °C

Surface Tension, Heat of Vaporization, and Vapor Pressure

Besides mercury, water has the highest **surface tension** for all liquids. Water's high surface tension is due to the hydrogen bonding in water molecules. Water also has an exceptionally high **heat of vaporization**. Vaporization occurs when a liquid changes to a gas, which makes it an endothermic reaction. Water's heat of vaporization is 41 kJ/mol. **Vapor pressure** is inversely related to intermolecular forces, so those with stronger intermolecular forces have a lower vapor pressure. Water has very strong intermolecular forces, hence the low vapor pressure, but it's even lower compared to larger molecules with low vapor pressures.

- Viscosity is the property of fluid having high resistance to flow. We normally think of liquids like honey or motor oil being viscous, but when compared to other substances with like structures, water is viscous. Liquids with stronger intermolecular interactions are usually more viscous than liquids with weak intermolecular interactions.
- Cohesion is intermolecular forces between like molecules; this is why water molecules are able to hold themselves together in a drop. Water molecules are very cohesive because of the molecule's polarity. This is why you can fill a glass of water just barely above the rim without it spilling.

Solid State (Ice)

All substances, including water, become less dense when they are heated and more dense when they are cooled. So if water is cooled, it becomes more dense and forms ice. Water is one of the few substances whose solid state can float on its liquid state! Why? Water continues to become more dense until it reaches 4°C. After it reaches 4°C, it becomes *LESS* dense. When freezing, molecules within water begin to move around more slowly, making it easier for them to form hydrogen bonds and eventually

arrange themselves into an open crystalline, hexagonal structure. Because of this open structure as the water molecules are being held further apart, the volume of water *increases* about 9%. So molecules are more tightly packed in water's liquid state than its solid state. This is why a can of soda can explode in the freezer.

Liquid State (Liquid Water)

It is very rare to find a compound that lacks carbon to be a liquid at standard temperatures and pressures. So it is unusual for water to be a liquid at room temperature! Water is liquid at room temperature so it's able to move around quicker than it is as solid, enabling the molecules to form fewer hydrogen bonds resulting in the molecules being packed more closely together. Each water molecule links to four others creating a tetrahedral arrangement, however they are able to move freely and slide past each other, while ice forms a solid, larger hexagonal structure.

Gas State (Steam)

As water boils, its hydrogen bonds are broken. Steam particles move very far apart and fast, so barely any hydrogen bonds have the time to form. So, less and less hydrogen bonds are present as the particles reach the critical point above steam. The lack of hydrogen bonds explains why steam causes much worse burns that water. Steam contains all the energy used to break the hydrogen bonds in water, so when steam hits your face you first absorb the energy the steam has taken up from breaking the hydrogen bonds it its liquid state. Then, in an exothermic reaction, steam is converted into liquid water and heat is released. This heat adds to the heat of boiling water as the steam condenses on your skin.

Water as the "Universal Solvent"

Because of water's polarity, it is able to dissolve or dissociate many particles. Oxygen has a slightly negative charge, while the two hydrogens have a slightly positive charge. The slightly negative particles of a compound will be attracted to water's hydrogen atoms, while the slightly positive particles will be attracted to water's oxygen molecule; this causes the compound to dissociate. Besides the explanations above, we can look to some attributes of a water molecule to provide some more reasons of water's uniqueness:

- Forgetting fluorine, oxygen is the most electronegative non-noble gas element, so while forming a bond, the electrons are pulled towards the oxygen atom rather than the hydrogen. This creates 2 polar bonds, which make the water molecule more polar than the bonds in the other hydrides in the group.
- A 104.5° bond angle creates a very strong dipole.
- Water has hydrogen bonding which probably is a vital aspect in waters strong intermolecular interaction

Why is this important for the real world?

The properties of water make it suitable for organisms to survive in during differing weather conditions. Ice freezes as it expands, which explains why ice is able to float on liquid water. During the winter when lakes begin to freeze, the surface of the water freezes and then moves down toward deeper water; this explains why people can ice skate on or fall through a frozen lake. If ice was not able to float, the lake would freeze from the bottom up killing all ecosystems living in the lake. However ice floats, so the fish are able to survive under the surface of the ice during the winter. The surface of ice above a lake also shields lakes from the cold temperature outside and insulates the water beneath it, allowing the lake under the frozen ice to stay liquid and maintain a temperature adequate for the ecosystems living in the lake to survive.

Resources

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3.6: Vapor Pressure

Pressure is the average force that material (gas, liquid or solid) exert upon the surface, e.g. walls of a container or other confining boundary. Vapor pressure or equilibrium vapor pressure is the pressure of a vapor in thermodynamic equilibrium with its condensed phases in a closed container. All liquids and solids have a tendency to evaporate or sublime into a gaseous form and all gases have a tendency to condense back to their liquid or solid form.

Introduction

When a liquid is in a confined, closed, container, an equilibrium exists between the liquid and its gaseous phase. This equilibrium exists regardless of the temperature inside the container and the temperature of the liquid. The equilibrium exists due to the fact that some of the particles in the liquid, essentially at any temperature, will always have enough energy to escape the intrinsic cohesive forces and enter the gaseous phase (Figure **3.6.1**).

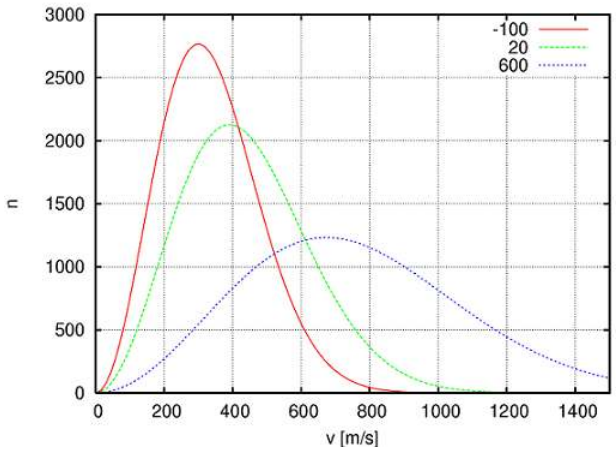


Figure **3.6.1**: The Boltzmann distribution shows that the molecules in a substance at any given temperature (measure of average kinetic energy) have a wide distribution of individual kinetic energies. Some of these individual molecules have enough energy to break from the liquid and enter the gaseous phase.

The vapor pressure of a substance is the pressure that the gaseous part of the substance exerts on the container of said substance.

Boiling a elevated altitudes

The fact that the vapor pressure is equal to the external pressure can become important when talking about boiling temperatures at various altitudes. At higher altitudes the pressure is lower than at sea level and therefore liquids such as water boil at lower temperatures. This would translate it into a longer time to cook something in the water as compared to cooking the same object at sea level. The opposite is also true if one boils water at an altitude lower than sea level.

Characteristics of Vapor Pressure

Vapor pressures are dependent only on temperature and nothing else. The vapor pressure of a liquid does not depend on the amount on the liquid in the container, be it one liter or thirty liters; at the same temperature, both samples will have the same vapor pressure. Vapor pressures have an exponential relationship with temperature and always increase as temperature increases (Figure 2: Vapor Pressure Curves). It is important to note that when a liquid is boiling, its vapor pressure is equal to the external pressure. For example, as water boils at sea level, its vapor pressure is 1 atmosphere because the external pressure is also 1 atmosphere.

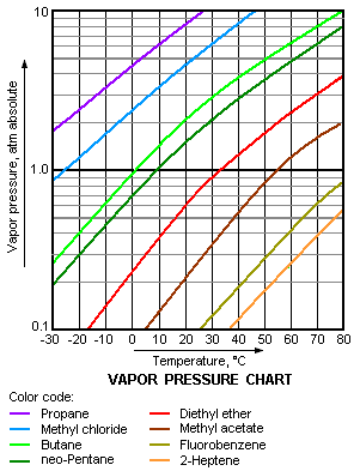


***Figure* 3.6.2:** *This chart shows the general relationship between a substance's vapor pressure and temperature change. Generally a substance's vapor pressure increases as temperature increases and decreases as temperature decreases (i.e. vapor pressure is directly proportional to temperature). This chart shows that this trend is true for various substances with differing chemical properties.*

The change in vapor pressure of a pure substance as temperature changes can be described using the equation known as the Clausius-Clapeyron Equation:

$$ln\frac{P_2}{P_1} = \frac{\Delta H_{vap}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{3.6.1}$$

Where:

- P_1 is the partial pressure of the liquid at T_1
- P_2 is the partial pressure of the liquid at T_2

Example 3.6.1

If the vapor pressure of water at 293 K is 17.5 mmHg, what is the vapor pressure of water at 300 K?

Solution

Step 1: Use the Clausius Clapeyron equation (Equation 3.6.1). Assume 293 K to be T_1 and 17.5 mmHg to be P_1 and 300 K to be T_2. We know the enthalpy of vaporization of water is 44000 J mol^{-1}. Therefore we plug in everything we are given into the equation.

$$ln\frac{P_2}{17.5mmHg} = \frac{44000Jmol^{-1}}{8.3145Jmol^{-1}K^{-1}}\left(\frac{1}{293K} - \frac{1}{300K}\right) \tag{3.6.2}$$

Step 2: Calculate everything possible, which is everything on the right side of the equation.

$$ln\frac{P_2}{17.5mmHg} = (5291.96K)(0.0000796K^{-1}) \tag{3.6.3}$$

Step 3: To isolate the variable, we need to get rid of the natural log function on the left side. To do so, we must exponentiate both sides of the equation after calculating the numerical value of the right side of the equation:

$$\frac{P_2}{17.5mmHg} = e^{0.421} \tag{3.6.4}$$

Step 4: To solve for P_2, we multiply both sides of the equation by 17.5mmHg.

$$P_2 = 26.7mmHg \tag{3.6.5}$$

Example 3.6.2

The vapor pressure of water at 298K is 23.8 mmHg. At what temperature is the vapor pressure of water 1075 mmHg?

Solution

Step 1: Once again this can be solved using the Clausius-Clapeyron equation. If we set P1 = 23.8 mmHg, T1 = 298K, and P2 = 1075 mmHg, all we need to do is to solve for T_2. So plug everything we know into the Clausius-Clapeyron Equation and we get:

$$\ln \frac{1075 mmHg}{23.8 mmHg} = \frac{44000 Jmol^{-1}}{8.3145 Jmol^{-1}K^{-1}} \left(\frac{1}{298K} - \frac{1}{T_2}\right) \tag{3.6.6}$$

Step 2: We can solve the right side of the equation for a numerical answer and we can simplify the right side of the equation to:

$$3.81 = (5291.96K)(\frac{1}{298K} - \frac{1}{T_2}) \tag{3.6.7}$$

Step 3: Further simplifying the equation by distributing the 5291.96 K, we get:

$$3.81 = (17.76) - \frac{5291.96K}{T_2} \tag{3.6.8}$$

Step 4: After subtracting 17.76 from both sides and multiplying both sides by T_2 to isolate the T_2 term, we get:

$$-13.95T_2 = -5291.96K \tag{3.6.9}$$

Step 5: Solving for T_2 we get:

$$T_2 = 383K \tag{3.6.10}$$

*Note: There may be some slight variations in this answer if you try working this problem out. The rounding in this problem will make a relatively large difference in mmHg (10-20 mmHg).

Vapor Pressure of Solutions: Raoult's Law

While the Clausius-Clapeyron equation is useful for describing the vapor pressure behavior of a pure substance, it does not quite help us when we need to describe the vapor pressure of a solution comprised of two ore more different liquids with different vapor pressures, that is where Raoult's Law comes in. Raoult's Law is:

$$P_{total} = \sum_i P_i X_i \tag{3.6.11}$$

Where P_i is the vapor pressure of that particular substance and X_i is the corresponding mole fraction of that substance. "i" is an indexing component that keeps track of each substance in the solution.

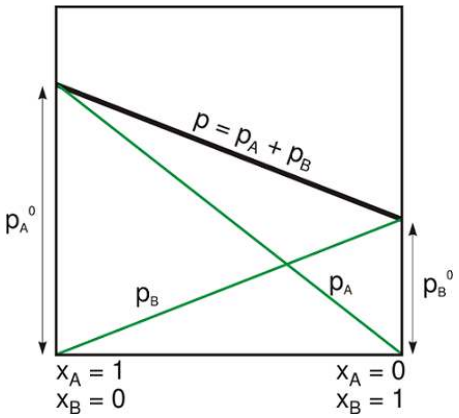


Figure* 3.6.3*: *Raoult's Law is used for calculating the vapor pressure of solutions with two or more substances in it. The total vapor pressure is a function of the vapor pressure of the individual vapor pressures of the components and their respective mole fractions.*

Essentially what Raoult's Law states is that the vapor pressure of a solution with two or more components is directly proportional to the vapor pressures of each component and their respective amounts in the solution (Figure 3). However, Raoult's Law is used to describe solutions that are essentially ideal solutions, meaning it is assumed that there are no interactions between the components of the solution. If the solution is non-ideal, it will deviate from the relationship described by Raoult's Law.

Example 3.6.3

A solution is comprised of 0.5000 mole H_2O, 1.000 mole ethanol, and 2.000 moles acetaldehyde at 293 K. What is the total vapor pressure of this solution? The partial pressures of these substances at 293 K are, respectively, 18 mmHg, 67.5 mmHg, and 740 mmHg (assume the liquids mix homogeneously).

Solution

Step 1: Calculate the mole fractions (moles of each substance divided by total moles) of each substance in the solution.

$$X_{water} = 0.5000/3.500 = 0.143 \tag{3.6.12}$$

$$X_{ethanol} = 1.000/3.500 = 0.286 \tag{3.6.13}$$

$$X_{acetaldehyde} = 2.000/3.500 = 0.571 \tag{3.6.14}$$

Step 2: Plug in all the values and solve for P_{total}

$$P_{total} = (18mmHg)(0.143) + (67.5mmHg)(0.286) + (740mmHg)(0.571mmHg) \tag{3.6.15}$$

$$P_{total} = 444.4mmHg \tag{3.6.16}$$

Example 3.6.4

A solution is comprised of only water and ethylene glycol and is at 293 K. Water's mole fraction in this solution is 0.379 and water's vapor pressure at this temperature is 18 mmHg (assume the water and ethylene glycol mix homogeneously). The total vapor pressure of this solution is 9.15 mmHg. Calculate the vapor pressure of pure ethylene glycol at this temperature.

Solution

Step 1: Since this solution is only comprised of water and ethylene glycol, we can easily calculate the mole fraction of ethylene glycol in this solution by subtracting water's mole fraction from 1.

$$X_{ethyleneglycol} = 1 - 0.379 = 0.621 \tag{3.6.17}$$

Step 2: Once we have the mole fraction of ethylene glycol, we have everything we need to solve for the partial pressure of pure ethylene glycol at 293 K using Raoult's Law:

$$9.15 = (18mmHg)(0.379) + (P_{ethyleneglycol})(0.621) \tag{3.6.18}$$

Solving for $P_{ethyleneglycol}$ we get:

$$P_{ethyleneglycol} = 3.75mmHg \tag{3.6.19}$$

Henry's Law

Both the Clausius-Clapeyron Equation (Equation 3.6.1) and Raoult's Law (Equation 3.6.11) describe liquids without any significant solutes in them. So what happens if the liquid contains a nonvolatile solute, in other words, a solute that does not evaporate and merely stays in the solution? Will the vapor pressure of the liquid increase or decrease? It turns out that having a nonvolatile solute in the liquid will decrease the vapor pressure of the liquid because the solutes will interfere with the high-energy liquid molecules' path to the surface to break free into the gaseous phase. An example of a nonvolatile solute in a liquid would be glucose in water (Figure 3.6.4: Henry's Law).

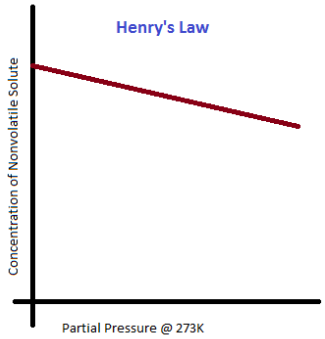


Figure **3.6.4**: Henry's Law can illustrate the the relationship between the partial pressure of a solvent and the concentration of a nonvolatile solute dissolved in it. As the concentration of the nonvolatile solute increases, the partial pressure of the solvent decreases.

Henry's Law can also be used the describe the partial pressure of a volatile solute in a liquid as a function of its concentration in the liquid. An example of this would be oxygen or carbon dioxide in a soda. Henry's Law is as follows:

$$C = (K_H)P_{gas} \tag{3.6.20}$$

Where P is the partial pressure of either the volatile solute or of the solvent with a nonvolatile solute in it and C is the solubility of the volatile solute or the concentration of the solvent with a nonvolatile solute in it. K_H is Henry's Constant and is different for various substances and differs with temperature and comes in many different units.

Example **3.6.5**: Henry's Law Application

Assume at 273 K and a CO_2 pressure of 3.6 atm, the aqueous solubility of CO_2 is 24.8 ml CO_2 per liter. What is the molarity of a saturated water solution when the CO_2 is under its normal partial pressure in air of 0.000395 atm.

Step 1: We need to calculate Henry's Constant for CO_2 when the partial pressure of CO_2 is 3.6 atm. To do this, we must first calculate the molarity of CO_2 under these conditions:

$$Molarity = \frac{0.0248 LCO_2 * \frac{1 molCO_2}{22.4 LCO_2}}{1 Lsolution} = 0.00111 MCO_2 \tag{3.6.21}$$

Step 2: Next we must solve for Henry's Constant under these conditions:

$$K_H = \frac{C}{P_{CO_2}} = 0.000308 \frac{MCO_2}{atm} \tag{3.6.22}$$

Step 3: Solve for the concentration (molarity) using Henry's Law:

$$C = K_H * P_{CO_2} = 0.000308 MCO_2 atm^{-1} * 0.000395 atm = 1.22 MCO_2 \tag{3.6.23}$$

"The bends"

One great use of Henry's Law is to calculate the various solubilities of gases in solutions under different pressures. One example of this is what is colloquially referred to as "the bends" (scientifically called decompression sickness). When divers go underwater, they are subjected to much higher pressures than they would be at sea level therefore their blood is much more soluble to gases and as such much larger quantities of gases such as nitrogen dissolve in the blood. If the divers then rise up back to the surface too quickly, these gases will be forced out of their dissolved form and form bubbles in the blood vessels. These gas bubbles can then cause the blood vessels to pop, causing much physical pain and serious medical issues. To avoid this, divers rise from deep depths slowly so their bodies can expel the extraneous gas through the lungs and allow the amounts of gas in the blood to equilibrate with the external pressure. This way the divers can avoid gas bubbles forming in blood vessels and therefore any personal injury.



Problems

The vapor pressure of water at 283 K is 9.2 mmHg, at what temperature is the vapor pressure of water 546 mmHg?

1. At 393 K the vapor pressure of water is 1489 mmHg; what is the vapor pressure of water at 343 K?
2. A solution's partial pressure is 34.93 mmHg. This solution is comprised of Chemical A and Chemical B. The partial pressure of Chemical A is 24.5 mmHg and its mole fraction is .145. What is the partial pressure of Chemical B?
3. Chemical A's partial pressure is 35.5 mmHg and Chemical B's partial pressure is 895.5 mmHg. Their respective mole fractions are 0.79 and 0.21. What is the the partial pressure of a homogenous solution of Chemical A and Chemical B?
4. Assume at 273 K and an O_2 pressure of 4.7 atm, the aqueous solubility of CO_2 is 79.6 ml CO_2 per liter. What is the molarity of a saturated water solution when the CO_2 is under its normal partial pressure in air of 0.21 atm.

Answers

1. 364K
2. 233.7mmHg
3. 36.7mmHg
4. 216.1mmHg
5. 0.000159 M O_2

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3.7: Viscosity

Viscosity is another type of bulk property defined as a liquid's resistance to flow. When the intermolecular forces of attraction are strong within a liquid, there is a larger viscosity. An example of this phenomenon is imagining a race between two liquids down a windshield. Which would you expect to roll down the windshield faster honey or water? Obviously from experience one would expect water to easily speed right past the honey, a fact that reveals honey has a much higher viscocity than water.

Introduction

Viscosity can be not only a fluid's resistance to flow but also a gas' resistance to flow, change shape or movement. The opposite of viscosity is fluidity which measures the ease of flow while liquids such as motor oil or honey which are "sluggish" and high in viscosity are known as *viscous*. One may ask the question of what is actually going on in the liquids to make one type flow faster and the other more resistant to flow such as the comparison between honey and water earlier. Because part of a fluid moves, it forces other adjacent parts of the liquid to move along with it causing an internal friction between the molecules which ultimately leads to a reduced rate of flow.

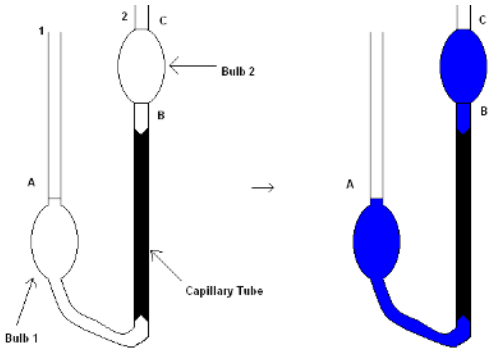
It is also important to note that the viscosity of liquids and gases are *affected by temperature* but in opposite ways meaning that upon heating, the viscosity of a liquid decreases rapidly, whereas gases flow more sluggishly. Why is this the case? As temperature increases, the average speed of molecules in a liquid also increases and as a result, they spend less time with their "neighbors." Therefore, as temperature increases, the average intermolecular forces decrease and the molecules are able to interact without being "weighed down" by one another. The viscosity of a gas, however, increases as temperature increases because there is an increase in frequency of intermolecular collisions at higher temperatures. Since the molecules are flying around in the void most of the time, any increase in the contact they have with one another will increase the intermolecular force which will ultimately lead to a disability for the whole substance to move.

Measuring Viscosity

There are numerous ways to measure viscosity. One of the most elementary ways is to allow a sphere, such as a metal ball, to drop through a fluid and time the fall of the metal ball: the slower the sphere falls, the greater the viscosity that is measured. Another more advanced design of measuring viscosity known as the Ostwald Viscometer that is much more accurate than dropping a metal ball. An Ostwald Viscometer consists of two reservoir bulbs and a capillary tube. The viscometer is filled with liquid until the liquid reaches the mark A with the aid of a pipette to accurately measure out the volume of needed liquid. The viscometer is then put into a water bath which equilibrates the temperature of the test liquid. As noted before, the equilibration is important to maintain a constant temperature as to not affect the viscosity otherwise. The liquid is then drawn through the side 2 of the U-tube by use of suction and lastly, the flow is time between marks C and B. The viscosity is calculated with Equation 3.7.1

$$\eta = Kt \tag{3.7.1}$$

where K is the value of a liquid with known viscosity and density such as water. Once the value of K is known, the viscosity can be determined by measuring the amount of time the test liquid flows between the two graduated marks.



Units of Measure:

1 Pascal-second (Pa•s) = 1 kg•m?1•s?1 1 Poise = 1 g•cm?1•s?1

Relationship between pascal-second to poise:

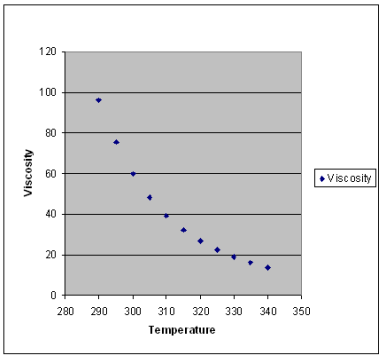
10 P = 1 kg•m?1•s?1 = 1 Pa•s 1 cP = 0.001 Pa•s = 1 mPa•s



When measuring viscosity with any type of viscometer, accurate temperature is so important that viscosity can double with a change of only 5 Celsius.

Table 1: Compound: Olive Oil

Temperature	Viscosity
290.00	96.102
295.00	75.392
300.00	59.906
305.00	48.167
310.00	39.153
315.00	32.150
320.00	26.649
325.00	22.283
330.00	18.785
335.00	15.956
340.00	13.651



notice how the increase in temperature lowers the viscosity of the fluid which in this case is olive oil

- Pitch (any highly viscous liquid which appear solid) has a viscosity of nearly 100 billion times the viscosity of water

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3.8: Wetting Agents

There are two general types of bulk intermolecular forces:

- Cohesive Forces: The forces exerted between molecules holding them together. If cohesive forces are strong, a liquid tends to form droplets on a surface.
- Adhesive Forces: The forces between liquid molecules and a surface. If adhesive forces are strong, a liquid tends to spread across a surface.

Wetting agents are substances that reduce the surface tension of water to allow it to spread drops onto a surface, increasing the spreading abilities of a liquid. Lowering the surface tension lowers the energy required to spread drops onto a film, thus weakening the cohesive properties of the liquid and strengthening its adhesive properties. One example of how wetting agents work is in the formation of micelles. Micelles consist of hydrophilic heads forming an outer layer around lipophilic tails. When in water, the micelles' tails can surround an oil droplet while the heads are attracted to the water.

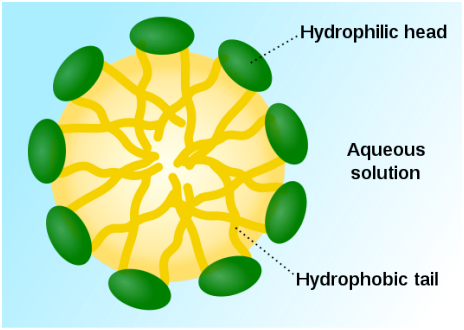


Figure **3.8.1**: Schematic diagram of a micelle of oil in aqueous suspension, such as might occur in an emulsion of oil in water. In this example the surfactant molecules' oil-soluble tails project into the oil, while the water-soluble ends remain in contact with the water phase. from Wikipedia (SuperManu)

Dish soap is a great example of a wetting agent. With all the food oils and such on the plate cohesive forces make it difficult for the water to spread and clean the plate. The soap dissolves all theses unwanted particles, exposing a clean surface. The soap also lowers the surface tension of water, allowing it to spread evenly across the entire surface.

There are four main types of wetting agents: anionic, cationic, amphoteric, and nonionic.

- Anionic, cationic, and amphoteric wetting agents ionize when mixed with water.
- Anions have a negative charge, while cations have a positive charge.
- Amphoteric wetting agents can act as either anions or cations, depending on the acidity of the solution.
- Nonionic wetting agents do not ionize in water. A possible advantage for using a nonionic wetting agent is that it does not react with other ions in the water, which could lead to formation of a precipitate.

How to Tell if a Liquid Contains a Wetting Agent

One method of knowing whether or not a liquid has a wetting agent in it is to spread the liquid on a surface that is coated in grease. If the liquid does not contain a wetting agent, the its cohesive forces would overpower adhesive forces, causing the liquid to for droplets on the surface (Figure **3.8.2**, left). If the liquid does contain a wetting agent, the grease would be dissolved and the surface tension of the liquid would be lowered, causing the adhesive forces to overpower the cohesive forces. This would result in the liquid spreading evenly along the surface (Figure **3.8.2**, right).

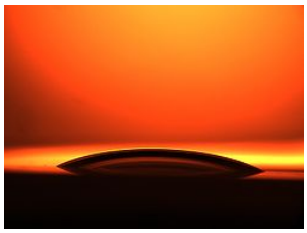


Figure **3.8.2**: (left) A water droplet is sitting on a **brass** surface while being immersed in oil as an example of poor wetting. (right) A water droplet is sitting on a glass surface while being immersed in oil as an example of better wetting. Images used with permission from Wikipedia (Guro Aspenes, SINTEF Petroleum Research).

Another method is to place the liquid in a test tube and observe the liquid's meniscus (Figure **3.8.3**). If the liquid contains a wetting agent, its adhesive forces are stronger than cohesive forces, which means the liquid molecules are more inclined to stick to the surface than other liquid molecules. This results in a concave meniscus. If the liquid does not contain a wetting agent and is naturally very cohesive, like mercury, it forms a convex meniscus. This is caused by the fact the the molecules of the liquid have a stronger attraction to each other than to the surface of the test tube.

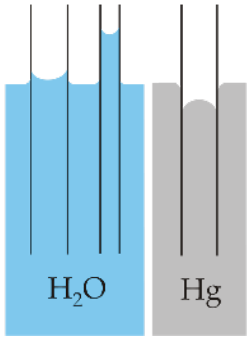


Figure used with permission from Wikipedia.

Intermolecular forces also cause a phenomenon called capillary action, which is the tendency of a polar liquid to rise against gravity into a small-diameter tube (a *capillary*), as shown in Figure **3.8.3**. When a glass capillary is put into a dish of water, water is drawn up into the tube. The height to which the water rises depends on the diameter of the tube and the temperature of the water but *not* on the angle at which the tube enters the water. The smaller the diameter, the higher the liquid rises.

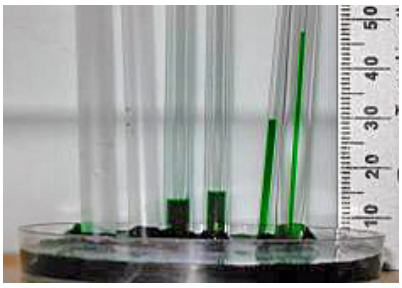


Figure **3.8.4**: The Phenomenon of Capillary Action. Capillary action seen as water climbs to different levels in glass tubes of different diameters. Credit: Dr. Clay Robinson, PhD, West Texas A&M University.

References

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Problems

1. Would it be beneficial to use a wetting agent when waxing a car?
2. An unknown liquid forms a convex meniscus when poured into a test tube. Does the liquid wet the test tube?
3. Do wetting agents increase or decrease the adhesive properties of a liquid?
4. Soap can form a precipitate when used as a wetting agent. Is it a nonionic or ionic wetting agent?
5. A liquid's cohesive forces overwhelm its adhesive forces. Do you think it contains a wetting agent?

Answers

1. No, when waxing a car, you do not want water to wet the car's surface.
2. No, if it forms a convex meniscus, its cohesive forces overpower its adhesive forces, causing the liquid's molecules to want to stick to each other as much as possible.
3. They increase the adhesive properties of a liquid.
4. It must be an ionic wetting agent, since nonionic wetting agents do not form precipitates.
5. The liquid most likely does not contain a wetting agent, since it is more inclined to stick to itself than to wet the surface.

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CHAPTER OVERVIEW

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4.2: Pressure-Volume Work
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4.4: Energy is a State Function
4.5: An Adiabatic Process is a Process in which No Energy as Heat is Transferred
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4.1: Overview of Classical Thermodynamics

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.

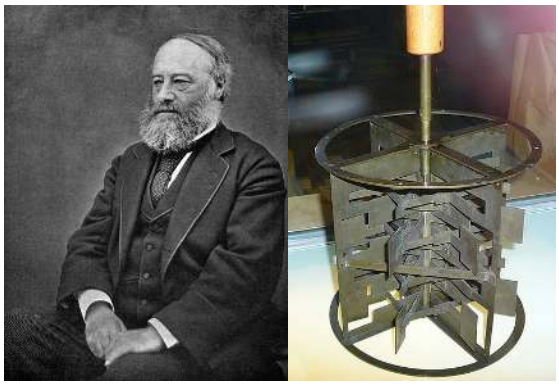


Figure **4.1.1**: (left) James Prescott Joule (1818 - 1889) (right) Joule's apparatus for measuring the work equivalent of heat. (CC BY-SA 3.0; Dr. Mirko Junge)

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

$$\Delta U = U_f - U_i \tag{4.1.1}$$

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.

4.1.1: 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 4.1.1: 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.

$$\left(\frac{\partial p}{\partial V}\right)_T = -\frac{RT}{V^2} \tag{4.1.2}$$

and

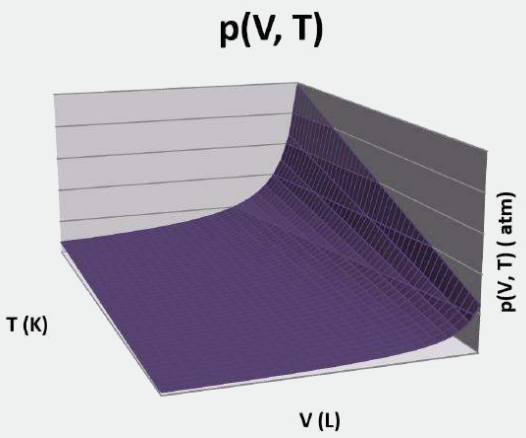
$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{R}{V} \tag{4.1.3}$$

So that the change in pressure can be expressed

$$dp = \left(\frac{\partial p}{\partial V}\right)_T dV + \left(\frac{\partial p}{\partial T}\right)_V dT \tag{4.1.4}$$

or by substituting Equations 4.1.2 and 4.1.3

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



Macroscopic changes can be expressed by integrating the individual pieces of Equation 4.1.4 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!

4.1.2: 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 4.1.2: 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

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

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

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4.2: 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.

4.2.1: 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:

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

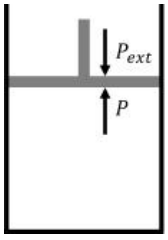


Figure 19.2.1 : A piston with internal pressure P and external pressure P_{ext}.

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:

$$w_{volume} = \int \left(\frac{F}{A}\right)(A\,ds) = \int P\,dV \tag{4.2.1}$$

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 4.2.1) 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.

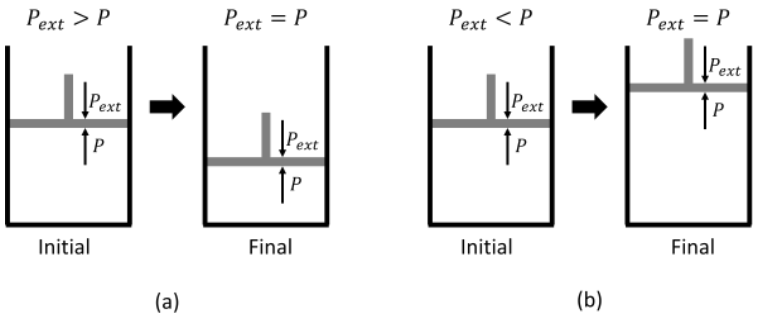


Figure 19.2.2 : Pistons showing a compression (left) and an expansion (right).

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

$$w = -P_{ext} \int_{V_{initial}}^{V_{final}} dV = -P_{ext} \Delta V \tag{4.2.2}$$

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.

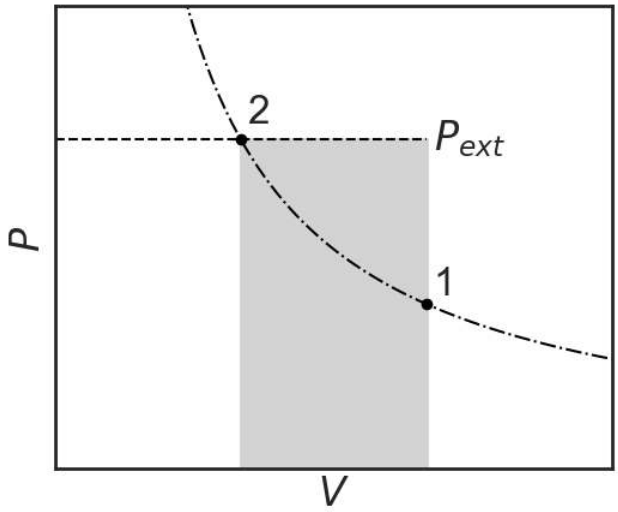


Figure 19.2.3 : A system is compressed under constant external pressure, P_{ext}, from state 1 to state 2. The shaded area shows the amount of work being done for the compression. The dash-dot line is an isotherm, a path of constant temperature, showing that the initial and final temperature of the irreversible 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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4.3: Work and Heat are not State Functions

4.3.1: 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**.

4.3.2: 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.

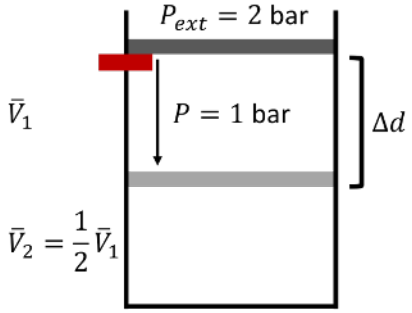


Figure 19.3.1 : A piston is being irreversibly and isothermally compressed under constant external pressure from state 1 to state 2.

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.

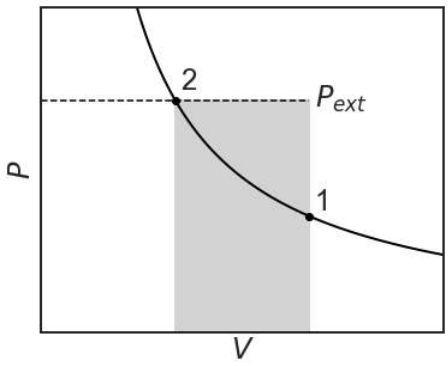


Figure 19.3.1 : The system is being irreversibly and isothermally compressed from state 1 to 2. The amount of work being done on the system is shown by the shaded area.

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 $P_{ext} = P_{system}$:

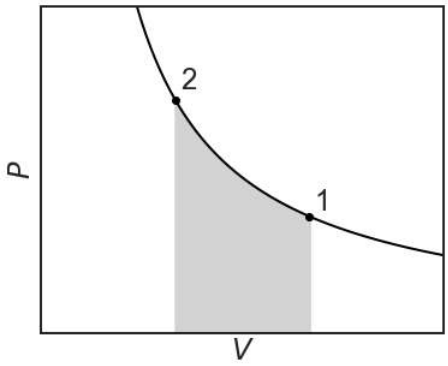


Figure 19.3.1 : The system is being reversibly and isothermally compressed from state 1 to 2. The amount of work being done on the system is shown by the shaded area. Note that for a compression, a reversible process does less work than an irreversible process.

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.

4.3.2.1: 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.

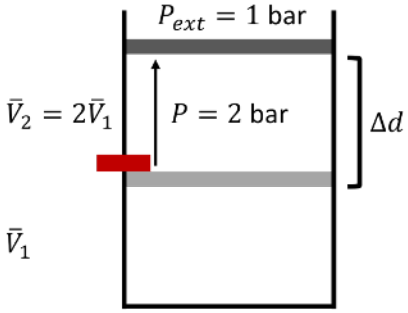


Figure 19.3.1 : A piston is being irreversibly and isothermally expanded under constant external pressure from state 1 to state 2.

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.

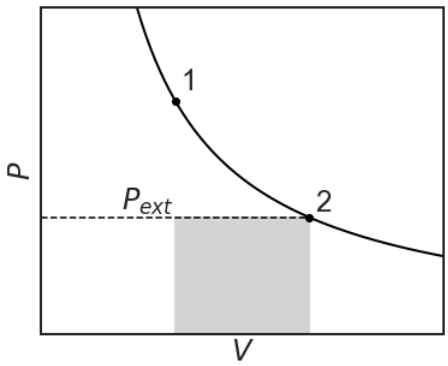


Figure 19.3.1 : The system is being irreversibly and isothermally expanded from state 1 to 2. The amount of work being done by the system is shown by the shaded area.

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 $P_{ext} = P_{system}$:

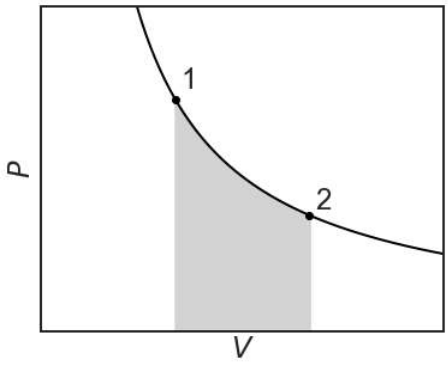


Figure 19.3.1 : The system is being reversibly and isothermally expanded from state 1 to 2. The amount of work being done by the system is shown by the shaded area. Note that for an expansion, a reversible process does more work than an irreversible process.

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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4.4: Energy is a State Function

4.4.1: 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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4.5: An Adiabatic Process is a Process in which No Energy as Heat is Transferred

4.5.1: Isothermal expansion of an ideal gas

For a monatomic ideal gas we have seen that energy $\langle E \rangle$ observed as $U = 3/2nRT$. This means that energy is only dependent on temperature and if a gas is compressed **isothermally**, then the internal energy does not change:

$$\Delta U_{isothermal-idealgas} = 0$$

This means that the reversible work must ***cancel*** the reversible heat:

$$\Delta U_{rev} = w_{rev} + q_{rev} = 0$$

Therefore

$$w_{rev} = -q_{rev}$$

so from the expression of the reversible work for expansion in the last section

$$q_{rev} = nRT \ln \frac{V_2}{V_1}$$

If $V_2 > V_1$ (expansion), then you (or the environment) **must** put heat into the system because this is a positive number.

4.5.2: Adiabatic expansion of an ideal gas

Now suppose you make sure that no heat can enter the cylinder. (Put it in styrofoam or so). Then the path can still be reversible (slow pulling) but the process is then adiabatic.

> *This bat- part comes from a Greek verb βαινω (baino) that means walking, compare acro**bat**, someone who goes high places (acro-). The δια (dia) part means 'through' (cf. diagram, diorama, diagonal etc.) and the prefix α- (a-) denies it all (compare atypical versus typical).*

So the styrofoam prevents the heat from walking through the wall. When expanding the gas from V_1 to V_2 it still does reversible work but where does that come from? It can only come from the internal energy itself. So in this case any energy change should consist of work (adiabatic means: $\delta q = 0$).

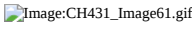
$$dU = \delta w_{rev}$$

This implies that the temperature must drop, because if U changes, then T must change.

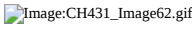
The change of energy with temperature at constant volume is known as the heat capacity (at constant volume) C_v

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

For an ideal gas U only changes with temperature, so that



or:



We can now compare two paths to go from state P_1, V_1, T_1 to state P_2, V_2, T_1:

1. Reversible isothermal expansion A
2. Reversible adiabatic expansion B followed by reversible isochoric heating C

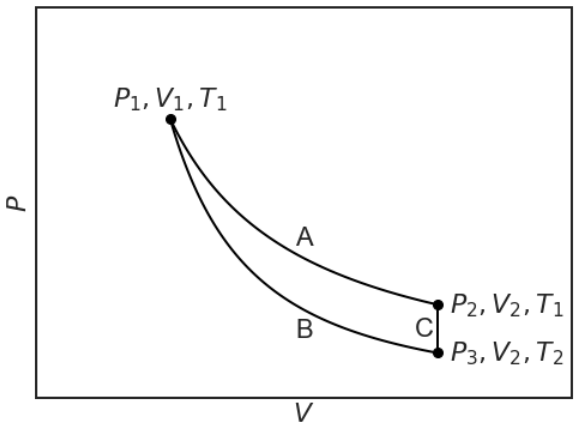


Figure __:

Notice that the temperature remains T_1 for path A (isotherm!), but that it drops to T_2 on the adiabat B, so that the cylinder has to be isochorically warmed up, C, to regain the same temperature.

ΔU_{tot} should be the same for both path A and the combined path B+C, because the end points are the same (U is a state function!). As the and points are at the same temperature and U only depends on T:

$$\Delta U_{tot} = 0$$

Along adiabat B:

$$q_{rev} = 0$$

Along isochoric heating C, there is no volume work because the volume is kept constant, so that:

Image:CH431_Image63.gif

This is the only reversible heat involved in path B+C. However, we know that ΔU_{tot} for path A is zero (isothermal!). This means that the volume work along B must cancel the heat along C:

The book keeping looks as follows, all paths are reversible:

$$\Delta U_{B+C} = \Delta U_A = 0 = q_B + w_B + q_C + w_C$$

We know that $q_B = 0$ since it is an adiabat and $w_C = 0$ since it is an isochore:

$$\Delta U_{B+C} = \Delta U_A = 0 = 0 + w_B + q_C + 0$$

Therefore:

$$w_B = -q_C$$

We had already seen before that along the isotherm A:

$$w_A = -q_A = -nRT \ln \frac{V_1}{V_2}$$

As you can see \w_A\) and w_B are ***not*** the same. Work is a path function, even if reversible. As we are working with an ideal gas we can be more precise about w_B and q_c as well. The term w_B along the adiabat is reversible volume work. Since there is no heat along B we can write a straight d instead of δ for the work contributions (It is the only contribution and must be identical to the state function dU):

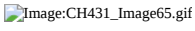
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4.5: An Adiabatic Process is a Process in which No Energy as Heat is Transferred is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

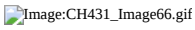
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4.6: The Temperature of a Gas Decreases in a Reversible Adiabatic Expansion

We can make the same argument for the heat along C. If we do the three processes A and B+C only to a tiny extent we can write:



And now we can integrate from V_1 to V_2 over the reversible adiabatic work along B and from T_1 to T_2 for the reversible isochoric heat along C. To separate the variables we do need to bring the temperature to the right side of the equation.:



The latter expression is valid for a reversible adiabatic expansion of a monatomic ideal gas (say Argon) because we used the C_v expression for such a system. We can use the gas law $PV = nRT$ to translate this expression in one that relates pressure and volume see Eq 19.23

We can mathematically show that the temperature of a gas decreases during an adiabatic expansion. Assuming an ideal gas, the internal energy along an adiabatic path is:

$$\begin{aligned} d\bar{U} &= \delta q + \delta w \\ &= 0 - Pd\bar{V} \\ &= -Pd\bar{V} \end{aligned}$$

The constant volume heat capacity is defined as:

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

We can rewrite this for internal energy:

$$d\bar{U} = \bar{C}_V dT$$

Combining these two expressions for internal energy, we obtain:

$$\bar{C}_V dT = -Pd\bar{V}$$

Using the ideal gas law for pressure of an ideal gas:

$$\bar{C}_V dT = -\frac{RT}{\bar{V}} d\bar{V}$$

Separating variables:

$$\frac{\bar{C}_V}{T} dT = -\frac{R}{\bar{V}} d\bar{V}$$

This is an expression for an ideal path along a reversible, adiabatic path that relates temperature to volume. To find our path along a PV surface for an ideal gas, we can start in TV surface and convert to a PV surface. Let's go from (T_1, V_1) to (T_2, V_2).

$$\int_{T1}^{T_2} \frac{\bar{C}_V}{T} dT = -\int_{\bar{V}_1}^{\bar{V}_2} \frac{R}{\bar{V}} d\bar{V}$$

$$\bar{C}_V \ln\left(\frac{T_2}{T_1}\right) = -R\ln\left(\frac{\bar{V}_2}{\bar{V}_1}\right) = R\ln\left(\frac{\bar{V}_1}{\bar{V}_2}\right)$$

$$\ln\left(\frac{T_2}{T_1}\right) = \frac{R}{\bar{C}_V}\ln\left(\frac{\bar{V}_1}{\bar{V}_2}\right)$$

$$\left(\frac{T_2}{T_1}\right) = \left(\frac{\bar{V}_1}{\bar{V}_2}\right)^{\frac{R}{\bar{C}_V}}$$

We know that:

$$R = \bar{C}_P - \bar{C}_V$$

$$\frac{R}{\bar{C}_V} = \frac{\bar{C}_P - \bar{C}_V}{\bar{C}_V} = \frac{\bar{C}_P}{\bar{C}_V} - 1$$

$$\frac{R}{\bar{C}_V} = \gamma - 1$$

Therefore:

$$\left(\frac{T_2}{T_1}\right) = \left(\frac{\bar{V}_1}{\bar{V}_2}\right)^{\gamma-1}$$

This expression shows that volume and temperature are inversely related. That is, as the volume increase from V_1 to V_2, the temperature must decrease from T_1 to T_2.

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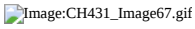
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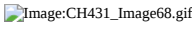
4.7: Work and Heat Have a Simple Molecular Interpretation

4.7.1: Statistical interpretation

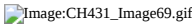
We can use what we know about the statistical side of thermodynamics to give a simple interpretation to a change dU:

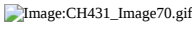
we see that because $\delta w_{rev} = -PdV$





See also section 17-5 :In this section it is shown that we can manipulate the partition function to find the pressure of a system by calculating the above moment of the distribution. Again we take the derivative of the logarithm of the partition function Q, this time versus V and show that the result resembles the last equation pretty closely (apart from a factor). Thus we get:





Once again we can find an important quantity of our system by manipulating the partition function Q.

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4.8: Pressure-Volume Work

4.8.1: 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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4.9: Heat Capacity is a Path Function

4.9.1: Determining enthalpies from heat capacities.

The functions H and C_p are related by differentiation:

$$\left(\frac{\partial H}{\partial T}\right)_P = C_P$$

This means that we can:

1. measure C_p as a function of temperature
2. integrate this function and find $H(T)$

However, there are problems with this approach:

1. Reference point: we have to deal with the lower limit of integration.

   Ideally we start at zero Kelvin (but we cannot get there), but how do we compare one compound to the other?

2. At temperatures where there is a phase transition there is a sudden jump in enthalpy. E.g. when ice melts we have to first add the heat of fusion until all ice is gone before the temperature can go up again (assuming all is done under reversible well-equilibrated conditions).
3. At the jumps in H, the C_p is infinite.

> *It should be stressed that there **are no absolute enthalpies**.*

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4.10: Relative Enthalpies Can Be Determined from Heat Capacity Data and Heats of Transition

It should be stressed that there **are no absolute enthalpies**. All that is properly defined are differences in enthalpy ΔH and these are only defined for ***processes***

When dealing with enthalpies

Define the Process

For example for the process of:

Process 1: ***heating ice from -20°C to -0°C***

We could write $\Delta H_1 = \int C_{P,ice}.\ dT$ from T=253K to T=273K = H(273) -H(253). But before moving beyond the melting point first a different process needs to take place, that of

Process 2: ***melting***

This gives us $\Delta_{fus}H = H_{liquid} - H_{solid}$ (both at 273K!). When we heat the liquid water further to say +20°C we would have to integrate over the heat capacity of the liquid.

Process 3: ***heating water from 0°C to +20°C***

We could write

$$\Delta H_3 = \int C_{P,water} dT$$

from T=273K to T=293K = H(293)-H(273).

The total change in enthalpy between -20 and +20 would be the sum of the three enthalpy changes.

$$\Delta H_{totalprocess} = \Delta H_1 + \Delta_{fus}H + \Delta H_3$$

Of course we could consider doing the same calculation for any temperature between -20 and +20 and summarize all our results in a graph. The three processes can thus schematically be shown in Figure 19.10.1 .

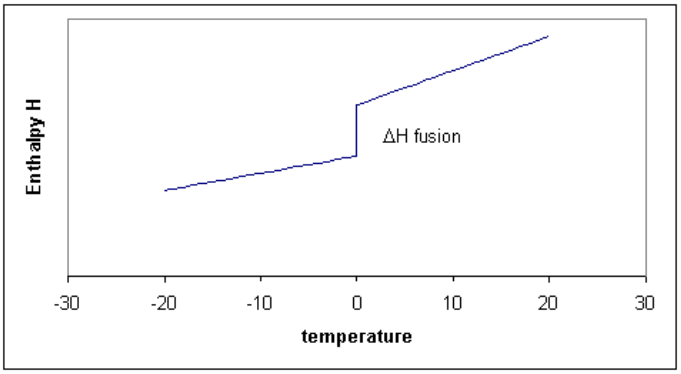


Figure 19.10.1 *: Schematic enthalpy function showing the jump at the melting point*

Notice that the slopes (i.e. the heat capacities!) before and after the melting point differ. The slope for the liquid is a little steeper because the liquid has more degrees of freedom and therefore the heat capacity of the liquid tends to be higher than of the solid. In the figure the enthlapy curves are shown as straight lines. This would be the case if the heat capacities are *constant* over the temperature interval. Although C_p is typically a 'slow' or 'weak' function of temperature it usually does change a bit, which means that the straight lines for H become curves.

> *Although C_p is typically a 'slow' or 'weak' function of temperature and is well approximated as a constant.*

Notice that for process two, the temperature is constant, that means that ΔT or dT is zero, but ΔH is finite, consequently ΔH/ΔT is infinitly large. Taking the limit for ΔT going to zero, we get a derivative:

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

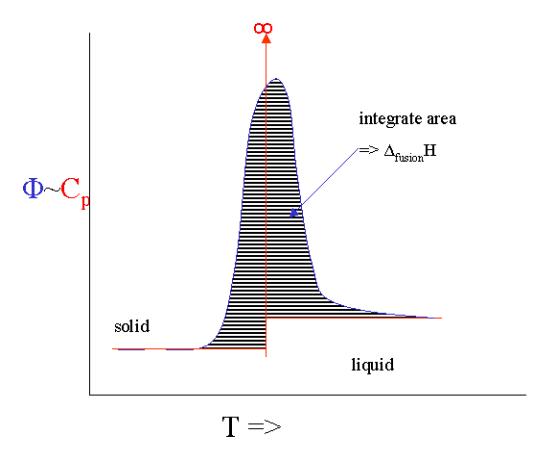
This derivative, the heat capacity must undergo a singularity: the slope is infinitely large (i.e, the H curve goes straight up). When there are more phase transitions, more discontinuities in H and singularities in C_p result (Figure 19.10.1). Note that $H(T) - H(0)$, not $H(T)$ is plotted to avoid the question what the absolute enthalpy is.

Scanningcalorimetry

There is technique that allows us to measure the heat capacity as a function of temperature fairly directly. It is called Differential Scanning Calorimetry (DSC). You put a sample in a little pan and put the pan plus an empty reference pan in the calorimeter. The instrument heats up both pans with a constant heating rate. Both pans get hotter by ***conduction***, but the heat capacity of the filled pan is obviously bigger. This means that the heat flow into the sample pan must be a bit bigger than into the empty one. This differential heat flow induces a tiny temperature difference ΔT between the two pans that can be measured. This temperature difference is proportional to the heat flow difference which is proportional to the heat capacity difference.

$$\Delta T\ \Delta\Phi\ \Delta_{betweenpans} C_p = C_p^{sample}\ (if the pans cancel)$$

However, there are number of serious broadening issues with the technique. If you melt something you will never get to see the infinite singularity of the heat capacity. Instead it broadens out into a peak. If you integrate the peak you get the $\Delta_{fusion}H$ and the onset is calibrated to give you the melting point.



The ideal heat capacity signal and its broadened DSC signal

It is even possible to heat the sample with a rate that fluctuates with a little sine wave. This "Modulated DSC" version can even give you the (small) difference in C_p before and after the melting event.

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4.11: Enthalpy Changes for Chemical Equations are Additive

4.11.1: Hess's law

As enthalpy and energy are state functions we should expect ***additivity*** of U and H when we study chemical reactions. This additivity is expressed in **Hess's Law**. The additivity has important consequences and the law finds wide spread application in the prediction of heats of reaction.

1. The reverse reaction has the negative enthalpy of the forward one.
2. If we can do a reaction in two steps we can calculate the enthalpy of the combined reaction by adding up:

Reaction	Enthalpy
$C_{(s)}$ + ½ $O_{2(g)}$ -> $CO_{(g)}$	$\Delta_r H$ = -110.5 kJ
$CO_{(g)}$ + ½ $O_{2(g)}$ -> $CO_{2(g)}$	$\Delta_r H$ = -283.0 kJ
This means that	----------+
$C_{(s)}$ + O2(g) -> CO2(g)	$\Delta_r H$ = -393.5 kJ

By this mechanism it is often possible to calculate the heat of a reaction even if this reaction is hard to carry out. E.g. we could burn both graphite and diamond and measure the heats of combustion for both. The difference would give us the heat of the transformation reaction from graphite to diamond.

4.11.1.1: Reaction-as-written convention (caution!)

The enthalpy is for the ***reaction-as-written***. That means that if we write:

$$2C(s) + O_2(g) \rightarrow 2CO(g)$$

with $\Delta_r H$ = -221 kJ (***not***: -110.5 kJ)

4.11.1.2: Reverse reactions

Because H is a state function the reverse reaction has the same enthalpy but with opposite sign

$$2CO(g) \rightarrow 2C(s) + O_2(g)$$

with $\Delta_r H$ = +221 kJ

4.11.1.3: Combining values

It is quite possible that you cannot really do a certain reaction in practice. For many reactions we can arrive at enthalpy values by doing some bookkeeping. For example, we can calculate the enthalpy for the reaction of PCl_3 with chlorine if we know the two reactions that the elements phosphorous and chlorine can undergo.

> *You do have to make sure you balance your equations properly!*

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4.12: Heats of Reactions Can Be Calculated from Tabulated Heats of Formation

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 4.12.1:

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

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

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

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

4.12.1: 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

$$\begin{aligned} \Delta_{rxn} &= (1\, mol)\left(\Delta H_f^o(CO_2)\right) + (2\, mol)\left(\Delta H_f^o(H_2O)\right) - (1\, mol)\left(\Delta H_f^o(CH_4)\right) && (4.12.1)\\ &= (1\, mol)(-393.5\, kJ/mol) + (2\, mol)\,(-285.8\, kJ/mol) && (4.12.2)\\ &\quad - (1\, mol)\,(-74.6\, kJ/mol) \\ &= -890.5\, kJ/mol && (4.12.3) \end{aligned}$$

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.

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

4.12.3: 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

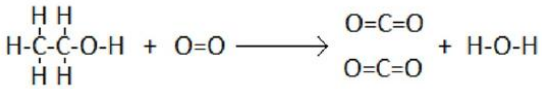
$$XY(g) \rightarrow X(g) + Y(g)$$

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

$$\begin{aligned}\Delta H_c &= 5(413\,kJ/mol) + 1(348\,kJ/mol) + 1(358\,kJ/mol) \\ &\quad + 1(495\,kJ/mol) - 4(799\,kJ/mol) - 2(463\,kJ/mol) \\ &= -856\,kJ/mol\end{aligned} \tag{4.12.4}$$

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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4.13: The Temperature Dependence of ΔH

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

$$\Delta H = \int_{T_2}^{T_2} C_p\,dT \tag{4.13.1}$$

Equation 4.13.1 is often referred to as *Kirchhoff's Law*. If C_p is independent of temperature, then

$$\Delta H = C_p\,\Delta T \tag{4.13.2}$$

If the temperature dependence of the heat capacity is known, it can be incorporated into the integral in Equation 4.13.1. A common *empirical* model used to fit heat capacities over broad temperature ranges is

$$C_p(T) = a + bT + \frac{c}{T^2} \tag{4.13.3}$$

After combining Equations 4.13.3 and 4.13.1, the enthalpy change for the temperature change can be found obtained by a simple integration

$$\Delta H = \int_{T_1}^{T_2} \left(a + bT + \frac{c}{T^2}\right) dT \tag{4.13.4}$$

Solving the definite integral yields

$$\Delta H = \left[aT + \frac{b}{2}T^2 - \frac{c}{T}\right]_{T_1}^{T_2} \tag{4.13.5}$$

$$= a(T_2 - T_1) + \frac{b}{2}(T_2^2 - T_1^2) - c\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{4.13.6}$$

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 **4.13.1:** *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 4.13.1: 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 4.13.1 with a temperature dependence C_p given by Equation 4.13.1 using the parameters in Table **4.13.1**. This results in the integral form (Equation 4.13.6):

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

when substituted with the relevant parameters of Pb(s) from Table **4.13.1**.

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

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 4.13.2: 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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4.14: Enthalpy is a State Function

Our expression for internal energy at constant pressure:

$$\Delta U = q_P + w = q_P - P\Delta V$$

Rearrange:

$$q_P = \Delta U + P\Delta V = U_2 - U_1 + P(V_2 - V_1)$$

$$q_P = (U_2 + PV_2) - (U_1 + PV_1)$$

We can define this term as enthalpy:

$$H \equiv U + PV$$

This is a new state function.

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4.E: The First Law of Thermodynamics (Exercises)

In the mid 1920's the German physicist Werner Heisenberg showed that if we try to locate an electron within a region Δx; e.g. by scattering light from it, some momentum is transferred to the electron, and it is not possible to determine exactly how much momentum is transferred, even in principle. Heisenberg showed that consequently there is a relationship between the uncertainty in position Δx and the uncertainty in momentum Δp.

$$\Delta p \Delta x \geq \frac{\hbar}{2} \tag{4.E.1}$$

You can see from Equation 4.E.1 that as Δp approaches 0, Δx must approach ∞, which is the case of the free particle discussed previously.

This uncertainty principle, which also is discussed in Chapter 4, is a consequence of the wave property of matter. A wave has some finite extent in space and generally is not localized at a point. Consequently there usually is significant uncertainty in the position of a quantum particle in space. Activity 1 at the end of this chapter illustrates that a reduction in the spatial extent of a wavefunction to reduce the uncertainty in the position of a particle increases the uncertainty in the momentum of the particle. This illustration is based on the ideas described in the next section.

? Exercise 4.E.1

Compare the minimum uncertainty in the positions of a baseball (mass = 140 gm) and an electron, each with a speed of 91.3 miles per hour, which is characteristic of a reasonable fastball, if the standard deviation in the measurement of the speed is 0.1 mile per hour. Also compare the wavelengths associated with these two particles. Identify the insights that you gain from these comparisons.

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CHAPTER OVERVIEW

5: Entropy and The Second Law of Thermodynamics

5.1: Energy Does not Determine Spontaneity
5.2: Nonequilibrium Isolated Systems Evolve in a Direction That Increases Their Energy Dispersal
5.3: Unlike heat, Entropy is a State Function
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5.6: We Must Always Devise a Reversible Process to Calculate Entropy Changes
5.7: Thermodynamics Provides Insight into the Conversion of Heat into Work
5.8: Entropy Can Be Expressed in Terms of a Partition Function
5.9: The Statistical Definition of Entropy is Analogous to the Thermodynamic Definition
5.E: Entropy and The Second Law of Thermodynamics (Exercises)

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5.1: Energy Does not Determine Spontaneity

There are many spontaneous events in nature. If you open the valve in both cases a spontaneous event occurs. In the first case the gas fills the evacuated chamber, in the second the gases will mix. The state functions U and H do not give us a clue what will happen. You might think that only those events are spontaneous that produce heat.

Not so:

- If you dissolve KNO_3 in water, it does so spontaneously, but the solution gets ***cold***.
- If you dissolve KOH in water, it does so spontaneously, but the solution gets ***hot***.

Clearly the first law is not enough to describe nature.

5.1.1: Two items left on our wish list

The development of the new state function entropy has brought us much closer to a complete understanding of how heat and work are related:

1. the spontaneity problem

   we now have a criterion for spontaneity for isolated systems

2. the asymmetry between work->heat (dissipation) and heat->work (power generation)

   at least we can use the new state law to predict the limitations on the latter.

Two problems remain:

1. we would like a spontaneity criterion *for all systems* (not just isolated ones)
2. we have a new state function S, but what is it?

5.1.2: Entropy on a microscopic scale

Let us start with the latter. Yes we can use S to explain the odd paradox between w and q both being forms energy on the one hand, but the conversion being easier in one direction than the other, but we have introduced the concept *entropy* purely as a phenomenon on iis own. Scientifically there is nothing wrong with such a phenomenological theory except that experience tells us that if you can understand the phenomenon itself better your theory becomes more powerful.

To understand entropy better we need to leave the macroscopic world and look at what happens on a molecular level and do statistics over many molecules. First, let us do a bit more statistics of the kind we will need.

5.1.2.1: Permutations

If we have n distinguishable objects, say playing cards we can arrange them in a large number of ways. For the first object in our series we have n choices, for number two we have $n-1$ choices (the first one being spoken for) etc. This means that in total we have

$$W = n(n-1)(n-2)\ldots.4.3.2.1 = n! \text{ choices.}$$

The quantity W is usually called the number of realizations in thermodynamics.

The above is true if the objects are all distinguishable. If they fall in groups within which they are not distinguishable we have to correct for all the swaps within these groups that do not produce a distinguishably new arrangement. This means that W becomes $\frac{n!}{a!b!c!\ldots z!}$ where a,b, c to z stands for the size of the groups. (Obviously $a+b+c+..+z=n$)

In thermodynamincs our 'group of objects' is typically an ensemble of systems, think of size N_{av} and so the factorial become horribly large. This makes it necessary to work with logarithms. Fortunately there is a good approximation (by Stirling) for a logarithmic factorial:

$$\ln N! \approx N \ln N - N$$

Causality vs. Correlation

In Europe nosey little children who are curious to find out where their newborn little brother or sister came from, often get told that the stork brought it during the night. When you look at the number of breeding pairs of this beautiful bird in e.g. Germany since 1960 you see a long decline to about 1980 when the bird almost got extinct. After that the numbers go up again due to breeding programs mostly. The human birth rate in the country follows a pretty much identical curve and the correlation between the two is very high (>0.98 or so). (Dr H. Sies in Nature (volume 332 page 495; 1988). Does this prove that storks indeed bring babies?



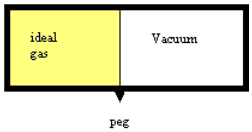
An adult White Stork. from Wikipedia (credit: Frank Vassen).

Answer:

No, it does ***not*** show causality, just a correlation due a common underlying factor. In this case that is the choices made by the German people. First they concentrated on working real hard and having few children to get themselves out of the poverty WWII had left behind and neglected the environment, then they turned to protect the environment and opened the doors to immigration of people, mostly from Muslim countries like Turkey or Morocco, that usually have larger families. The lesson from this is that you can only conclude causality ***if*** you are sure that there are no other intervening factors.

5.1.3: Changing the size of the box with the particles in it

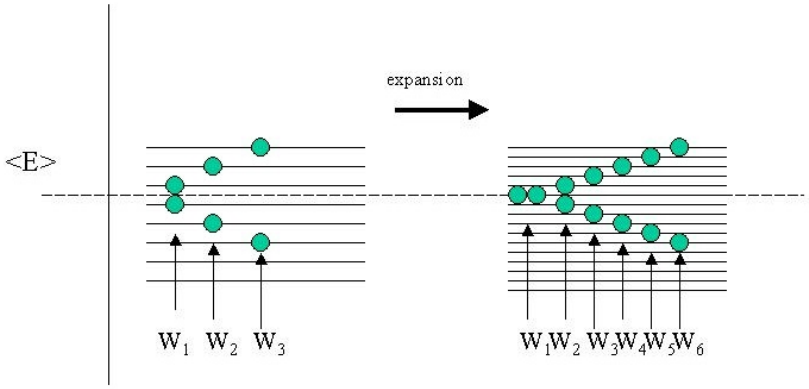
The expansion of an ideal gas against vacuum is really a wonderful *model experiment*, because *nothing else happens* but a spontaneous expansion and a change in entropy. No energy change, no heat, no work, no change in mass, no interactions, nothing. In fact, it does not even matter whether we consider it an isolated process or not. We might as well do so.



Physicists and Physical Chemists love to find such experiments that allows them to retrace *causality*. All this means that if we look at what happens at the atomic level, we should be able to retrace the ***cause*** of the entropy change. As we have seen before, the available energy states of particles in a box depend on the size of the box.

$$E_{kin} = \frac{h^2}{8ma^2}\left[n_1^2 + n_2^2 + n_2^2\right]$$

Clearly if the side (a and therefore the volume of the box changes, the energy spacing between the states will become smaller. Therefore during our expansion against vacuum, the energy states inside the box are changing. Because U does not change the *average* energy $\langle E \rangle$ is constant. Of course this average is taken over a great number of molecules (*systems*) in the gas (the *ensemble*), but let's look at just two of them and for simplicity let us assume that the energy of the states are equidistant (rather than quadratic in the quantum numbers n).



As you can see there is more than one way to skin a cat, or in this case to *realize* the same average $\langle E \rangle$ of the complete ensemble (of only two particles admittedly). Before expansion I have shown three realizations W_1, W_2, W_3 that add up to the same $\langle E \rangle$. After expansion however, there are more energy states available and the schematic figure shows twice as many realizations W in the same energy interval.

Boltzmann was the first to postulate that this is what is at the root of the entropy function, not so much the (total) energy itself (that stays the same!), but the number of ways the energy can be distributed in the ensemble. Note that because the ensemble average (or total) energy is identical, we could also say that the various realizations W represent the degree of *degeneracy* Ω of the ensemble.

Boltzmann considered a much larger (*canonical*) ensemble consisting of a great number of identical *systems* (e.g. molecules, but it could also be planets or so). If each of our systems already has a large number of energy states the systems can all have the same (total) energy but distributed in rather different ways. This means that two systems within the ensemble can either have the same distribution or a different one. Thus we can divide the ensemble A in subgroups a_j having the same energy distribution and calculate the number of ways to distribute energy in the ensemble A as

$$W = \frac{A!}{a1!a2!\ldots}.$$

Boltzmann postulated that entropy was directly related to the number of realizations W, that is the number of ways the same energy can be distributed in the ensemble. This leads immediately to the concept of order versus disorder, e.g, if the number of realizations is $W = 1$, all systems must be in the same state (W=A! / A!0!0!0!…) which is a very orderly arrangement of energies.

If we were to add two ensembles to each other the total number of possible arrangements W_{tot} becomes the product W_1W_2 but the entropies should be additive. As logarithms transform products into additions Boltzmann assumed that the relation between W and S should be logarithmic and wrote:

$$S = k \ln W$$

Again, if we consider a very ordered state, e.g. where all systems are in the ground state the number of realizations A!/A!= 1 so that the entropy is zero. If we have a very messy system where the number of ways to distribute energy over the many many different states is very large S becomes very large. Thus entropy is very large.

This immediately gives us the driving force for the expansion of a gas into vacuum or the mixing of two gases. We simply get more energy states to play with, this increases W. This means an increase in S. This leads to a spontaneous process.

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5.2: Nonequilibrium Isolated Systems Evolve in a Direction That Increases Their Energy Dispersal

In spontaneous processes for an isolated system, there is a competition between minimizing the energy of the system and increasing the dispersal of energy within the system. If energy is constant, then the system will evolve to maximize energy dispersal. If energy dispersal is not a factor, the system will evolve to minimize its energy. We already have a quantitative basis for the energy of a system and we need to do the same for energy dispersal. Suppose we have a small reversible change dU in the energy of an ideal gas. We know that U only depends on temperature:

$$dU = C_v dT$$

We also know that any reversible work would be volume work.

$$\delta w_{rev} = -PdV$$

This means that we can write:

$$\begin{aligned} \delta q_{rev} &= dU - \delta w_{rev} \\ &= C_v dT + PdV \end{aligned}$$

Let us examine if this represents an **exact differential**. If δq were an exact differential, we could write the total differential:

$$\delta q_{rev} = \left(\frac{\partial q}{dT}\right)_V dT + \left(\frac{\partial q}{dV}\right)_T dV$$

And the following would be true:

$$\frac{\partial^2 q_{rev}}{\partial T \partial V} = \frac{\partial^2 q_{rev}}{\partial V \partial T}$$

From our equation above, we know that:

$$\frac{\partial q_{rev}}{\partial T} = C_V$$

$$\frac{\partial q_{rev}}{\partial V} = P$$

Therefore, the following should be true:

$$\frac{\partial C_V}{\partial V} = \frac{\partial P}{\partial T}$$

However,

$$\frac{\partial C_v}{\partial V} = 0$$

Because C_v does not depend on volume (only T, just like U: it is its derivative). And:

$$\frac{\partial P}{\partial T} = \frac{\partial nRT}{\partial T} = \frac{nR}{V}$$

Which is not zero!! Clearly, δq_{rev} is **not a state function**, but look what happens if we multiply everything with an 'integration factor' $1/T$:

$$\frac{\delta q_{rev}}{T} = \frac{C_v}{T} dT + \frac{P}{T} dV$$

$$\frac{\partial C_v/T}{\partial V} = 0$$

Because $\frac{C_v}{T}$ does not depend on volume. However,

$$\frac{\partial(P/T)}{\partial T} = \frac{\partial(nR/V)}{\partial T} = 0$$

Thus, the quantity $dS = \frac{\delta q_{rev}}{T}$ is an exact differential, so S is a state function and it is called **entropy**. Entropy is the dispersal of energy, or equivalently, the measure of the number of possible microstates of a system.

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5.3: Unlike heat, Entropy is a State Function

5.3.1: Circular integrals

Because entropy is a state function, it integrates to zero over any circular path going back to initial conditions, just like U and H:

$$\oint dS = 0$$

$$\oint dH = 0$$

$$\oint dU = 0$$

As discussed previously, we can use this fact to revisit the isotherm + isochore + adiabat circular path (Figure 20.3.1).

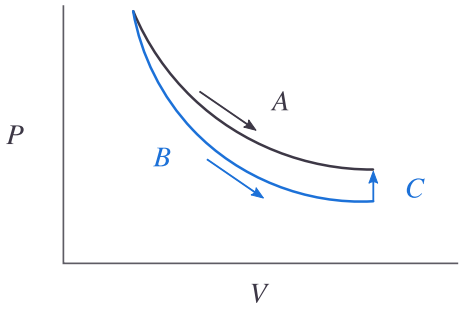


Figure 20.3.1 : A: isothermal expansion, B:adiabat, C:isochore (CC BY-NC; Ümit Kaya via LibreTexts)

Along adiabat B and isochore C:

- There is no heat transfer along adiabat B:

$$q_{rev,B} = 0$$

- There is no work along isochore C:

$$\delta w = 0$$

- But the temperature changes from T_2 back to T_1. This requires heat:

$$q_{rev,C} = C_V \Delta T$$

Along the isotherm A:

- We have seen that

$$q_{rev,A} = nRT \ln \frac{V_2}{V_1}$$

The quantities $q_{rev,A}$, $q_{rev,B}$, and $q_{rev,C}$ are ***not*** the same, which once again underlines that heat is a path function. How about entropy?

First, consider the combined paths of B and C:

$$q_{rev,B+C} = \int_{T_2}^{T_1} C_v dT$$

$$\int dS_{B+C} = \int \frac{dq_{rev,B+C}}{T} = \int_{T_2}^{T_1} \frac{C_v}{T} dT$$

We had seen this integral before from Section 19-6, albeit from T_1 to T_2:

$$\Delta S_{B+C} = nR \ln \frac{V_2}{V_1} \tag{5.3.1}$$

(Notice sign in Equation 5.3.1 is positive)

Along the isotherm A:

$$q_{rev,A} = nRT \ln \frac{V_2}{V_1}$$

T is a constant so we can just divide $q_{rec,A}$ by T to get ΔS_A:

$$\Delta S_A = nR \ln \frac{V_2}{V_1}$$

We took two different paths to get start and end at the same points. Both paths had the same change in entropy. Clearly entropy is a *state function* while q_{rev} is not.

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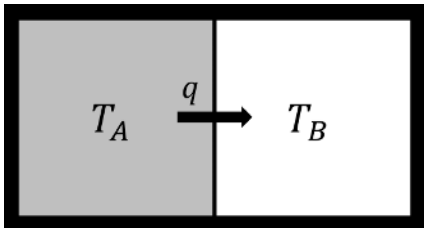
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5.4: The Second Law of Thermodynamics

5.4.1: Spontaneity of an isolated system

> An **isolated system** is a little more than just adiabatic. In the latter heat cannot get in or out. In an isolated system *nothing* gets in or out, neither heat nor mass nor even any radiation, such as light. The isolated system is like a little universe all to itself.

Let us consider a zero law process. We have two identical blocks of metal, say aluminum. They are each at thermal equilibrium, but at different temperatures. They are brought into contact with each other but isolated from the rest of the universe.



- ***Zeroth law***: *Heat will flow from hot to cold*
- ***First law***: *There is no change in total energy*

so:

$$dU_A = -dU_B$$

There is also no work so:

$$dU_A = \delta q_A + 0$$

Because U is a state function this makes q a state function as well, otherwise this equality does not hold. As there is only one term on the right there is only one path (along q). So we could write:

$$dU_A = dq_A$$

This implies that we do not need to worry about reversible and irreversible paths as there is only one path. Since:

$$dS = \frac{\delta q_{rev}}{T}$$

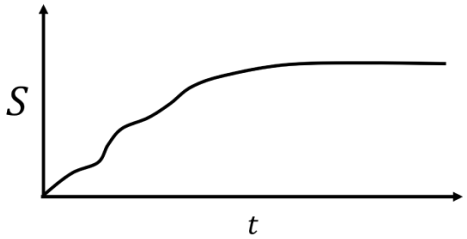
In this particular case:

$$TdS = \delta q_{rev} = dU$$

Thus we get:

$$dS = \frac{dU_A}{T_A} + \frac{dU_B}{T_B} = \frac{dU_A}{T_A} - \frac{dU_A}{T_B} = dU_A\left(\frac{1}{T_A} - \frac{1}{T_B}\right)$$

Clearly as long as the two temperatures are not the same dS is not zero and entropy is not conserved. Instead it is **increasing**. Over time, the temperatures will become the same (if the blocks are identical, the final temperature is the average of T_A and T_B) and the entropy will reach a maximum.



For our two identical blocks of metal (with same heat capacity, C_V), we can, in fact, derive that the entropy change:

$$\Delta S = C_V \ln \left[\frac{T_A^2 + T_B^2}{4 T_A T_B} \right].$$

This is indeed a positive quantity. In general, we can say for an isolated system:

$$dS \geq 0$$

Thus if we are dealing with a spontaneous (and isolated) process $dS > 0$ and ***entropy is being produced***. This gives us a ***criterion for spontaneity***.

5.4.2: Entropy exchange of an open system

In an isolated system dS represents the produced entropy dS_{prod} and this is a good criterion for spontaneity. Of course the requirement that the system is isolated is very restrictive and makes the criterion as good as useless... What happens in a system that can exchange heat with the rest of the universe? We do have entropy changes in that case, but part of them may have nothing to do with production, because we also have to consider the heat that is exchanged.

$$dS = dS_{prod} + dS_{exchange}$$

If the process is reversible (that is completely non-spontaneous) we are dealing with δq_{rev} so that $dS_{exchange} = \delta q_{rev}/T$, but that is also what dS_{tot} is equal to (by definition). This leaves no room for entropy production.

So we have:

Isolated: $dS = dS_{prod} + 0$

Reversible $dS = 0 + \delta q_{rev}/T$

Notice that this demonstrates that for non-isolated systems entropy change is *not* a good criterion for spontaneity at all... In the case the heat exchange is ***irreversible*** *part* of the entropy is entropy production by the system:

Irreversible: $dS = dS_{prod} + \delta q_{irrev}/T$

$dS > \delta q_{irrev}/T$ in this case.

Generalizing the isolated, irreversible and reversible cases we may say:

$$dS \geq \frac{\delta q}{T}$$

This is the ***Clausius inequality***.

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5.5: The Famous Equation of Statistical Thermodynamics is S=k ln W

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:

$$S = k_b \ln(W) \tag{5.5.1}$$

W is the number of available microstates in a macrostate (ensemble of systems) and can be taken as the quantitative measure of energy dispersal in a macrostate:

$$W = \frac{A!}{\prod_j a_j!}$$

Where a_j is the number of systems in the ensemble that are in state j and A represents the total number of systems in the ensemble:

$$A = \sum_j a_j$$

Equation 20.5.1 is a rather famous equation etched on Boltzmann's grave marker in commemoration of his profound contributions to the science of thermodynamics (Figure 5.5.1).



Figure 5.5.1: Ludwig Boltzmann (1844 - 1906)

Example 5.5.1:

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 5.5.1):

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

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

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

5.5.1: Contributors and Attributions

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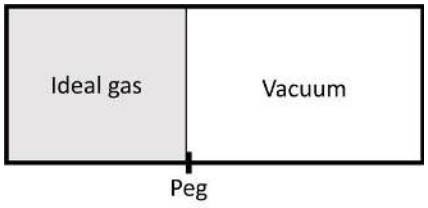
5.6: We Must Always Devise a Reversible Process to Calculate Entropy Changes

The second law of thermodynamics can be formulated in many ways, but in one way or another they are all related to the fact that the state function entropy, S, tends to increase over time in isolated systems. For a long time, people have looked at the entire universe as an example of an isolated system and concluded that its entropy must be steadily increasing until $\delta S_{universe}$ becomes zero. As we will see below, the second law has important consequences for the question of how we can use heat to do useful work.

> Of late, cosmologists like the late Richard Hawkins have begun to question the assumption that the entropy of the universe is steadily increasing. The key problem is the role that gravity and relativity play in creating black holes.

5.6.1: Vacuum Expansion

Let's compare two expansions from V_1 to V_2 for an ideal gas, both are isothermal. The first is an irreversible one, where we pull a peg an let the piston move against vacuum:



The second one is a reversible isothermal expansion from V_1 to V_2 (and P_1 to P_2) that we have examined before. In both cases, the is no change in internal energy since T does not change. During the irreversible expansion, however, there is also no volume work because the piston is expanding against a vacuum and the following integral:

$$\int -P_{ext} dV = 0$$

integrates to zero. The piston has nothing to perform work against until it slams into the right hand wall. At this point $V = V_2$ and then dV becomes zero. This is not true for the reversible isothermal expansion as the external pressure must always equal the internal pressure.

> *No energy and no work means no heat!*

Clearly the zero heat is irreversible heat ($q_{irr} = 0$) and this makes it hard to calculate the entropy of this spontaneous process. But then this process ends in the same final state as the reversible expansion from V_1 to V_2. We know that dU is still zero, but now $\delta w_{rev} = -\delta q_{rev}$ is nonzero. We calculated its value before:

$$q_{rev} = nRT \ln \left(\frac{V_2}{V_1} \right) \tag{5.6.1}$$

The Claussius definition of entropy change can be used to find ΔS (under constant temperature).

$$\Delta S = \frac{q_{rev}}{T} \tag{5.6.2}$$

Substituting Equation 5.6.1 into Equation 5.6.2 results in

$$\Delta S = nR \ln \left(\frac{V_2}{V_1} \right)$$

As S is a state function this equation also holds for the irreversible expansion against vacuum.

> Always calculate the entropy difference between two points along a **reversible** path.

For the irreversible expansion into vacuum we see that

$$\begin{aligned}\Delta S_{\text{total}} &= \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \\ &= nR\ln\left(\frac{V_2}{V_1}\right) + 0 \\ &= nR\ln\left(\frac{V_2}{V_1}\right)\end{aligned}$$

For the reversible expansion, heat is transferred to the system while the system does work on the surroundings in order to keep the process isothermal:

$$\Delta S_{\text{sys}} = nR\ln\left(\frac{V_2}{V_1}\right)$$

The entropy change for the surrounding is the opposite of the system:

$$\Delta S_{\text{surr}} = -nR\ln\left(\frac{V_2}{V_1}\right)$$

This is because the amount of heat transferred to the system is the same as the heat transferred from the surroundings and this process is reversible so the system and surroundings are at the same temperature (equilibrium). Heat is related to entropy by the following equation:

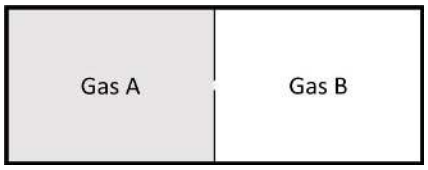
$$dS = \frac{\delta q}{T}$$

Therefore, the total entropy change for the reversible process is zero:

$$\begin{aligned}\Delta S_{\text{total}} &= \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \\ &= nR\ln\left(\frac{V_2}{V_1}\right) - nR\ln\left(\frac{V_2}{V_1}\right) \\ &= 0\end{aligned}$$

5.6.2: The Mixing of Two Gases

Consider two ideal gases at same pressure separated by a thin wall that is punctured. Both gases behave as if the other one is not there and again we get a spontaneous process, mixing in this case.



If the pressure is the same the number of moles of each gas should be proportional to the original volumes, V_A and V_B, and the total number of moles to the total volume V_{tot}.

For gas A we can write:

$$\Delta S_A = n_A R\ln\frac{V_{tot}}{V_A} = n_A R\ln\frac{n_{tot}}{n_A}$$

and similarly for gas B we can write:

$$\Delta S_B = n_B R\ln\frac{V_{tot}}{V_B} = n_B R\ln\frac{n_{tot}}{n_B}$$

The total entropy change is therefore the sum of constituent entropy changes:

$$\Delta S = \Delta S_A + \Delta S_B$$

and the entropy change total per mole of gas is:

$$\frac{\Delta S}{n_{tot}} = R\frac{\left[n_B\ln\frac{n_{tot}}{n_B} + n_A\ln\frac{n_{tot}}{n_A}\right]}{n_{tot}} \tag{5.6.3}$$

Equation 5.6.3 can be simplified using mole fractions:

$$\chi_A = \frac{n_A}{n_{tot}}$$

and the mathematical relationship of logarithms that:

$$\ln\left(\frac{x}{y}\right) = -\ln\left(\frac{y}{x}\right)$$

to:

$$\Delta\bar{S} = -R\left[\chi_A \ln \chi_A + \chi_B \ln \chi_B\right] \tag{5.6.4}$$

In the case of mixing of more than two gases, Equation 5.6.4 can be expressed as:

$$\Delta\bar{S} = -R\sum \chi_i \ln \chi_i \tag{5.6.5}$$

This entropy expressed in Equations 5.6.4 and 5.6.5 is known as the **entropy of mixing**; its existence is the major reason why there is such a thing as diffusion and mixing when gases, and also solutions (even solid ones), are brought into contact with each other.

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5.7: Thermodynamics Provides Insight into the Conversion of Heat into Work

Heat and work are both forms of transferring energy, and under the right circumstance, one form may be transformed into the other. However, the second law of thermodynamics puts a limitation on this. To go from work to heat is called dissipation and there is no limitation on this at all. In fact it was through dissipation (by friction) that we discovered that heat and work were both forms of energy. There is, however, a limitation on converting heat to work.

5.7.1: The Carnot Cycle

Let's consider a circular, reversible path of an ideal gas on a PV diagram in Figure **5.7.1**:

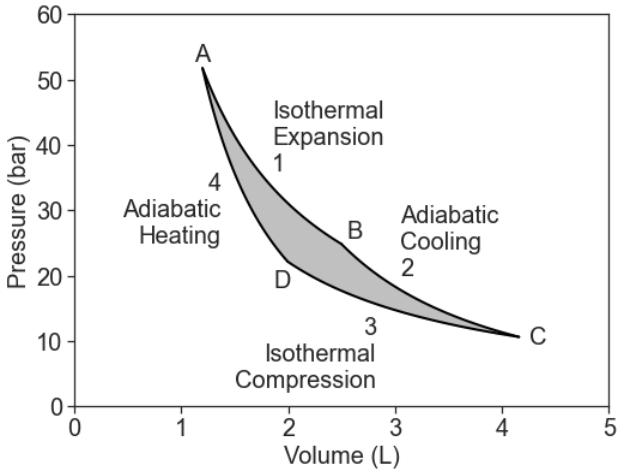


Figure **5.7.1**: A circular, reversible path of a Carnot cycle as an ideal gas on a PV diagram. (CC BY 4.0; Jerry LaRue via LibreTexts)

This cycle forms the 4-stage Carnot cycle heat engine. A heat engine converts heat energy into work. The cycle consists of:

1. Isothermal expansion at the hot temperature, T_h:

$$\Delta U_1 = w_1 + q_h = 0$$

2. Adiabatic cooling from T_h to T_c:

$$\Delta U_2 = w_2$$

3. Isothermal compression at the cold temperature, T_c:

$$\Delta U_3 = w_3 + q_c = 0$$

4. Adiabatic heating from T_c to T_h:

$$\Delta U_4 = w_4$$

The total four-step process produces work because $w_{hot} > w_{cold}$. The work is the integral under the upper isotherm minus the one under the lower curve, i.e. the surface *area in between*.

Sadi Carnot

Sadi Carnot was a French engineer at the beginning of the 19th century. He considered a cyclic process involving a cylinder filled with gas. This cycle the Carnot cycle contributed greatly to the development of thermodynamics and the improvement of the steam engine. Carnot demonstrated that the cold temperature on the right is as important as the heat source on the left in defining the possible efficiency of a heat engine

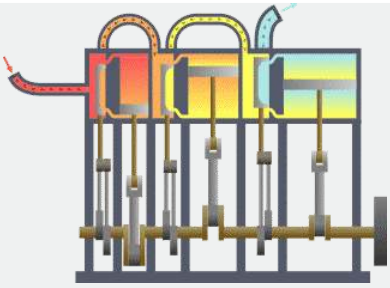


Figure 5.7.2: Animation of a typical vertical triple-expansion engine. (CC SA-BY 2.5; Emoscopes)

5.7.2: Efficiency

Of course we spend good money on the fuel to start the cycle by heating things up. So how much work do we get for the heat we put in? In other words, we want to know how efficient our heat engine is. The efficiency, η of a heat engine is:

$$\eta = \frac{|w_{\text{cycle}}|}{q_h} = \frac{q_h + q_c}{q_h} = 1 + \frac{q_c}{q_h}$$

To get the work of the cycle, we can make use of internal energy as a state function. As the path is circular the circular integrals for U is zero:

$$\begin{aligned} \oint dU &= \Delta U_{\text{cycle}} \\ &= \sum \Delta U_i \\ &= w_1 + q_h + w_2 + w_3 + q_c + w_4 \\ &= 0 \end{aligned}$$

Rearranging:

$$\begin{aligned} q_h + q_c &= -w_1 - w_2 - w_3 - w_4 \\ &= -w_{\text{cycle}} \end{aligned}$$

An ideal engine would take $q_h \rightarrow q_c$ with 100% efficiency. The work of the cycle will be equivalent to the heat transfer. For ideal gases:

1. $w_1 = -RT_h \ln\left(\frac{V_B}{V_A}\right) = -q_h$
2. $dU = \delta w = \bar{C}_V dT \rightarrow w_2 = \bar{C}_V (T_c - T_h)$
3. $w_3 = -RT_c \ln\left(\frac{V_D}{V_C}\right) = -q_c$
4. $w_4 = \bar{C}_V (T_h - T_c)$

Finding an expression for w_{cycle}:

$$\begin{aligned} w_{\text{cycle}} &= -RT_h \ln\left(\frac{V_B}{V_A}\right) + \bar{C}_V (T_c - T_h) - RT_c \ln\left(\frac{V_D}{V_C}\right) + \bar{C}_V (T_h - T_c) \\ &= -RT_h \ln\left(\frac{V_B}{V_A}\right) - RT_c \ln\left(\frac{V_D}{V_C}\right) = -R(T_h - T_c) \ln\left(\frac{V_B}{V_A}\right) \end{aligned}$$

We have an expression for work, so we can evaluate the efficiency, η. The efficiency of the Carnot engine is:

$$\eta = \frac{|w_{\text{cycle}}|}{q_h} = \frac{R(T_h - T_c) \ln\left(\frac{V_B}{V_A}\right)}{RT_h \ln\left(\frac{V_B}{V_A}\right)} = \frac{T_h - T_c}{T_h} = 1 - \frac{T_c}{T_h}$$

Paths (2) and (4) are adiabats, so we can also use entropy, S, to get the same solution:

$$\oint dS = \frac{q_h}{T_h} + \frac{q_c}{T_c} = 0$$

Therefore:

$$\frac{q_c}{q_h} = -\frac{T_c}{T_h}$$

And we get that:

$$\eta = 1 + \frac{q_c}{q_h} = 1 - \frac{T_c}{T_h} \tag{5.7.1}$$

As you see we can only get full efficiency if T_{cold} is 0 K, which is never (i.e., we always waste energy). Another implication is that if $T_c = T_h$ then **no work** can be obtained, no matter how much energy is available in the from of heat. Or in other words, if one dissipates work into heat isothermally, *none* of it can be retrieved. Equation 5.7.1 is not very forgiving at all. Just imaging that you have a heat source of say 400 K (a superheated pool of water, e.g. a geyser) and you are dumping in the river at room temperature 300 K. The best efficiency you'll ever get is:

$$\eta = 1 - \frac{300}{400} = 24\%$$

Sadly, you'd be dumping three quarters of your energy as heat in the river (and that is best case scenario as there are always more losses, e.g. due to friction). The arrow saying Q_C in Figure 5.7.3 should then be three times as fat as the one that says w.

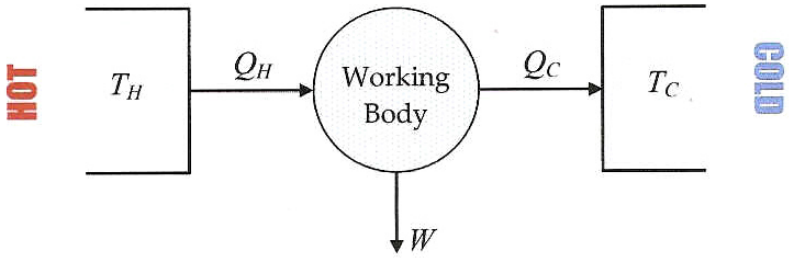


Figure 5.7.3: Carnot engine diagram (modern) - where an amount of heat Q_H flows from a high temperature $T_H$furnace through the fluid of the "working body" (working substance) and the remaining heat Q_C flows into the cold sink T_C, thus forcing the working substance to do mechanical work W on the surroundings, via cycles of contractions and expansions. (Public Domain; Eric Gaba)

5.7.3: Heat pumps

So getting our work from heat is hard and always less than 100% successful. The other way around should be easy. After all, we can dissipate work into heat freely even under isothermal conditions!

What happens if we let the heat engine run backwards? Consider reversing all the flows in the above diagram. Obviously we must *put in work* to make the cycle run in reverse. The heat will now flow from cold to hot, say from your cold garden into your nice and warm apartment. The amount of heat you get in your humble abode will be the sum of all the work (say 100 Joules) you dissipate *plus* the heat you pumped out of the garden (say 300 Joules). Thus if you are willing to pay for the energy you dissipate (100 Joules), you may well end up with a total of 400 Joules of heat in your apartment! Obviously if it is heat you after this is a better deal than just dissipating the work in your apartment (by burning some oil). Then you'd only get 100 J for your precious buck.

Dissipating it as electrical heating is even worse because you would

1. first burn (a lot more!) oil to generate heat
2. use this heat to produce electrical work at great expense because a lot of the heats gets dumped at the low temperature side (the river or so)
3. dissipate the work again in your apartment (without using it to pump any heat out of the garden)

Refrigerators are also heat pumps. They heat the kitchen by pumping heat from its innards to the kitchen. If I keep the door open, however, all it does is dissipate precious electrical work, because the pumped heat will flow back into its innards and spoil the milk.

5.7.4: Stirling Engine

Let's consider another type of heat engine, the Stirling engine. The Stirling engine uses a circular reversible path in an ideal PV diagram in Figure 5.7.4:

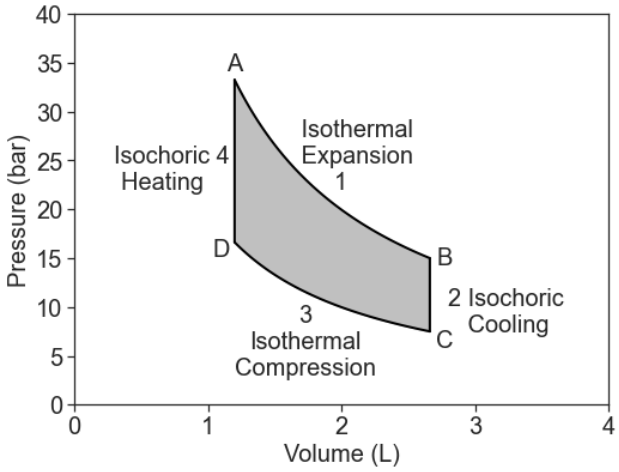


Figure **5.7.4**: an ideal PV diagram of the Stirling engine. (CC BY 4.0; Jerry LaRue via LibreTexts)

The path consists of four steps:

1. *Isothermal* expansion at the hot temperature T_h:

   $$q_1 = q_h = -w$$

   and we get work **out** (i.e., negative work):

   $$w_h = -RT_h \ln\left(\frac{V_B}{V_A}\right)$$

2. *Isochoric* heating from T_c to T_h (with constant C_V):

   $$q_2 = \frac{C_V}{\Delta T} \tag{5.7.2}$$

3. *Isothermal* compression at the cold temperature T_c:

   $$q_3 = q_c = -w$$

   and we must put work **in** (i.e., positive work):

   $$w_c = -RT_c \ln\left(\frac{V_D}{V_C}\right) = RT_c \ln\left(\frac{V_B}{V_A}\right)$$

4. *Isochoric* cooling from T_h to T_c (with constant C_V):

   $$q_4 = -\frac{C_V}{\Delta T} \tag{5.7.3}$$

Notice that this gray area *vanishes* if $T_h = T_c$. Obviously how cold the cold side is of great importance! The amount of work is also equal to the difference in the heat picked up at high temperature q_h and dumped at low temperature q_c. The isochoric heats cancel. The problem is that q_c is only zero if the cold temperature is 0 K. That means that we can never get all the heat we pick up at high temperatures to come out as work.

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5.8: Entropy Can Be Expressed in Terms of a Partition Function

We have seen that the partition function of a system gives us the key to calculate thermodynamic functions like energy or pressure as a moment of the energy distribution. We can extend this formulism to calculate the entropy of a system once its Q is known. We can start with Boltzmann's (statistical) definition of entropy:

$$S = k\ln(W) \tag{5.8.1}$$

with

$$W = \frac{A!}{\prod_j a_j!}$$

Combining these equations, we obtain:

$$S_{ensemble} = k\ln\frac{A!}{\prod_j a_j!}$$

Rearranging:

$$S_{ensemble} = k\ln A! - k\sum_j \ln a_j!$$

Using Sterling's approximation:

$$\begin{aligned} S_{ensemble} &= kA\ln A - kA - k\sum_j a_j \ln a_j + k\sum_j a_j \\ &= kA\ln A - k\sum_j a_j \ln a_j \end{aligned}$$

Since:

$$\sum_j a_j = A$$

The probability of finding the system in state a_j is:

$$p_j = \frac{a_j}{A}$$

Rearranging:

$$a_j = p_j A$$

Plugging in:

$$S_{ensemble} = kA\ln A - k\sum_j p_j A \ln p_j A$$

Rearranging:

$$S_{ensemble} = kA\ln A - k\sum_j p_j A\ln p_j - k\sum_j p_j A\ln A$$

If A is constant, then:

$$k\sum_j p_j A\ln A = kA\ln A\sum_j p_j$$

Since:

$$\textstyle\sum_j p_j = 1$$

We get:

$$S_{ensemble} = kA \ln A - k \sum_j p_j A \ln p_j - kA \ln A$$

The first and last term cancel out:

$$S_{ensemble} = -k \sum_j p_j A \ln p_j$$

We can divide by A to get the entropy of the system:

$$S_{system} = -k \sum_j p_j \ln p_j \tag{5.8.2}$$

If all the p_j are zero except for the for one, then the system is perfectly ordered and the entropy of the system is zero. The probability of being in state j is

$$p_j = \frac{e^{-\beta E_j}}{Q} \tag{5.8.3}$$

Plugging Equation 5.8.3 into Equation 5.8.2 results in

$$\begin{aligned} S &= -k \sum_j \frac{e^{-\beta E_j}}{Q} \ln \frac{e^{-\beta E_j}}{Q} \\ &= -k \sum_j \frac{e^{-\beta E_j}}{Q} (-\beta E_j - \ln Q) \\ &= -\beta k \sum_j \frac{E_j e^{-\beta E_j}}{Q} + \frac{k \ln Q}{Q} \sum_j e^{-\beta E_j} \end{aligned}$$

Making use of:

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

And:

$$\sum \frac{e^{-\beta E_j}}{Q} = \sum p_j = 1$$

We obtain:

$$S = \frac{U}{T} + k \ln Q \tag{5.8.4}$$

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5.9: The Statistical Definition of Entropy is Analogous to the Thermodynamic Definition

The laws of thermodynamics can be understood in two ways: by looking at large-scale properties like temperature and pressure, or by examining how countless tiny atoms move and interact. Both perspectives lead to the same laws, even though the reasoning behind them is quite different.

We learned earlier that entropy, S, is related to the number of microstates, W, in an ensemble with A systems:

$$S_{ensemble} = k_B \ln W \tag{5.9.1}$$

and

$$W = \frac{A!}{\prod_j a_j!} \tag{5.9.2}$$

Combining Equations 5.9.1 and 5.9.2 to get:

$$\begin{aligned} S_{ensemble} &= k_B \ln \frac{A!}{\prod_j a_j!} \\ &= k_B \ln A! - k_B \sum_j \ln a_j! \end{aligned}$$

Using Sterling's approximation:

$$\ln A! \approx A \ln A - A$$

We obtain:

$$S_{ensemble} = k_B A \ln A - k_B A - k_B \sum_j a_j \ln a_j + k_B \sum a_j$$

Since:

$$A = \sum a_j$$

The expression simplifies to:

$$S_{ensemble} = k_B A \ln A - k_B \sum_j a_j \ln a_j$$

We can make use of the fact that the number of microstates in state j is equal to the total number of microstates multiplied by the probability of finding the system in state j, p_j:

$$a_j = p_j A$$

Plugging in, we obtain

$$\begin{aligned} S_{ensemble} &= k_B A \ln A - k_B \sum_j p_j A \ln p_j A \\ &= k_B A \ln A - k_B \sum_j p_j A \ln p_j - k_B \sum_j p_j A \ln A \end{aligned}$$

Since A is a constant and the sum of the probabilities of finding the system in state j is always 1:

$$\sum p_j = 1$$

The first and last term cancel out:

$$S_{ensemble} = -k_B A \sum_j p_j \ln p_j$$

We can use that the entropy of the system is the entropy of the ensemble divided by the number of systems:

$$S_{system} = S_{ensemble}/A$$

Dividing by A, we obtain:

$$S_{system} = -k_B \sum_j p_j \ln p_j$$

We can differentiate this equation and dropping the subscript:

$$dS = -k_B \sum_j (dp_j + \ln p_j dp_j)$$

Since $\sum_j p_j = 1$, the derivative $\sum_j dp_j = 0$:

$$dS = -k_B \sum_j \ln p_j dp_j$$

In short:

$$\sum_j \ln p_j dp_j = -\frac{\delta q_{rev}}{k_B T}$$

Plugging in:

$$dS = \frac{\delta q_{rev}}{T} \tag{5.9.3}$$

The thermodynamic definition of entropy comes from macroscopic observations. In classical thermodynamics, entropy is defined as the measure of energy dispersal in a system (Equation 5.9.3). It tells us how much heat is spread out or distributed in a system at temperature. This definition is practical and works well at the bulk level but does not say why entropy behaves this way.

The statistical definition of entropy in Equation 5.9.1, developed by Boltzmann, defines entropy in terms of the number of possible microstates that correspond to the same overall macroscopic state (macrostate). This shows that entropy measures the degree of microscopic disorder or multiplicity of arrangements consistent with what we see at the macroscopic level.

Both definitions describe the same underlying concept:

- The thermodynamic view says entropy measures the spread of energy in terms of heat and temperature.
- The statistical view says entropy measures the spread of possible microstates that energy can occupy.

They are equivalent because a system with more accessible microstates (higher disorder) will also tend to have greater energy dispersal, and thus higher entropy. In fact, the statistical definition explains why the thermodynamic definition works: macroscopic energy dispersal arises from the overwhelming number of microscopic ways energy can be arranged.

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5.E: Entropy and The Second Law of Thermodynamics (Exercises)

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CHAPTER OVERVIEW

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6.E: Entropy and the Third Law of Thermodynamics (Exercises)

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6.1: Entropy Increases With Increasing Temperature

Learning Objectives

- Define entropy and its relation to energy flow.

6.1.1: Entropy versus temperature

We can put together the first and the second law for a reversible process with no other work than volume (PV) work and obtain:

$$dU = \delta q_{rev} + \delta w_{rev}$$

Entropy is the dispersal of energy and is related to heat:

$$\delta q_{rev} = TdS$$

Work is related to the change in volume:

$$\delta w_{rev} = -PdV$$

Plugging these into our expression for dU for reversible changes:

$$dU = TdS - PdV$$

We no longer have any path functions in the expression, as U, S and V are ***all state functions***. This means this expression must be an exact differential. We can generalize the expression to hold for irreversible processes, but then the expression becomes an inequality:

$$dU \leq TdS - PdV$$

This equality expresses U as a function of two variables, entropy and volume: $U(S,V)$. S and V are the ***natural variables*** of U.

6.1.1.1: Entropy and heat capacity

At constant volume, dU becomes:

$$dU = TdS$$

Recall that internal energy is related to constant volume heat capacity, C_V:

$$C_V = \left(\frac{dU}{dT}\right)_V$$

Combining these two expressions, we obtain:

$$dS = \frac{C_V}{T}dT$$

Integrating:

$$\Delta S = \int_{T_1}^{T_2} \frac{C_V(T)}{T}dT$$

If we know how C_V changes with temperature, we can calculate the change in entropy, ΔS. Since heat capacity is always a positive value, entropy must increase as the temperature increases. There is nothing to stop us from expressing U in ***other*** variables, e.g. T and V. In fact, we can derive some interesting relationships if we do.

Example 21.1.1

1. Write U as a function of T and V.
2. Write U as a function of its natural variables.
3. Rearrange (2) to find an expression for dS.
4. Substitute (1) into (3) and rearrange. This is the definition of C_V.

5. Write out S as a function of T and V.

We can also derive an expression for the change in entropy as a function of constant pressure heat capacity, C_P. To start, we need to change from internal energy, U, to enthalpy, H:

$$\begin{aligned} H &= U + PV \\ dH &= dU + d(PV) \\ &= dU + PdV + VdP \end{aligned}$$

For reversible processes:

$$\begin{aligned} dH &= dU + PdV + VdP \\ &= TdS - PdV + PdV + VP \\ &= TdS + VdP \end{aligned}$$

The natural variables of the enthalpy are S and P (not: V). A similar derivation as above shows that the temperature change of entropy is related to the constant pressure heat capacity:

$$dH = TdS + VdP$$

At constant pressure:

$$dH = TdS + VdP$$

Recall that:

$$C_P = \frac{dH}{dT}$$

Combining, we obtain:

$$dS = \frac{C_P}{T} dT$$

Integrating:

$$\Delta S = \int_{T_1}^{T_2} \frac{C_P(T)}{T} dT$$

This means that if we know the heat capacities as a function of temperature we can calculate how the entropy changes with temperature. Usually it is easier to obtain data under constant P conditions than for constant V, so that the route with C_p is the more common one.

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6.2: The 3rd Law of Thermodynamics Puts Entropy on an Absolute Scale

Learning Objectives

- Recall the third law of thermodynamics.

In the unlikely case that we have C_p data all the way from 0 K we could write:

$$S(T) = S(0) + \int_0^T C_p(T)\, dT$$

It is tempting to set the $S(0)$ to zero and make the entropy thus an absolute quantity. As we have seen with enthalpy, it was not really possible set $H(0)$ to zero. All we did was define ΔH for a particular process, although if C_p data are available we could construct an enthalpy function (albeit with a floating zero point) by integration of C_P (instead of C_p/T!). The situation is different for entropy S than for H. Here we can actually put things on an ***absolute*** scale. Both Nernst and Planck have proposed to do so. Nernst postulated that for a pure and perfect crystal S should indeed to go to zero as T goes to zero (Figure 6.2.1).

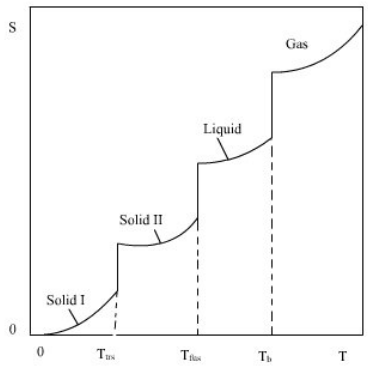


Figure 6.2.1: Entropy as a Function of Temperature. The entropy (S) of a substance (compound or element) as a function of temperature (T). Note that there are three phase transitions in this system with evolution through two solid phases. These result in positive jumps in the entropy.

Example 6.2.1: Sulfur

Sulfur has two solid crystal structure, rhombic and monoclinic. At 368.5 K, the entropy of the phase transition from rhombic to monoclinic, $S_{(rh)} \rightarrow S_{(mono)}$, is:

$$\Delta_{trs} S(368.5\ \text{K}) = 1.09\ \frac{\text{J} \cdot \text{mol}}{\text{K}}$$

As the temperature is lowered to 0 K, the entropy of the phase transition approaches zero:

$$\lim_{T \to 0} \Delta_r S = 0$$

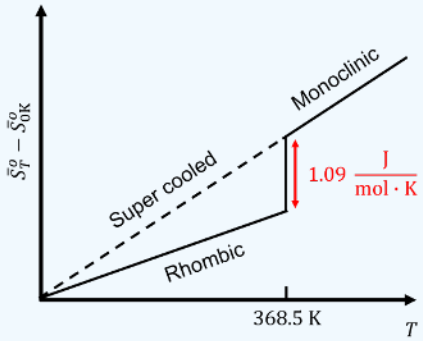


Figure 6.2.2: Schematic showing the entropy of the rhombic and monoclinic structures of sulfur as a function of temperature.

This shows that the entropy of the two crystalline forms are the same. The only way is if all species have the same absolute entropy at 0 K. For energy dispersal at 0 K:

1. Energy is as concentrated as it can be.
2. Only the very lowest energy states can be occupied.

For a pure, perfect crystalline solid at 0 K, there is only one energetic arrangement to represent its lowest energy state. We can use this to define a natural zero, giving entropy an absolute scale. The **third Law of Thermodynamics** states that the entropy of a pure substance in a perfect crystalline form is 0 $\frac{J}{mol \cdot K}$ at 0 K:

$$\bar{S}^{\circ}_{0\,\mathrm{K}} = 0$$

This is consistent with our molecular formula for entropy:

$$S = k \ln W$$

For a perfect crystal at 0 K, the number of ways the total energy of a system can be distributed is one ($W = 1$). The $\ln W$ term goes to zero, resulting in the perfect crystal at 0 K having zero entropy (Figure **6.2.3***a*).

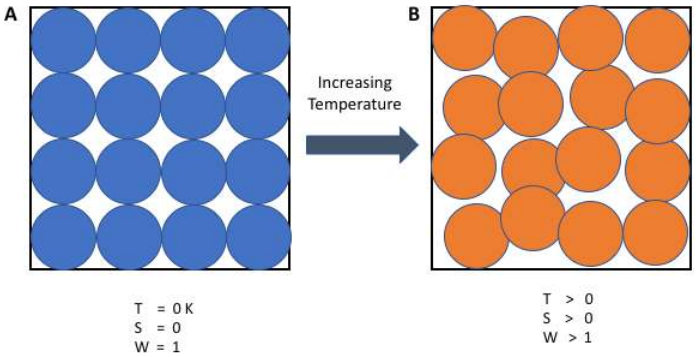


Figure **6.2.3**: (a) Single possible configuration for a system at absolute zero, i.e., only one microstate is accessible. Thus $S = k \ln W = 0$. (b) At temperatures greater than absolute zero, multiple microstates are accessible due to atomic dislocation (exaggerated in the figure). Since the number of accessible microstates is greater than 1, $S = k \ln W > 0$. (CC BY-SA 4.0; BlyumJ via Wikipedia)

It is certainly true that for the great majority of materials we end up with a crystalline material at sufficiently low materials (although there are odd exceptions like liquid helium). However, it should be mentioned that a completely *perfect* crystal can only be grown at zero Kelvin! It is not possible to grow anything at 0 K however. At any finite temperature the crystal always incorporates defects, more so if grown at higher temperatures. When cooled down very slowly the defects tend to be ejected from the lattice for the crystal to reach a new equilibrium with less defects. This tendency towards less and less disorder upon cooling is what the third law is all about.

However, the ordering process often becomes impossibly slow, certainly when approaching absolute zero. This means that real crystals always have *some* frozen in imperfections. Thus there is always *some* residual entropy. Fortunately, the effect is often too small to be measured. This is what allows us to ignore it in many cases (but not all). We could state the Third law of thermodynamics as follows:

Definition: Third law of thermodynamics

The entropy of a perfect crystal approaches zero when T approaches zero (but perfect crystals do not exist).

$$\lim_{T \to 0} S^{\circ}(T) = 0 \qquad (6.2.1)$$

Another complication arises when the system undergoes a phase transition, e.g. the melting of ice. As we can write:

$$\Delta_{fus} H = q_P$$

If ice and water are in equilibrium with each other the process is quite reversible and so we have:

$$\Delta_{fus}S = \frac{q_{rev}}{T} = \frac{\Delta_{fus}H}{T}$$

This means that at the melting point the curve for S makes a sudden jump by this amount because all this happens at one an the same temperature. Entropies are typically calculated from calorimetric data (e.g., C_P measurements) and tabulated in standard molar form.

There are some clear trends in the entropy values of elements and molecules, e.g. when the noble gas gets heavier this induces more entropy. This is a direct consequence of the particle in the box formula. It has mass in the denominator and therefore the energy levels get more crowded together when m increases: more energy levels, more entropy.

> *The energy levels get more crowded together when m increases: more energy levels, more entropy*

There are tables for $H^\circ(T) - H^\circ(0)$, $S^\circ(T)$ and $G^\circ(T) - H^\circ(0)$ as a function of temperature for numerous substances. As we discussed before the plimsoll defines are standard state in terms of pressure (1 bar) and of concentration reference states, if applicable, but temperature is the one of interest.

Residual Entropy in Carbon Monoxide

For most substances, the assumption made in Equation 6.2.1 regarding the Third Law is generally valid; however, there are notable exceptions, such as carbon monoxide. In its solid state, carbon monoxide molecules would ideally be fully ordered at absolute zero. However, due to the similar sizes of carbon and oxygen atoms and the molecule's weak dipole, it is possible for some molecules to be positioned "upside down"—with oxygen occupying a carbon site and vice versa (i.e., the C≡O and O≡C orientations are nearly isoenergetic in the lattice). When the crystal forms at higher temperatures, this disorder increases entropy, thereby lowering the Gibbs energy (G). Essentially, if each molecule can be placed into the lattice in two different orientations, the total number of possible configurations (W_{disorder}) for N molecules is 2^N.

This leads to an additional contribution to the entropy of

$$S_{disorder} = k \ln W_{disorder} = k \ln 2^N = Nk \ln 2 = 5.7\,\text{J/(mol K)}$$

At lower temperatures, the entropy term in $\Delta G = \Delta H - T\Delta S$ diminishes in significance, and the crystal should theoretically transition to a more ordered state with lower entropy. However, in practice, the kinetics of this process are extremely slow, preventing the ordering from occurring. As a result, solid CO retains **a nonzero entropy** even as it approaches absolute zero (Equation 6.2.1).

In principle *all* crystalline materials have this effect to some extent, but CO is unusual because the concentration of 'wrongly aligned' entities is of the order of 50% rather than say 1 in 10^{13} (a typical defect concentration in say single crystal silicon). The experimental residual entropy of CO is approximately 4.4 J/(mol K); this indicates that the two orientations of CO are not exactly identical in energy (i.e., equal probability of forming), which would give a residulate entropy of 5.7 J/(mol K).

? Exercise 6.2.1

The entropy of a crystal composed of one mole of identical molecules is measured to be 9.134 J/K at 0 K. Determine the number of possible orientations each molecule can adopt within the crystal. Additionally, illustrate a molecule that would be expected to exhibit this behavior.

6.2.1: Summary

Residual entropy quantifies the remaining disorder or randomness in a system even at absolute zero temperature (0 K). According to the Third Law of Thermodynamics, the entropy of a perfect crystal approaches zero as the temperature nears absolute zero. However, some systems retain a nonzero entropy at 0 K, exhibiting residual entropy. This phenomenon represents an exception to the Third Law rather than a contradiction. The law assumes a perfect crystal with a singular, unique ground state, whereas systems with residual entropy, such as carbon monoxide, possess multiple degenerate ground states.

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6.3: The Entropy of a Phase Transition can be Calculated from the Enthalpy of the Phase Transition

Phase transitions (e.g. melting) often occur under equilibrium conditions. We have seen that both the H and the S curves undergo a discontinuity at constant temperature during melting, because there is an enthalpy of fusion to overcome. For a general phase transition at equilibrium at constant T and P, we can say that:

$$\begin{aligned}\Delta_{trs}G &= \Delta_{trs}H - T_{trs}\Delta_{trs}S \\ &= 0 \\ \Delta_{trs}H &= T_{trs}\Delta_{trs}S \\ \frac{\Delta_{trs}H}{T_{trs}} &= \Delta_{trs}S\end{aligned}$$

For melting of a crystalline solid, we now see *why* there is a sudden jump in enthalpy. The reason is that the solid has a much more ordered structure than the crystalline solid. The decrease in order implies a finite $\Delta_{trs}S$. We should stress at this point that we are talking about ***first order*** transitions here. The reason for this terminology is that the discontinuity is in a function like S, that is a first order derivative of G (or A):

$$\left(\frac{\partial \bar{G}}{\partial T}\right)_P = -\bar{S}$$

Second order derivatives (e.g. the heat capacity) will display a singularity ($+\infty$) at the transition point.

Every phase transition will have a change in entropy associated with it. The different types of phase transitions that can occur are:

$l \rightarrow g$	Vaporization / boiling
$g \rightarrow l$	Condensation
$s \rightarrow l$	Fusion / melting
$l \rightarrow s$	Freezing
$s \rightarrow g$	Sublimation
$g \rightarrow s$	Deposition
$s \rightarrow s$	Solid to solid phase transition

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6.4: The Debye Function is Used to Calculate the Heat Capacity at Low Temperatures

The Debye function is a mathematical expression used in solid-state physics to calculate the heat capacity of solids at low temperatures. Unlike the classical Dulong–Petit law, which assumes that each atom contributes a constant amount of heat capacity, the Debye model incorporates quantum mechanics by considering the vibrational modes of a crystal lattice as quantized phonons. At low temperatures, only the low-frequency vibrational modes are thermally accessible, causing the heat capacity to decrease sharply rather than remain constant. The Debye function provides a way to describe this temperature dependence, predicting the characteristic behavior at very low temperatures and approaching the classical limit at higher temperatures:

$$C_P = aT^3 \tag{6.4.1}$$

Using quantum mechanics, Debye showed that the vibrational energy of a crystal lattice could be modeled as a collection of quantized normal modes, or phonons, leading to a temperature-dependent heat capacity that accurately describes low-temperature behavior in Equation 6.4.1.

However, for metallic crystals, the situation is slightly more complex. In addition to lattice vibrations, the conduction electrons contribute to the heat capacity, resulting in a modified equation at low temperatures. The total heat capacity $C(T)$ for metals is often expressed as:

$$C_P = aT + bT^3 \tag{6.4.2}$$

where a and b are constants.

The aT term in Equation 6.4.2 represents the linear contribution from conduction electrons, while the bT^3 term arises from the lattice vibrations described by the Debye model (form Equation 6.4.1. This combination allows for an accurate prediction of the low-temperature heat capacity of metals.

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6.5: Practical Absolute Entropies Can Be Determined Calorimetrically

Practical absolute entropies can also be determined experimentally using calorimetry, based on the Third Law of Thermodynamics. The Third Law states that a perfect crystalline substance has zero entropy at absolute zero (0 K). From this reference point, the entropy at any higher temperature can be obtained by measuring the heat capacity of the substance as it is warmed from 0 K up to the temperature of interest (often 298 K for standard entropies).

From section 21.1, we learned that the entropy at constant pressure changes with temperature by:

$$\Delta S = \int_{T_1}^{T_2} \frac{C_P(T)}{T} dT \tag{6.5.1}$$

where C_p is the molar heat capacity at constant pressure.

Equation 6.5.1 accounts for the continuous increase in entropy as the substance absorbs heat with rising temperature but does not address the increase in entropy if the substances undergoes a phase transition. From section 21.3, we learned that the entropy of a phase transition (e.g., melting or vaporization) is:

$$\Delta S_{trs} = \frac{\Delta H_{trs}}{T_{trs}} \tag{6.5.2}$$

Note that third law of thermodynamics can be used to set the entropy at absolute zero ($T_1 = 0K$) to zero in the integral in Equation 6.5.1 and the expression in Equation 6.5.2 applies to all possible phase transitions. These aspects combined with Equations 6.5.1 and 6.5.2 results in an expression for the absolute entropy of a substance at temperature T:

$$S(T) = \int_0^T \frac{C_p(T)}{T} dT + \sum \frac{\Delta H_{\text{trs}}}{T_{\text{trs}}} \tag{6.5.3}$$

The summation term adds contributions from multiple possible phase transitions, where entropy changes abruptly due to latent heats (ΔH) at specific transition temperatures.

The values of C_p, ΔH_{trs}, and T can be experimentally determined using calorimetry. We can calculate the practical absolute entropy of a substance for any temperature.

Example 6.5.1

What is the absolute entropy of $\mathbf{CO_2}$ gas at 300 K?

Solution

The entropy of $\mathbf{CO_2}$ gas at 300 K can be calculated by:

$$S(T) = \int_{0K}^{T_{sub}} \frac{C_P(T)}{T} dT + \frac{\Delta H_{sub}}{T_{sub}} + \int_{T_{sub}}^{300\text{ K}} \frac{C_P^g(T)}{T} dT$$

where the temperature of sublimation (T_{sub}) is 194.7 K.

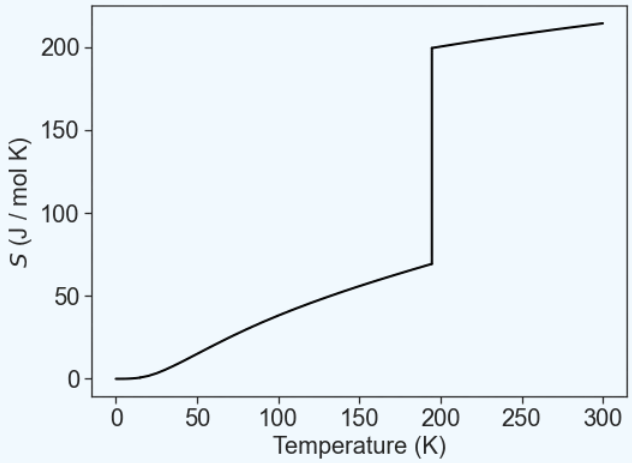


Figure **6.5.1**. The molar entropy of CO_2 from 0 K to 300 K.

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6.6: Practical Absolute Entropies of Gases Can Be Calculated from Partition Functions

Recall that the entropy of a system, S, can be calculated if the partition function, Q, is known:

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

where Q is:

$$Q = \sum_j e^{-\frac{E_j}{kT}}$$

The internal energy of the system can also be calculated from the partition function:

$$U = k_B T^2 \left(\frac{\delta \ln Q}{\delta T} \right)$$

Combining these equations, we obtain:

$$S = k_B \ln Q + k_B T \left(\frac{\delta \ln Q}{\delta T} \right)$$

The third law of thermodynamics states that entropy of a perfect crystal at absolute zero is zero. We can show that our equation for entropy in terms of the partition function is consistent with the third law. Plugging in our equation for the partition function into our equation for entropy, we obtain:

$$S = k_B \ln \sum_j e^{-\frac{E_j}{kT}} + k_B T \left(\frac{\delta \ln \sum_j e^{-\frac{E_j}{kT}}}{\delta T} \right)$$

As T goes to zero, all the states will be in their lowest energy configuration. If the ground state is n degenerate, then n states will be in the ground state:

$$E_1 = E_2 = ... = E_m$$

This is true for all the next states. For example, if the next state is m degenerate, then:

$$E_{n+1} = E_{n+2} = ... = E_{n+m}$$

This gives us the result:

$$\sum_j e^{-\frac{E_j}{kT}} = ne^{-\frac{E_1}{kT}} + me^{-\frac{E_{n+1}}{kT}} + ...$$

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6.7: Standard Entropies Depend Upon Molecular Mass and Structure

Entropy is related to the number of microstates a collection of particles can occupy. As both the molecular mass and molecular structure of the particles will affect the number of available microstates, they also affect the entropy of the collection of particles. So why does $S°$ depend on molecular mass and molecular structure?

Standard molar entropies depend strongly on both molecular mass and molecular structure. Heavier molecules generally have higher entropies because their greater mass leads to more accessible translational and vibrational energy states at a given temperature. Molecular complexity also plays a key role: larger or more structurally intricate molecules have more ways to store energy through rotations and vibrations, giving rise to a greater number of microstates. For example, methane (CH_4) has a higher standard entropy than carbon dioxide (CO_2) because it possesses more rotational and vibrational modes, while oxygen (O_2) has a higher entropy than nitrogen (N_2) due to its larger molecular mass. In essence, both increased mass and increased structural complexity expand the possible distributions of molecular energy, leading to higher entropy values.

From quantum theory, we know that increasing the molecular mass of a particle decreases the energy spacing between states. For a given temperature, more states are available to be occupied, increasing the number of available microstates the system may occupy, and hence the entropy of the system. Heavier molecules have more closely spaced translational and vibrational energy levels, so at room temperature a larger number of these quantum states can be populated, giving rise to higher entropy. Molecular structure also determines how many distinct types of motion are possible: nonlinear and polyatomic molecules possess more rotational and vibrational modes than simpler, linear, or diatomic molecules. Each additional degree of freedom increases the total number of accessible quantum states. Thus, as molecular mass increases or as structure becomes more complex, the system gains a vastly greater multiplicity of microstates, and the entropy correspondingly increases.

The table below shows the molar entropies for the noble gases. As the mass of increases, so does the molar entropy.

Table: Molar entropies for the noble gases

Noble Gas	He	Ne	Ar	Kr	Xe	Rn
Mass $\left(\frac{g}{mol}\right)$	4.0	20.2	39.9	84.8	131.3	222.0
$S°_{g,1\ bar}$ $\left(\frac{J}{mol \cdot K}\right)$	**126.15**[1]	**146.33**[1]	**154.84**[1]	**164.08**[1]	**169.68**[1]	**176.2**[1]

The same is true for the number of atoms in a molecule. A molecule with more atoms will, in general, have a more degrees of freedom to take up energy, increasing its number of available microstates and entropy.

6.7.1: References

1. Chase, M.W., Jr., *NIST-JANAF Themochemical Tables*, *Fourth Edition*, **J. Phys. Chem. Ref. Data, Monograph 9**, 1998, 1-1951.

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6.8: Spectroscopic Entropies sometimes disgree with Calorimetric Entropies

The entropy of gases can be experimentally measured using calorimetry (S°_{exp}) or calculated using spectroscopic methods (S°_{calc}). For most molecules, the experiment and calculated values are in a good agreement, however, this is not true for all molecules. The discrepancy is referred to as residual entropy:

$$\bar{S}_{\text{calc}} - \bar{S}_{\text{exp}}$$

Residual entropy arises from a material that can have many different states a 0 K. The third law of thermodynamics states that at zero kelvin, a substance will have an entropy of zero. In substances, such as glass, ice, and carbon monoxide, the substance can exist in many different configurations; it is not a perfect crystal, but must still have zero entropy according to third law. The material has residual entropy.

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6.9: Standard Entropies Can Be Used to Calculate Entropy Changes of Chemical Reactions

Entropy is a state function, so we can calculate values for a process using any path. This allows us to calculate the entropy change of a chemical reaction using standard entropies. Specifically, we sum the entropies of the products and subtract the entropies of the reactions:

$$\Delta_{rxn}S^\circ = \sum_{\text{Products}} v_i S_i^\circ - \sum_{\text{Reactants}} v_i S_i^\circ$$

Where v_i is the stoichiometric coefficient. Let's look at the combustion of methane:

$$\mathrm{CH_4}\,(g) + 2\mathrm{O_2}\,(g) \rightarrow 2\mathrm{H_2O} + \mathrm{CO_2}\,(g)$$

The standard entropies are:

Molecule	Entropy $\left(\frac{\mathrm{J}}{\mathrm{mol \cdot K}}\right)$
$\mathrm{CH_4}$	186.25[1]
$\mathrm{O_2}$	205.15[1]
$\mathrm{H_2O}$	188.84[1]
$\mathrm{CO_2}$	213.79[1]

The entropy for the combustion of methane is:

$$\Delta S^\circ = [2\,(188.84) + 1\,(213.70)] - [1\,(186.25) + 2\,(205.15)] = -5.17\,\frac{\mathrm{J}}{\mathrm{mol \cdot K}}$$

6.9.1: References

1. Chase, M.W., Jr., *NIST-JANAF Themochemical Tables, Fourth Edition*, **J. Phys. Chem. Ref. Data, Monograph 9**, 1998, 1-1951.

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6.E: Entropy and the Third Law of Thermodynamics (Exercises)

6.E.0.1: Problem 1

Liquid water has a nearly constant molar heat capacity of $\bar{C}_P = 75.4.\ \mathrm{J \cdot mol^{-1} K^{-1}}$. What is the change in entropy as 200. g of water are cooled from 70.0°C to 20.0°C?

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CHAPTER OVERVIEW

7: Helmholtz and Gibbs Energies

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7.3: The Maxwell Relations
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7.E: Helmholtz and Gibbs Energies (Exercises)

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7.1: Helmholtz Energy

We have answered the question: what is entropy, but we still do not have a general criterion for spontaneity, just one that works in an isolated system. We will consider what happens when we hold volume and temperature constant. As discussed previously, the expression for the change in internal energy:

$$dU = TdS - PdV$$

is only valid for *reversible* changes. Let us consider a spontaneous change. If we assume constant volume, the $-PdV$ work term drops out. From the *Clausius inequality* $dS > \frac{\delta q}{T}$ we get:

$$dU \underset{\text{constant V}}{\leq} TdS$$

$$dU - TdS \underset{\text{constant V}}{\leq} 0$$

Consider a new state function, **Helmholtz energy**, **A**:

$$A \equiv U - TS$$

$$dA = dU - TdS - SdT \tag{7.1.1}$$

If we also set T constant, we see that Equation 7.1.1 becomes

$$dA = dU - TdS \underset{\text{constant V and T}}{\leq} 0$$

This means that the Helmholtz energy, A, is a ***decreasing quantity*** for spontaneous processes (regardless of isolation!) when T and V are held constant. A becomes constant once a reversible equilibrium is reached.

Example 22.1.1 : What A stands for

A good example is the case of the mixing of two gases. Let's assume isothermal conditions and keep the total volume constant. For this process, ΔU is zero (isothermal, ideal) but the

$$\Delta S_{molar} = -y_1 R \ln y_1 - y_2 R \ln y_2$$

This means that

$$\Delta A_{molar} = RT(y_1 \ln y_1 + y_2 \ln y_2).$$

This is a negative quantity because the mole ratios are smaller than unity. So yes this spontaneous process has a negative ΔA. If we look at $\Delta A = \Delta U - T\Delta S$ we should see that the latter term is the same thing as $-q_{rev}$ So we have :

$$\Delta A = \Delta U - q_{rev} = w_{rev}$$

This is however the *maximal work that a system is able to produce* and so the Helmholtz energy is a direct measure of how much work one can get out of a system. A is therefore often called the Helmholtz ***free*** energy. Interestingly this work **cannot** be volume work as volume is constant. so it stands for the maximal ***other*** work (e.g. electrical work) that can be obtained under the unlikely condition that volume is constant.

7.1.1: Natural variables of A

Because $A \equiv U - TS$ we can write

$$\begin{aligned} dA &= dU - TdS - SdT \\ &= TdS - PdV - TdS - SdT \\ &= -PdV - SdT \end{aligned}$$

The natural variables of A are volume V and temperature T.

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7.2: Gibbs Energy Determines the Direction of Spontaneity at Constant Pressure and Temperature

The Helmholtz energy A is developed for isochoric changes and as we have often said before it is much easier to deal with isobaric ones where $P =$ constant. We can therefore repeat the above treatment for the enthalpy and introduce another state function the Gibbs energy

$$\begin{aligned} G &\equiv H - TS \\ &= U + PV - TS \\ &= A + PV \end{aligned}$$

If we take both T and P constant we get

$$\begin{aligned} dU - TdS + PdV &\leq 0 \\ dG &\leq 0 \end{aligned}$$

G either decreases (spontaneously) or is constant (at equilibrium). Calculating the state function between two end points we get:

$$\Delta G = \Delta H - T\Delta S \leq 0 (T, P \text{ constant})$$

This quantity is key to the question of spontaneity under the conditions we usually work under. If for a process ΔG is positive it does not occur spontaneous and can only be made to occur if it is 'pumped', i.e. coupled with a process that has a negative ΔG. The latter is spontaneous.

> If $\Delta G = 0$ then the system is as ***equilibrium***.

7.2.1: Direction of the spontaneous change

Because the ΔS term contains the temperature T as coefficient the spontaneous direction of a process, e.g. a chemical reaction can **change** with temperature depending on the values of the enthalpy and the entropy change ΔH and ΔS. This is true for the melting process, e.g. for water below 0°C we get water=>ice, above this temperature ice melts to water, but it also goes for chemical reactions.

Example

Consider

$$NH_3(g) + HCl(g) \rightleftharpoons NH_4Cl(s)$$

$\Delta_r H$ at 298K / 1 bar is -176.2 kJ. The change in entropy is -0.285 kJ/K so that at 298K ΔG is -91.21 kJ. Clearly this is a reaction that will proceed to the depletion of whatever is the limiting reagent on the left.

However at 618 K this is a different story. Above this temperature ΔG is positive! (assuming enthalpy and entropy have remained the same, which is almost but not completely true) The reaction will not proceed. Instead the *reverse* reaction would proceed spontaneously. The salt on the right would decompose in the two gases -base and acid- on the left.

7.2.2: Meaning of the ΔG term

As we have seen, ΔA can be related to the maximal amount of work that a system can perform at constant V and T. We can hold an analogous argument for ΔG except that V is not constant so that we have to consider volume work (zero at constant volume) .

$$dG = d(U + PV - TS) = dU - TdS - SdT - PdV + VdP$$

As $dU = TdS + \delta w_{rev}$

$$dG = \delta w_{rev} - SdT + VdP + PdV$$

As the later term is $-\delta w_{volume}$

$$dG = \delta w_{rev} - SdT + VdP - \delta w_{volume}$$

At constant T and P the two middle terms drop out

$$dG = \delta w_{rev} - \delta w_{volume} = \delta w_{otherusefulwork}$$

Note

ΔG stands for the (maximal) reversible, isobaric isothermal non-PV work that a certain spontaneous change can perform. The volume work may not be zero, but is corrected for.

7.2.3: Natural variables of G

Because $G \equiv H - TS$, we can write

$$\begin{aligned} dG &= dH - TdS - SdT \\ &= TdS + VdP - TdS - SdT \\ &= VdP - SdT \end{aligned}$$

The natural variables of G are pressure P and temperature T. This is what makes this function the most useful of the four U, H, A, and G: these are the natural variables of most of your laboratory experiments!

7.2.4: Summary

We now have developed the basic set of concepts and functions that together form the framework of thermodynamics. Let's summarize four very basic state functions:

state function	natural variables
$dU = -PdV + TdS$	$U(V,S)$
$dH = +VdP + TdS$	$H(P,S)$
$dA = -PdV - SdT$	$A(V,T)$
$dG = +VdP - SdT$	$G(P,T)$

Note:

1. The replacement of δq by TdS was based on *reversible* heat. This means that in the irreversible case the expressions for dU and dH become inequalities
2. We only include *volume* work in the above expressions. If other work (elastic, electrical e.g.) is involved extra terms need to be added: $dU = TdS - PdV + xdX$ etc.

We are now ready to begin applying thermodynamics to a number of very diverse situations, but we will first develop some useful partial differential machinery.

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7.3: The Maxwell 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 $dU = dq + dw$):

$$dU = TdS - pdV \tag{7.3.1}$$

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!

7.3.1: 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 7.3.1 can be expressed:

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV \tag{7.3.2}$$

Also, by inspection (comparing the two expressions for dU in Equations 7.3.1 and 7.3.2) it is apparent that:

$$\left(\frac{\partial U}{\partial S}\right)_V = T \tag{7.3.3}$$

and

$$\left(\frac{\partial U}{\partial V}\right)_S = -p \tag{7.3.4}$$

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 7.3.3 and 7.3.4, 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.

$$dH = TdS + Vdp \tag{7.3.5}$$

And much as in the case of internal energy, this suggests that the natural variables of H are S and p. Or

$$dH = \left(\frac{\partial H}{\partial S}\right)_p dS + \left(\frac{\partial H}{\partial p}\right)_S dV \tag{7.3.6}$$

Comparing Equations 7.3.5 and 7.3.6 show that

$$\left(\frac{\partial H}{\partial S}\right)_p = T \tag{7.3.7}$$

and

$$\left(\frac{\partial H}{\partial p}\right)_S = V \tag{7.3.8}$$

It is worth noting at this point that both Equation 7.3.3

$$\left(\frac{\partial U}{\partial S}\right)_V$$

and Equation 7.3.7

$$\left(\frac{\partial H}{\partial S}\right)_p$$

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 7.3.1.

Table 7.3.1: 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 7.3.1

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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7.4: The Enthalpy of an Ideal Gas is Independent of Pressure

How does pressure affect enthalpy H? As we showed above we have the following relations of first and second order for G

$$\left(\frac{\partial G}{\partial T}\right)_P = -S$$

$$\left(\frac{\partial G}{\partial P}\right)_T = -V$$

$$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$$

We also know that by definition:

$$G = H - TS \tag{7.4.1}$$

Consider an isothermal change in pressure, so taking the partial derivative of each side of Equation 7.4.1, we get:

$$\left(\frac{\partial G}{\partial P}\right)_T = \left(\frac{\partial H}{\partial P}\right)_T - T\left(\frac{\partial S}{\partial P}\right)_T$$

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P \tag{7.4.2}$$

For an ideal gas

$$\frac{\partial V}{\partial T} = \frac{nR}{P}$$

so Equation 7.4.2 becomes

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{nR}{P}\right) = 0$$

As we can see for an ideal gas, there is no dependence of H on P.

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7.5: Thermodynamic Functions have Natural Variables

The fundamental thermodynamic equations follow from five primary thermodynamic definitions and describe internal energy, enthalpy, Helmholtz energy, and Gibbs energy in terms of their natural variables. Here they will be presented in their differential forms.

7.5.1: Introduction

The fundamental thermodynamic equations describe the thermodynamic quantities U, H, G, and A in terms of their natural variables. The term "natural variable" simply denotes a variable that is one of the convenient variables to describe U, H, G, or A. When considered as a whole, the four fundamental equations demonstrate how four important thermodynamic quantities depend on variables that can be controlled and measured experimentally. Thus, they are essentially equations of state, and using the fundamental equations, experimental data can be used to determine sought-after quantities like G or H.

7.5.2: First Law of Thermodynamics

The first law of thermodynamics is represented below in its differential form

$$dU = đq + đw$$

where

- U is the internal energy of the system,
- q is heat flow of the system, and
- w is the work of the system.

The "đ" symbol represent **inexact differentials** and indicates that both q and w are path functions. Recall that U is a state function. The first law states that internal energy changes occur only as a result of heat flow and work done.

It is assumed that w refers only to PV work, where

$$w = -\int pdV$$

The fundamental thermodynamic equation for internal energy follows directly from the first law and the principle of Clausius:

$$dU = đq + đw$$

$$dS = \frac{\delta q_{rev}}{T}$$

we have

$$dU = TdS + \delta w$$

Since only PV work is performed,

$$dU = TdS - pdV \tag{7.5.1}$$

The above equation is the fundamental equation for U with natural variables of entropy S and volume$V$.

7.5.2.1: Principle of Clausius

The *Principle of Clausius* states that the entropy change of a system is equal to the ratio of heat flow in a reversible process to the temperature at which the process occurs. Mathematically this is written as

$$dS = \frac{\delta q_{rev}}{T}$$

where

- S is the entropy of the system,
- q_{rev} is the heat flow of a reversible process, and
- T is the temperature in Kelvin.

7.5.3: Enthalpy

Mathematically, enthalpy is defined as

$$H = U + pV \tag{7.5.2}$$

where H is enthalpy of the system, p is pressure, and V is volume. The fundamental thermodynamic equation for enthalpy follows directly from it deffinition (Equation 7.5.2) and the fundamental equation for internal energy (Equation 7.5.1) :

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

The above equation is the fundamental equation for H. The natural variables of enthalpy are S and p, entropy and pressure.

7.5.4: Gibbs Energy

The mathematical description of Gibbs energy is as follows

$$\begin{aligned} G &= U + pV - TS \\ &= H - TS \end{aligned} \tag{7.5.3}$$

where G is the Gibbs energy of the system. The fundamental thermodynamic equation for Gibbs Energy follows directly from its definition 7.5.3 and the fundamental equation for enthalpy 7.5.2:

$$\begin{aligned} dG &= dH - d(TS) \\ & dH - TdS - SdT \end{aligned}$$

Since

$$\begin{aligned} dH &= TdS + VdP \\ dG &= TdS + VdP - TdS - SdT \\ &= VdP - SdT \end{aligned} \tag{7.5.4}$$

The above equation is the fundamental equation for G. The natural variables of Gibbs energy are P and T.

7.5.5: Helmholtz Energy

Mathematically, Helmholtz energy is defined as

$$A = U - TS \tag{7.5.5}$$

where A is the Helmholtz energy of the system, which is often written as the symbol F. The fundamental thermodynamic equation for Helmholtz energy follows directly from its definition (Equation 7.5.5) and the fundamental equation for internal energy (Equation 7.5.1):

$$\begin{aligned} dA &= dU - d(TS) \\ &= dU - TdS - SdT \end{aligned}$$

Since

$$\begin{aligned} dU &= TdS - pdV \\ dA &= TdS - pdV - TdS - SdT \\ &= -pdV - SdT \end{aligned} \tag{7.5.6}$$

Equation 7.5.6 is the fundamental equation for A with natural variables of V and T. For the definitions to hold, it is assumed that **only** PV work is done and that **only reversible** processes are used. These assumptions are required for the first law and the principle of Clausius to remain valid. Also, these equations do not account include n, the number of moles, as a variable. When n is included, the equations appear different, but the essence of their meaning is captured without including the n-dependence.

7.5.6: Chemical Potential

The fundamental equations derived above were not dependent on changes in the amounts of species in the system. Below the n-dependent forms are presented[1,4].

$$dU = TdS - PdV + \sum_{i=1}^{N} \mu_i dn_i$$

$$dH = TdS + VdP + \sum_{i=1}^{N} \mu_i dn_i$$

$$dG = -SdT + Vdp + \sum_{i=1}^{N} \mu_i dn_i$$

$$dA = -SdT - PdV + \sum_{i=1}^{N} \mu_i dn_i$$

where μ_i is the chemical potential of species i and dn_i is the change in number of moles of substance i.

7.5.7: Importance/Relevance of Fundamental Equations

The differential fundamental equations describe U, H, G, and A in terms of their natural variables. The natural variables become useful in understanding not only how thermodynamic quantities are related to each other, but also in analyzing relationships between measurable quantities (i.e. P, V, T) in order to learn about the thermodynamics of a system. Below is a table summarizing the natural variables for U, H, G, and A:

Thermodynamic Quantity	Natural Variables
U (internal energy)	S, V
H (enthalpy)	S, P
G (Gibbs energy)	T, P
A (Helmholtz energy)	T, V

7.5.8: Maxwell Relations

The fundamental thermodynamic equations are the means by which the Maxwell relations are derived[1,4]. The Maxwell Relations can, in turn, be used to group thermodynamic functions and relations into more general "families"[2,3].

As we said dA is an **exact differential**. Let's write is out in its natural variables (Equation 7.5.6) and take a cross derivative. The dA expression in natural variables is

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

The partial derivatives of A of first order can already be quite interesting we see e.g. in step 2 that the first partial of A versus V (at T constant) is the negative of the pressure.

$$\left(\frac{\partial A}{\partial V}\right)_T = -P$$

Likewise we find the (isochoric) slope with temperature gives us the negative of the entropy. Thus entropy is one of the ***first order derivatives*** of A.

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

When we apply a cross derivative

$$\left(\frac{\partial^2 A}{\partial V \partial T}\right) = \left(\frac{\partial(-S)}{\partial V}\right)_T + \left(\frac{\partial(-P)}{\partial T}\right)_V$$

we get what is known as a ***Maxwell relation***:

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$$

? Exercise

What does Equation three mean for the heat capacity? answer

A similar treatment of dG (Equation 7.5.4 gives:

$$\left(\frac{\partial G}{\partial T}\right)_P = -S$$

$$\left(\frac{\partial G}{\partial P}\right)_T = V$$

and another Maxwell relation

$$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$$

? Exercise 7.5.1

If the assumptions made in the derivations above were not made, what would effect would that have? Try to think of examples were these assumptions would be violated. Could the definitions, principles, and laws used to derive the fundamental equations still be used? Why or why not?

Answer

If it was not assumed that PV-work was the only work done, then the work term in the second law of thermodynamics equation would include other terms (e.g. for electrical work, mechanical work). If reversible processes were not assumed, the Principle of Clausius could not be used. One example of such situations could the movement of charged particles towards a region of like charge (electrical work) or an irreversible process like combustion of hydrocarbons or friction.

? Exercise 7.5.2

For what kind of system does the number of moles not change? This said, do the fundamental equations without n-dependence apply to a wide range of processes and systems?

Answer

In general, a closed system of non-reacting components would fit this description. For example, the number of moles would not change for a closed system in which a gas is sealed (to prevent leaks) in a container and allowed to expand/is contracted.

? Exercise 7.5.3

Derive the Maxwell Relations.

Answer

See the Maxwell Relations section.

? Exercise 7.5.4

1. Derive the expression

$$\left(\frac{\partial H}{\partial P}\right)_{T,n} = -T\left(\frac{\partial V}{\partial T}\right)_{P,n} + V$$

Then apply this equation to an ideal gas. Does the result seem reasonable?

Answer

$(\frac{\partial H}{\partial P})_{T,n} = 0$ for an ideal gas. Since there are no interactions between ideal gas molecules, changing the pressure will not involve the formation or breaking of any intermolecular interactions or bonds.

? Exercise 7.5.5

Using the definition of Gibbs energy and the conditions observed at phase equilibria, derive the Clapeyron equation.

Answer

See the third outside link.

7.5.9: References

1. DOI: 10.1063/1.1749582
2. DOI: 10.1063/1.1749549
3. DOI:10.1103/PhysRev.3.273
4. *A Treatise on Physical Chemistry*, 3rd ed.; Taylor, H. S. and Glasstone, S., Eds.; D. Van Nostrand Company: New York, 1942; Vol. 1; p 454-485.

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7.6: The Standard State for a Gas is an Ideal Gas at 1 Bar

Tabulated data are expressed in terms of a pure ideal gas (no mixing) at 1 bar, known as standard state conditions (SSC). Standard states are indicated with the ∘ symbol. These values are tabulated at a specific temperature, but that temperature can vary and is not included in the definition of SSC. No real gas has perfectly ideal behavior, but this definition of the standard state allows corrections for non-ideality to be made consistently for all the different gases.

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7.7: The Gibbs-Helmholtz Equation

7.7.0.1: Ideal gas

For a mole of ideal gas we can use the gas law to integrate volume over pressure and we get

$$\Delta G_{molar} = RT \ln\left(\frac{P_2}{P_1}\right)$$

It is customary to identify one of the pressures (P_1} with the *standard state* of **1 bar** and use the plimsoll to indicate the fact that we are referring to a standard state by writing:

$$G_{molar}(P) = G^o_{molar} + RT \ln\left(\frac{P}{1}\right) = G^o_{molar} + RT \ln[P]$$

The fact that we are making the function intensive (per mole) is usually indicated by putting a bar over the G symbol, although this is often omitted for $G^{\ominus}_{molar}$

7.7.0.1: Solids

For solids the volume does not change very much with pressure (the *isothermal compressibility* κ is small), so can assume it more or less constant:

$$G(P_{final}) = G(P_{initial}) + \int V dP(\text{from init to final})$$
$$\approx G(P_{initial}) + V \int dP(\text{from init to final}) = G(P_{initial}) + V\Delta P$$

7.7.1: The Gibbs-Helmholtz Expression

$$\frac{G}{T} = \frac{H}{T} - S$$

Take the derivative under constant pressure of each side to get

$$\left(\frac{\partial G/T}{\partial T}\right)_P = -\frac{H}{T^2} + \frac{1}{T}\left(\frac{\partial H}{\partial T}\right)_P - \left(\frac{\partial S}{\partial T}\right)_P$$

We make use of the relationship between C_p and H and C_p and S

$$\left(\frac{\partial G/T}{\partial T}\right)_P = -\frac{H}{T^2} + \frac{\cancel{C_P}}{\cancel{T}} - \frac{\cancel{C_P}}{\cancel{T}} \tag{7.7.1}$$
$$= -\frac{H}{T^2} \tag{7.7.2}$$

We said before that S is a first order derivative of G. As you can see from this derivation the enthalpy H is also a first order derivative, albeit not of G itself, but of G/T.

$$\left(\frac{\partial \Delta G/T}{\partial T}\right)_P = -\frac{\triangle H}{T^2}$$

The last step in the derivation simply takes the step before twice -say for the G and H at the begin and end of a *process*- and subtracts the two identical equations leading to a Δ symbol. In this differential form the Gibbs-Helmholtz equation can be applied to any process.

7.7.2: Gibbs Energy as a Function of Temperature

If heat capacities are know from 0 K we could determine both enthalpy and entropy by integration:

$$S(T) = S(0) + \int_0^T \frac{C_p}{T} dT$$

$$H(T) = H(0) + \int_0^T C_p \, dT$$

As we have seen we must be careful at phase transitions such as melting or vaporization. At these points the curves are *discontinuous* and the derivative C_p is undefined.

$$H(T) = H(0) + \int_0^{T_{fus}} C_p(T)_{solid} dT + \Delta H_{fus} + \int_{T_{fus}}^{T_{boil}} C_p(T)_{liquid} dT + \Delta H_{vap} + etc. \tag{7.7.3}$$

$$S(T) = S(0) + \int_0^{T_{fus}} \frac{C_p(T)_{solid}}{T} dT + \Delta S_{fus} + \int_{T_{fus}}^{T_{boil}} \frac{C_p(T)_{liquid}}{T} dT + \Delta S_{vap} + etc. \tag{7.7.4}$$

$$= S(0) + \int_0^{T_{fus}} \frac{C_p(T)_{solid}}{T} dT + \frac{\Delta H_{fus}}{T_{fus}} + \int_{T_{fus}}^{T_{boil}} \frac{C_p(T)_{liquid}}{T} dT + \frac{\Delta H_{vap}}{T_{boil}} + etc. \tag{7.7.5}$$

with $H(T = 0) = \textbf{undefined}$ and $S(T = 0) = 0$ from the third law of thermodynamics.

> We also discussed the fact that the third law allows us to define $S(0)$ as zero in most cases. For the enthalpy we cannot do that so that our curve is with respect to an undefined zero point. We really should plot $H(T) - H(0)$ and leave $H(0)$ undefined.

Because the Gibbs free energy $G = H - TS$ we can also construct a curve for G as a function of temperature, simply by combining the H and the S curves (Equations 7.7.3 and 7.7.5):

$$G(T) = H(T) - TS(T)$$

Interestingly, if we do so, the **discontinuties** at the phase transition points will **drop out** for G because at these points $\Delta_{trs}H = T_{trs}\Delta_{trs}S$. Therefore, G is **always** continuous.

The $H(0)$ problem does not disappear so that once again our curve is subject to an arbitrary offset in the y-direction. The best thing we can do is plot the quantity $G(T) - H(0)$ and leave the offset $H(0)$ undefined.

We have seen above that the derivative of G with temperature is $-S$. As entropy is always positive, this means that the G-curve is always *descending* with temperature. It also means that although the curve is *continuous* even at the phase transitions, the slope of the G curve is not, because the derivative $-S$ makes a jump there. Fig. 22.7 in the book shows an example of such a curve for benzene. Note the kinks in the curve at the mp and the boiling point.

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7.8: Fugacity Measures Nonideality of a Gas

We have seen that, for a closed system, the Gibbs energy is related to pressure and temperature as follows:

$$dG = VdP - SdT$$

For a constant temperature process:

$$dG = VdP \tag{7.8.1}$$

Equation 7.8.1 can be evaluated for an ideal gas:

$$d\bar{G} = \frac{RT}{P}dP$$

At constant temperature, T:

$$d\bar{G} = RT\, d\ln P$$

This expression by itself is strictly applicable to ideal gases. However, Lewis, in 1905, suggested extending the applicability of this expression to all substances by defining a new thermodynamic property called **fugacity**, f, such that:

$$d\bar{G} = RT\, d\ln f$$

This definition implies that for ideal gases, f must be equal to P. For non ideal gases, f is not equal to P. The ratio between fugacity and pressure is:

$$\phi = \frac{f}{P}$$

where ϕ is the fugacity coefficient. The fugacity coefficient takes a value of unity when the substance behaves like an ideal gas. Therefore, the fugacity coefficient is also regarded as a *measure of non-ideality*; the closer the value of the fugacity coefficient is to unity, the closer we are to the ideal state. In the zero-pressure limit, fugacity approaches ideal gas behavior:

$$\lim_{P\to 0} d\bar{G} = RT\, d\ln P$$

For mixtures, this expression is written as:

$$d\bar{G}_i = RT\, d\ln f_i$$

where $\bar{G}_i$ and f_i are the partial molar Gibbs energy and fugacity of the i-th component, respectively. Fugacity can be readily related to chemical potential because of the one-to-one relationship of Gibbs energy to chemical potential, which we have discussed previously. Therefore, the definition of fugacity in terms of chemical potential becomes:

$$d\bar{\mu}_i = RT\, d\ln f_i$$

Even though the concept of thermodynamic equilibrium is given in terms of chemical potentials, the above definitions allow us to restate the same principle in terms of fugacity. To do this, previous expressions can be integrated to obtain:

$$\bar{\mu} = \bar{\mu}^\circ + RT\ln\frac{f}{P^\circ}$$

At equilibrium:

$$0 = \bar{\mu}^\circ + RT\ln\frac{f}{P^\circ}$$

$$\bar{\mu}^\circ = -RT\ln\frac{f}{P^\circ}$$

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7.E: Helmholtz and Gibbs Energies (Exercises)

22.E: Helmholtz and Gibbs Energies (Exercises)

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CHAPTER OVERVIEW

8: Phase Equilibria

Phase equilibria is the term used to describe with two or more phases co-exist (in equilibrium). The stability of phases can be predicted by the chemical potential, in that the most stable form of the substance will have the minimum chemical potential at the given temperature and pressure. A key tool in exploring phase equilibria is a phase diagram which is used to show conditions (pressure, temperature, volume, etc.) at which thermodynamically distinct phases (such as solid, liquid or gaseous states) occur and coexist at equilibrium.

8.1: A Phase Diagram Summarizes the Solid-Liquid-Gas Behavior of a Substance

8.2: Gibbs Energies and Phase Diagrams

8.3: The Chemical Potentials of a Pure Substance in Two Phases in Equilibrium

8.4: The Clausius-Clapeyron Equation

8.5: Chemical Potential Can be Evaluated From a Partition Function

8.E: Phase Equilibria (Exercises)

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8.1: 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.

8.1.1: 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.

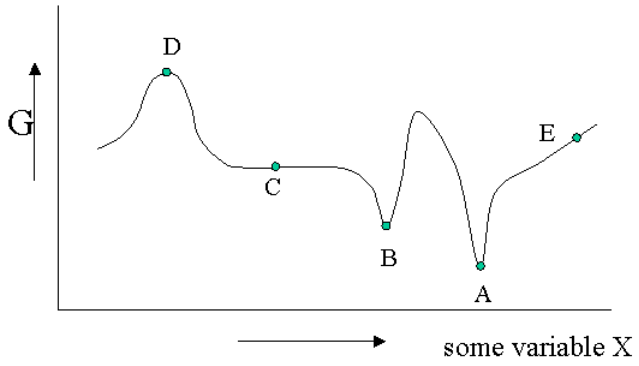


Figure 23.1.1 : A schematic G curve showing various Points of stability. Due to statistical fluctuations the value of G is not quite constant over time, because less likely realizations of the ensemble (having a slightly less favorable value of G) do occur from time to time. After all, the Boltzmann 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*.

8.1.2: 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).

8.1.2.0.1: 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.

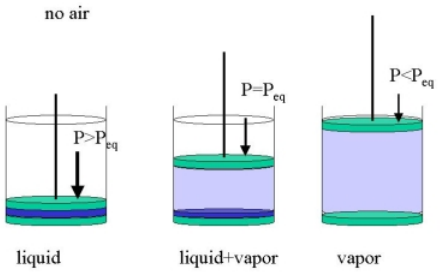


Figure 23.1.2 *: A cylinder with one substance*

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.

8.1.2.0.1: 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

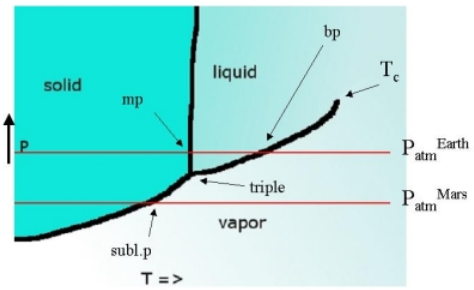
small, but not negligible. As for liquids we can construct a line representing the equilibrium pressures for sublimation as function of temperature and add it to the phase diagram.

8.1.2.0.1: Liquid-solid Equilibrium Curve

The $\mathbf{solid \rightleftharpoons liquid}$ 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.

8.1.2.1: 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.

8.1.3: 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.

8.1.3.1: 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.

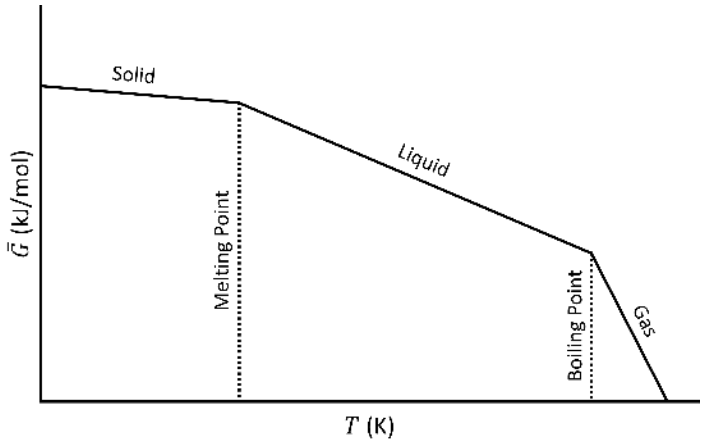
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8.2: Gibbs Energies and Phase Diagrams

8.2.1: 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 ∞)

8.2.2: Second Order Transitions

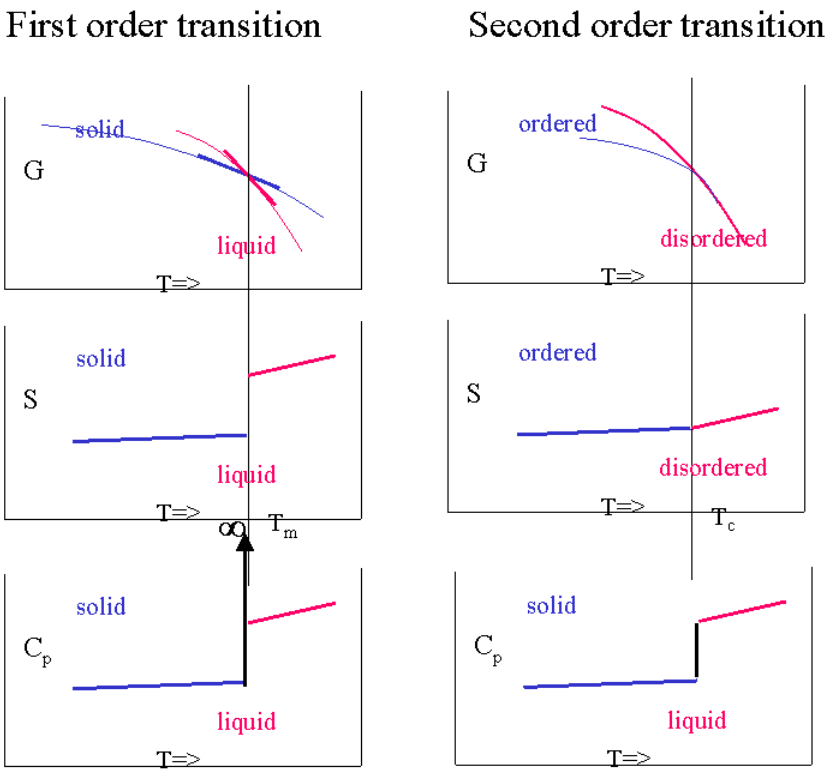
More subtle transitions where G is continuous, H and S are also continuous but have a kink and the discontinuity is only found in the second order derivatives (such as C_P) also exist. They are called *second order transitions*. In such a case:

- 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.

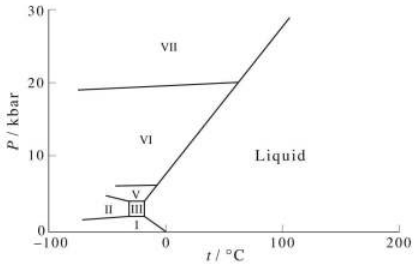


Figure 13.4: Some of the ice polymorphs.

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.

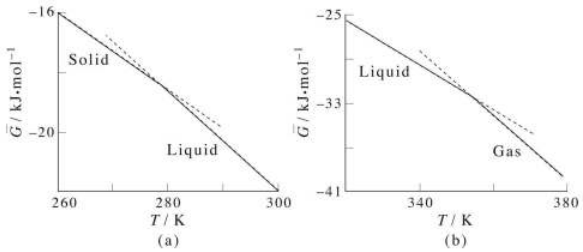


Figure 13.5: Behavior of the Gibbs free energy across the solid-liquid phase (left) and liquid-gas (right) transitions for benzene.

Now, recall that

$$S = -\frac{\partial G}{\partial T} \tag{8.2.1}$$

Consider the slopes in the solid and liquid parts of the graph:

$$\frac{\partial G^{(\text{solid})}}{\partial T} = -S^{(\text{solid})}, \quad \frac{\partial G^{(\text{liquid})}}{\partial T} = -S^{(\text{liquid})} \tag{8.2.2}$$

However, since

$$\frac{\partial G^{(\text{liquid})}}{\partial T} < \frac{\partial G^{(\text{solid})}}{\partial T} \tag{8.2.3}$$

(*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:

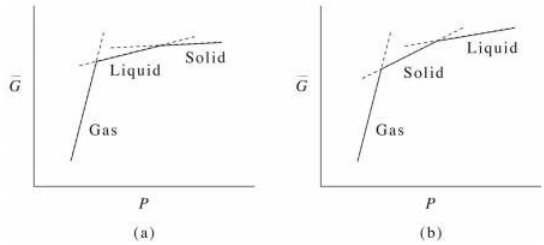


Figure 13.6: Dependence of the Gibbs free energy as a function of pressure for benzene (left) and water (right). For benzene, the temperature is above the triple point, whereas for water, it is set below triple point.

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

$$\bar{V} = \frac{\partial \bar{G}}{\partial P} \tag{8.2.4}$$

From the graph, we see that the slopes obey

$$\bar{V}^{(\text{gas})} \gg \bar{V}^{(\text{liquid})} > \bar{V}^{(\text{solid})} \tag{8.2.5}$$

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

$$\bar{V}^{(\text{gas})} \gg \bar{V}^{(\text{solid})} > \bar{V}^{(\text{liquid})} \tag{8.2.6}$$

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.

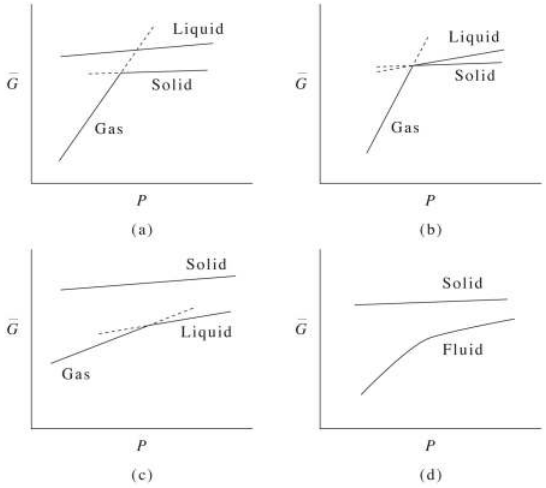


Figure 13.7: Behavior of the Gibbs free energy as a function of P across different phases at different temperatures for benzene. (a): Temperature is less than the triple point; (b): Temperature is equal to the triple point; (c): Temperature is just below the critical temperature; (d): Temperature is greater than the critical temperature.

8.2.3: 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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8.3: The Chemical Potentials of a Pure Substance in Two Phases in Equilibrium

8.3.1: 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.

8.3.2: 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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8.4: The Clausius-Clapeyron Equation

8.4.1: 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

$$\frac{1}{P}\cdot\frac{dP}{dT} = \frac{d\ln P}{dT} = \frac{\Delta H_{molar}^{vap}}{RT^2} \tag{8.4.1}$$

Equation 8.4.1 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).

8.4.2: 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

$$\mu_\alpha(P,T) = \mu_\beta(P,T) \tag{8.4.2}$$

Next, suppose that the pressure and temperature are changed by dP and dT. The changes in the chemical potentials of each phase are

$$d\mu_\alpha(P,T) = d\mu_\beta(P,T) \tag{8.4.3}$$

$$\left(\frac{\partial\mu_\alpha}{\partial P}\right)_T dP + \left(\frac{\partial\mu_\alpha}{\partial T}\right)_P dT = \left(\frac{\partial\mu_\beta}{\partial P}\right)_T dP + \left(\frac{\partial\mu_\beta}{\partial T}\right)_P dT \tag{8.4.4}$$

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

$$\bar{G}(P,T) = \frac{G(n,P,T)}{n} = \mu(P,T) \tag{8.4.5}$$

Moreover, the derivatives of $\bar{G}$ are

$$\left(\frac{\partial \bar{G}}{\partial P}\right)_T = \bar{V}, \qquad \left(\frac{\partial \bar{G}}{\partial T}\right)_P = -\bar{S} \tag{8.4.6}$$

Applying these results to the chemical potential condition in Equation 8.4.4, we obtain

$$\left(\frac{\partial \bar{G}_\alpha}{\partial P}\right)_T dP + \left(\frac{\partial \bar{G}_\alpha}{\partial T}\right)_P dT = \left(\frac{\partial \bar{G}_\beta}{\partial P}\right)_T dP + \left(\frac{\partial \bar{G}_\beta}{\partial T}\right)_P dT \tag{8.4.7}$$

$$\bar{V}_\alpha dP - \bar{S}_\alpha dT = \bar{V}_\beta dP - \bar{S}_\beta dT \tag{8.4.8}$$

Dividing through by dT, we obtain

$$\bar{V}_\alpha \frac{\partial P}{\partial T} - \bar{S}_\alpha = \bar{V}_\beta \frac{\partial P}{\partial T} - \bar{S}_\beta \tag{8.4.9}$$

$$(\bar{V}_\alpha - \bar{V}_\beta)\frac{\partial P}{\partial T} = \bar{S}_\alpha - \bar{S}_\beta \tag{8.4.10}$$

$$\frac{dP}{dT} = \frac{\bar{S}_\alpha - \bar{S}_\beta}{\bar{V}_\alpha - \bar{V}_\beta} \tag{8.4.11}$$

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

$$\bar{S}_\alpha - \bar{S}_\beta = \frac{\bar{H}_\alpha - \bar{H}_\beta}{T} \tag{8.4.12}$$

and the pressure derivative dP/dT becomes

$$\frac{dP}{dT} = \frac{\bar{H}_\alpha - \bar{H}_\beta}{T(\bar{V}_\alpha - \bar{V}_\beta)} = \frac{\Delta_{\alpha\beta}\bar{H}}{T\Delta_{\alpha\beta}\bar{V}} \tag{8.4.13}$$

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 8.4.13 becomes

$$\frac{dP}{dT} = \frac{\Delta\bar{H}_{\text{vap}}}{T(\bar{V}_g - \bar{V}_l)} \tag{8.4.14}$$

In this case, $\bar{V}_g \gg \bar{V}_l$, and we can approximate Equation 8.4.14 as

$$\frac{dP}{dT} \approx \frac{\Delta\bar{H}_{\text{vap}}}{T\bar{V}_g} \tag{8.4.15}$$

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 8.4.15 becomes

$$\frac{dP}{dT} = \frac{\Delta \bar{H}_{\text{vap}} P}{RT^2} \tag{8.4.16}$$

$$\frac{1}{P}\frac{dP}{dT} = \frac{\Delta \bar{H}_{\text{vap}}}{RT^2} \tag{8.4.17}$$

$$\frac{d \ln P}{dT} = \frac{\Delta \bar{H}_{\text{vap}}}{RT^2} \tag{8.4.18}$$

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

$$\int_{P_1}^{P_2} d \ln P = \int_{T_1}^{T_2} \frac{\Delta \bar{H}_{\text{vap}}}{RT^2} dT \tag{8.4.19}$$

$$\ln \left(\frac{P_2}{P_1}\right) = -\frac{\Delta \bar{H}_{\text{vap}}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{8.4.20}$$

$$= \frac{\Delta \bar{H}_{\text{vap}}}{R}\left(\frac{T_1 - T_1}{T_1 T_2}\right) \tag{8.4.21}$$

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

$$\ln \left(\frac{P_3}{P_1}\right) = -\frac{\Delta \bar{H}_{\text{vap}}}{R}\left(\frac{1}{T_3} - \frac{1}{T_1}\right) \tag{8.4.22}$$

Subtracting the two results, we obtain

$$\ln \left(\frac{P_2}{P_3}\right) = -\frac{\Delta \bar{H}_{\text{vap}}}{R}\left(\frac{1}{T_2} - \frac{1}{T_3}\right) \tag{8.4.23}$$

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

$$\ln P_2(\text{bar}) = -\frac{(40.65\ \text{kJ/mol})(1000\ \text{J/kJ})}{8.3145\ \text{J/mol}\cdot\text{K}}\left(\frac{1}{473\ \text{K}} - \frac{1}{373\ \text{K}}\right) = 2.77 \tag{8.4.24}$$

$$P_2(\text{bar}) = (1\ \text{bar})\, e^{2.77} = 16\ \text{bar} \tag{8.4.25}$$

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 8.4.1).

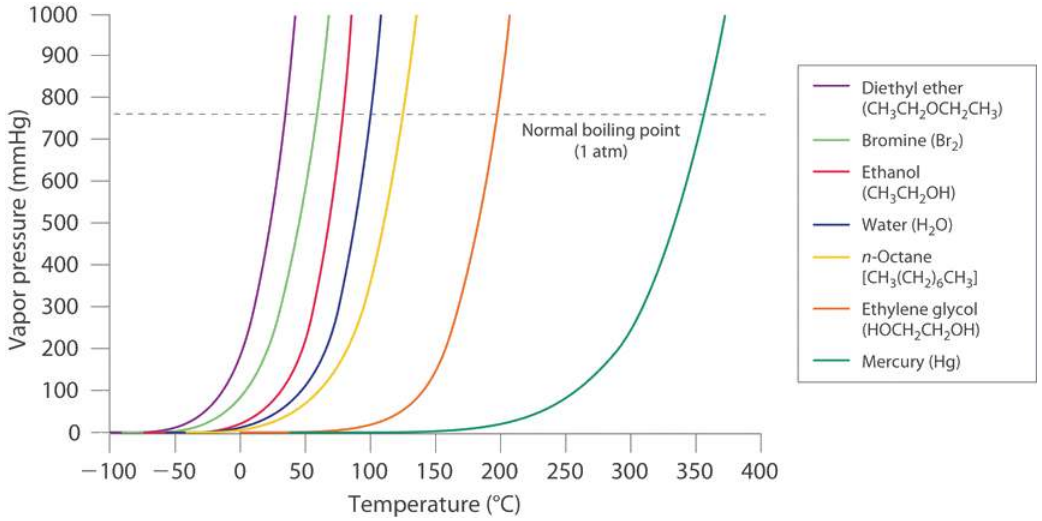


Figure 8.4.1: The Vapor Pressures of Several Liquids as a Function of Temperature. The point at which the vapor pressure curve crosses the P = 1 atm line (dashed) is the normal boiling point of the liquid. (CC BY-SA-NC 3.0; Anonymous)

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,

$$P \propto \exp\left(-\frac{\Delta H_{vap}}{RT}\right) \tag{8.4.26}$$

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 8.4.26 between two pressure-temperature endpoints:

$$\ln\left(\frac{P_1}{P_2}\right) = \frac{\Delta H_{vap}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{8.4.27}$$

where $\boldsymbol{P_1}$ and $\boldsymbol{P_2}$ are the vapor pressures at two temperatures $\boldsymbol{T_1}$ and $\boldsymbol{T_2}$. Equation 8.4.27 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 8.4.27 matters as the Clausius-Clapeyron Equation is sometimes written with a negative sign (and switched order of temperatures):

$$\ln\left(\frac{P_1}{P_2}\right) = -\frac{\Delta H_{vap}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{8.4.28}$$

Example 8.4.1: 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 8.4.28), 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 8.4.2: 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 8.4.2

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 8.4.3: 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 8.4.28

$$\ln\left(\frac{150}{760}\right) = \frac{-\Delta H_{vap}}{8.314}\left[\frac{1}{313} - \frac{1}{351}\right]$$

$$\ln 150 - \ln 760 = \frac{-\Delta H_{vap}}{8.314}\left[\frac{1}{313} - \frac{1}{351}\right]$$

$$-1.623 = \frac{-\Delta H_{vap}}{8.314}\left[0.0032 - 0.0028\right]$$

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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8.5: Chemical Potential Can be Evaluated From a Partition Function

The chemical potential can be given in terms of a partition function. Internal energy can be defined as:

$$U = RT^2 \left(\frac{\partial \ln Q}{\partial T}\right)_{n,V}$$

And entropy can be defined as:

$$S = RT \left(\frac{\partial \ln Q}{\partial T}\right)_{n,V} + R \ln Q$$

We know that Helmholtz energy is:

$$A = U - TS$$

Using our two equations above, we obtain:

$$A = -RT \ln Q$$

Now, let's change gears a bit to show how Helmholtz energy is related to chemical potential. The total differential for Helmholtz energy is:

$$dA = \left(\frac{\partial A}{\partial T}\right)_{n,V} + \left(\frac{\partial A}{\partial V}\right)_{n,T} + \left(\frac{\partial A}{\partial n}\right)_{V,T}$$

And the fundamental equation is:

$$dA = -SdT - PdV + \left(\frac{\partial A}{\partial n}\right)_{V,T} dn$$

Using the relationship between Helmholtz energy and Gibbs energy:

$$G = A + PV$$

We obtain:

$$\begin{aligned} dG &= dA + d(PV) \\ &= -SdT + VdP + \left(\frac{\partial A}{\partial n}\right)_{V,T} dn \end{aligned}$$

We know that the change in Gibbs energy is:

$$\begin{aligned} dG &= -SdT + VdP + \left(\frac{\partial G}{\partial n}\right)_{P,T} dn \\ &= -SdT + VdP + \mu dn \end{aligned}$$

Inspecting these equations, we see that:

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

This shows us that, as long as the natural variables for each thermodynamic potential are held constant, the partial derivatives of Gibbs energy and Helmholtz energy with respect to the number of moles, n are equal to the chemical potential. We can now plug in our expression above for Helmholtz energy in terms of the partition function:

$$\mu = -RT \left(\frac{\partial \ln Q}{\partial n}\right)_{V,T}$$

We now have chemical potential written in terms of the partition function, Q.

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8.E: Phase Equilibria (Exercises)

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CHAPTER OVERVIEW

9: Solutions

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9.E: Solutions I- Liquid-Liquid Solutions (Exercises)

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9.1: Partial Molar Quantities in Solutions

So far, we have only discussed systems that are comprised of one component. Because a lot of chemistry occurs in mixtures or produces a mixture, chemists need to consider the thermodynamics of mixtures. A mixture can consist of many different components, however, for the sake of simplicity, we will restrict ourselves for now to two-component mixtures. Two-component mixtures can consist of two gases, two liquids, two solids, or even a liquid and a gas.

9.1.1: Partial Quantities and Scaling

Let's consider a two-component system where the volume and number of moles are changing. For example, we could have a system of a certain size of 1 and reduce its size stepwise in successive steps by taking half of it and throwing the other half away. The number of moles of each component, n_1 and n_2, will change as the volume of the system, V, changes:

$$dn_1 = n_1 dV$$

$$dn_2 = n_2 dV$$

The extensive Gibbs free energy will be affected the same way:

$$dG = GdV$$

At constant T and P we can write:

$$dG = \cancel{-SdT} + \cancel{VdP} + \mu_1 dn_1 + \mu_2 dn_2$$

So:

$$dG = \mu_1 dn_1 + \mu_2 dn_2$$

$$GdV = \mu_1 n_1 dV + \mu_2 n_2 dV$$

If we integrate this from the original size, 1, down to 0 (or 0 to 1, it does not matter). We get:

$$\int_0^1 GdV = \int_0^1 \mu_1 n_1 dV + \int_0^1 \mu_2 n_2 dV$$

$$G\int_0^1 dV = \mu_1 n_1 \int_0^1 dV + \mu_2 n_2 \int_0^1 dV$$

$$G = \mu_1 n_1 + \mu_2 n_2$$

By the same argument we have:

$$V = \bar{V}_1 n_1 + \bar{V}_2 n_2$$

where $\bar{V}_i$ is the partial molar volume for component i. These partial molar volumes are generally a function of composition (and P, T) and have been tabulated for a number of liquid systems. They allow us to calculate the real volume of a binary mixture. Volumes are generally speaking ***not strictly additive***. This fact is typically ignored in volumetric analysis and the use of molarities. Fortunately the deviations are often negligible in dilute solutions.

For phase diagrams, molarity (moles per liter) is not a very suitable quantity to use for concentration due to its volume dependence. Usually we work with mole fractions or molalities (moles per kilogram), where there are no volume dependencies.

9.1.2: Gaseous Mixtures

Gases can always mix in any ratio and mixtures typically act close to ideal unless heavily compressed or brought to low temperatures. The only exception is if the gases react (e.g, HCl and NH_3). Gas molecules experience little interaction with each other and, therefore, it does not matter much whether the molecules are different or the same. The total pressure can be computed by adding the partial pressures of the two components (Dalton's Law of Partial Pressures):

$$P_{total} = P_1 + P_2 \tag{9.1.1}$$

9.1.3: Liquid Mixtures

There are binary liquid systems that are fully miscible and are said to act as *ideal solutions*. Liquid molecules typically experience *strong* interactions with their neighbors. For the solution to be ideal, the interactions must remain *equally strong* even when the neighboring substance is different. This means they must be chemically similar. For this reason, liquid binaries are often *not* ideal. The next nearest thing are **regular solutions**. Even these systems can display phase segregation and limited mutual solubilities at low temperatures. Many liquid-liquid binaries diverge from ideality even more than the regular solutions and many of them are hardly miscible at all.

Table 24.1.1: Solutions

Solution/mixture	Interactions	Miscibility
Ideal gas	none	complete
Ideal liquid	strong but similar	complete
Regular liquid	strong, modestly dissimilar	not always complete
Real liquid	often strongly dissimilar	partial or none

9.1.4: Solid Mixtures

Solid binaries tend to be even less miscible than liquid binaries to the point that immiscibility is the rule and miscibility is the exception. Even totally miscible systems like electrum (the alloys of silver and gold) are far from ideal.



Figure 24.1.1: Electrum coin of the Byzantine Emperor Alexius I Comnenus. (CC-BY-SA-3.0; Classical Numismatic Group, Inc. http://www.cngcoins.com)

Another point of practical (kinetic rather than thermodynamic) importance is that even if two compounds are able to form a homogeneous solid solution, it usually takes heating for prolonged periods to get them to mix because solid diffusion is typically very slow. Nevertheless, solid solubility is an important issue for many systems, particularly for metal alloys. Two molecular solid substances that differ vastly in shape, size, polarity and or hydrogen bonding (e.g. organic compounds) typically have *negligible* mutual solid solubility. The latter fact is frequently exploited in organic chemistry to purify compounds through recrystallization.

Note

Solid solutions are relatively infrequent and never ideal.

9.1.5: Ideal liquid/Ideal Gas Phase Diagrams

Let's mix two liquids together. Liquids typically have different boiling points, with one being more volatile than the other. The vapor pressure of a component scales simply with the equilibrium vapor pressure of the pure component. In the gas phase, ***Dalton's law*** is applicable:

$$y_i = \frac{P_i}{P_{total}} \tag{9.1.2}$$

This is a consequence of the fact that ideal gases do not interact. The latter implies that the total pressure is simply the sum of the partial ones:

$$P_{total} = \sum_{i}^{N} P_i$$

If the liquid solution is ideal, then the vapor pressure of both components follow ***Raoult's law***, which states that the equilibrium vapor pressure above the mixture is the equilibrium pressure of the pure component times the mole fraction:

$$P_i = \chi_i P_i^\circ \tag{9.1.3}$$

- P_i is the vapor pressure of component i in the mixture
- P_i° is equilibrium vapor pressure of the pure component i.
- χ_i is the mole fraction of i^{th} component in the liquid phase.

Note that values for pure components are typically indicated by adding an asterisk $^\circ$ superscript.

The idea behind Raoult's law is that if the interactions are similar, it is a matter of random chance which component sits at the interface at any given moment. The equilibrium vapor pressure has to do with the probability that a molecule escapes from the interface into the gas phase and is dependent on both the substances volatility and the number that cover the surface. This leads to Raoult's Law, where we must multiply the vapor pressure of the pure liquid (volatility) by the mole fraction (number on the surface).

Note: Applicability of Raoult's Law

Raoult's law seldom holds completely, which is more applicable if the two components are almost chemically identical like two isomers, e.g., 1-propanol and 2-propanol.

9.1.6: The Pressure Phase Diagram

If we assume that temperature is constant, we can plot the total pressure for both Dalton and Raoult's laws versus composition (of gas: y_1 and liquid: χ_1 on the same axis).

Liquid Phase:

$$\begin{aligned} P_{total} &= P_1 + P_2 \\ &= \chi_1 P_1^\circ + \chi_2 P_2^\circ \\ &= \chi_1 P_1^\circ + (1-\chi_1) P_2^\circ \\ &= P_2^\circ - \chi_1 (P_2^\circ - P_1^\circ) \end{aligned} \tag{9.1.4}$$

Clearly this is a straight line going from P_2° at $x = 0$ to P_1° at $x = 1$.

However the composition of the vapor in equilibrium with a liquid at a given mole fraction χ is *different* than that of the liquid. So y is not χ. If we take Dalton's law (Equation 9.1.2) and substitute Raoult's Law (Equation 9.1.3) in the numerator and the straight line in the denominator we get:

$$y_1 = \frac{\chi_1 P_1^\circ}{P_2^\circ - \chi_1 (P_2^\circ - P_1^\circ)} \tag{9.1.5}$$

? Exercise

Suppose $P_1^\circ = 50$ Torr and $P_2^\circ = 25$ Torr. If $\chi_1 = 0.6$ what is the composition of the vapor?

We can rearrange Equations 9.1.4 and 9.1.5 to plot the total pressure as function of y_1:

$$P_{total} = \frac{P_1^\circ P_2^\circ}{P_1^\circ + (P_2^\circ - P_1^\circ) y_1} \tag{9.1.6}$$

This is *not* a straight line.

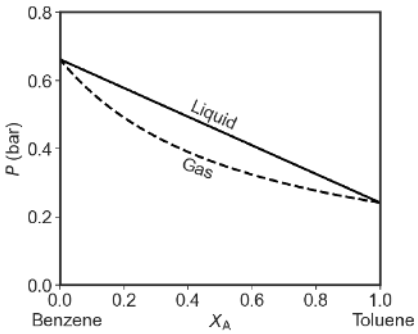


Figure 24.1.1: an ideal-ideal phase diagram for the binary system of toluene (A) and benzene (B). The curves are calculated from Equations 9.1.4 and 9.1.6.

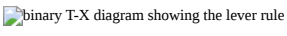
As you can see when we plot both lines we get a diagram with three regions. At high pressures we just have a liquid. At low pressures we just have a gas. In between we have a ***phase gap*** or ***two phase region***. Points inside this region represent states that the system cannot achieve homogeneously. The horizontal ***tie-line*** shows which *two* phases coexists. I used the same 25 and 50 Torr values for the pure equilibrium pressures as in the question above. If you try to make a system with *overall* composition x and impose a pressure that falls in the forbidden zone you get two phases: a gaseous one that is richer in the more volatile component and a liquid one that is poorer in the volatile component than the overall composition would indicate.

9.1.7: The Temperature Phase Diagram

Note that the question: *what phase do we have when?* is really a function of ***both P and T***, so that if we want to represent *all* our knowledge in a diagram we should make it a three dimensional picture. This is not so easy to draw and not easy to comprehend visually either. This is why we usually look at a 2D cross section of the 3D space.

The above diagram is *isothermal*: we vary P, keeping T constant. It is, however, more usual (and easier) to do it the other way around. We keep pressure constant (say 1 bar, that's easy) and start heating things up isobarically.

The boiling points of our mixtures can also be plotted against x (the liquid composition) and y (the gaseous one) on the same horizontal axis. Again because in general y is not equal x we get two different curves. Neither of them are straight lines in this case and we end up with a lens-shaped two phase region:



binary T-X diagram showing the lever rule

What happens to a mixture with a given overall composition x(=x_1) when it is brought to a temperature where it boils can be seen at the intersection of a vertical line (an isopleth) at $x_{overall}$ and a horizontal one (an isotherm) at T_{boil}. If the intersection points in inside the two phase region a vapor phase and a liquid phase result that have a different composition from the overall one. The vapor phase is always richer in the more volatile component (the one with the lowest boiling point, on the left in the diagram). The liquid phase is enriched in the less volatile one.

9.1.7.1: The Lever Rule

How much of each phase is present is represented by the arrows in the diagram. The amount of liquid is proportional to the left arrow, the amount of gas to the right one (i.e. it works crosswise). The composition of the liquid in equilibrium with the vapor is:

$$x_2 = \frac{n_2^{liq}}{n_{1+2}^{liq}}$$

$$x_2^* n_{1+2}^{liq} = n_2^{liq}$$

The composition of the vapor is:

$$y_2 = \frac{n_2^{gas}}{n_{1+2}^{gas}}$$

$$y_2^* n_{1+2}^{gas} = n_2^{gas}$$

The overall composition is:

$$x_{all} = \frac{n_2^{liq+gas}}{n_{1+2}^{liq+gas}}$$

$$x_{all}^* n_{1+2}^{liq+gas} = n_2^{gas} + n_2^{liq}$$

$$x_{all}^* n_{1+2}^{liq+gas} = y_2^* n_{1+2}^{gas} + x_2^* n_{1+2}^{liq}$$

$$x_{all}^* n_{1+2}^{gas} + x_{all}^* n_{1+2}^{liq} = y_2^* n_{1+2}^{gas} + x_2^* n_{1+2}^{liq}$$

Thus:

$$\frac{n_{1+2}^{liq}}{n_{1+2}^{gas}} = \frac{y_2 - x_{all}}{x_{all} - x_2}$$

9.1.7.2: Distillation

The difference in composition between the gas and the liquid can be exploited to separate the two components, at least partially. We could trap the vapor and cool it down to form a liquid with a different composition. We could then boil it again and repeat the process. Each time the vapor will be more enriched in the volatile phase whereas the residual liquid is more enriched in the less volatile one. This process is known as ***distillation***. In practice the process is done one a fractionation column which makes it possible to have a series of vapor-liquid equilibria at once.

A good degree of purity can be reached this way, although 100% purity would take an infinite number of distillation steps.

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9.2: The Gibbs-Duhem Equation

At **equilibrium**, there is no change in chemical potential for the system:

$$\sum_i n_i d\mu_i = 0 \tag{9.2.1}$$

This is the Gibbs-Duhem relationship and it places a compositional constraint upon any changes in the chemical potential in a mixture at constant temperature and pressure for a given composition. This result is easily derived when one considers that μ_i represents the partial molar Gibbs function for component i. And as with other partial molar quantities:

$$G_{\text{tot}} = \sum_i n_i \mu_i$$

Taking the derivative of both sides yields:

$$dG_{\text{tot}} = \sum_i n_i d\mu_i + \sum_i \mu_i dn_i$$

But dG can also be expressed as:

$$dG = Vdp - sdT + \sum_i \mu_i dn_i$$

Setting these two expressions equal to one another:

$$\sum_i n_i d\mu_i + \cancel{\sum_i \mu_i dn_i} = Vdp - sdT + \cancel{\sum_i \mu_i dn_i}$$

And after canceling terms, one gets:

$$\sum_i n_i d\mu_i = Vdp - sdT \tag{9.2.2}$$

For a system at constant temperature and pressure:

$$V\ dp - s\ dT = 0 \tag{9.2.3}$$

Substituting Equation 9.2.3 into 9.2.2 results in the **Gibbs-Duhem equation** (Equation 9.2.1). This expression relates how the chemical potential can change for a given composition while the system maintains equilibrium.

9.2.1: **Gibbs-Duhem for** Binary Systems

For a binary system consisting of components two components, A and B:

$$n_B d\mu_B + n_A d\mu_A = 0$$

Rearranging:

$$d\mu_B = -\frac{n_A}{n_B} d\mu_A$$

Consider a Gibbs free energy that only includes μ_n conjugate variables as we obtained it from our scaling experiment at T and P constant:

$$G = \mu_A n_A + \mu_B n_B$$

Consider a change in G:

$$\begin{aligned} dG &= d(\mu_A n_A) + d(\mu_B n_B) \\ &= n_A d\mu_A + \mu_A dn_A + n_B d\mu_B + \mu_B dn_B \end{aligned}$$

However, if we simply write out a change in G due to the number of moles we have:

$$dG = \mu_A dn_A + \mu_B dn_B$$

Consequently the other terms must add up to zero:

$$0 = n_A d\mu_A + n_B d\mu_B$$

$$d\mu_A = -\frac{n_B}{n_A} d\mu_B$$

$$d\mu_A = -\frac{\chi_B}{\chi_A} d\mu_B$$

In the last step we have simply divided both denominator and numerator by the total number of moles. This expression is the Gibbs-Duhem equation for a 2-component system. It relates the change in one thermodynamic potential ($d\mu_A$) to the other ($d\mu_B$).

> *The Gibbs-Duhem equation relates the change in one thermodynamic potential ($d\mu_A$) to the other ($d\mu_B$).*

9.2.2: Gibbs-Duhem in the Ideal Case

In the ideal case we have:

$$\mu_B = \mu_B^* + RT \ln x_B$$

Gibbs-Duhem gives:

$$d\mu_A = -\frac{\chi_B}{\chi_A} d\mu_B$$

As:

$$d\mu_B = 0 + \frac{RT}{\chi_B}$$

with x_B being the only active variable at constant temperature, we get:

$$d\mu_A = -\frac{\chi_B}{\chi_A} \frac{RT}{\chi_B} = \frac{RT}{\chi_A}$$

If we now wish to find μ_A we need to integrate $d\mu_A$, e.g. form pure 1 to χ_A. This produces:

$$\mu_A = \mu_A^* + RT \ln \chi_A$$

This demonstrates that Raoult's law can only hold over the whole range for one component ***if*** it also holds for the other over the whole range.

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9.3: Chemical Potential of Each Component Has the Same Value in Each Phase in Which the Component Appears

In much the same fashion as the partial molar volume is defined, the **partial molar Gibbs function** is defined for compound i in a mixture:

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_{j\neq i}} \tag{9.3.1}$$

The partial molar function is of particular importance and is called the **chemical potential**. The chemical potential tells how the Gibbs function will change as the composition of the mixture changes. Since systems tend to seek a minimum aggregate Gibbs function, the chemical potential will point to the direction the system can move in order to reduce the total Gibbs function and reach equilibrium. In general, the total change in the Gibbs function (dG) can be calculated from:

$$dG = \left(\frac{\partial G}{\partial P}\right)_{T,n_i} dP + \left(\frac{\partial G}{\partial T}\right)_{P,n_i} dT + \sum_i \left(\frac{\partial G}{\partial n_i}\right)_{T,n_{j\neq i}} dn_i$$

Or, by substituting the definition for the chemical potential, and evaluating the pressure and temperature derivatives:

$$dG = VdP - SdT + \sum_i \mu_i dn_i$$

But as it turns out, the chemical potential can be defined as the partial molar quantity of any of the four major thermodynamic functions U, H, A, or G:

Table **9.3.1**: Chemical potential can be defined as the partial molar derivative any of the four major thermodynamic functions

$dU = TdS - PdV + \sum_i \mu_i dn_i$	$\mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_{j\neq i}}$
$dH = TdS - VdT + \sum_i \mu_i dn_i$	$\mu_i = \left(\frac{\partial H}{\partial n_i}\right)_{S,P,n_{j\neq i}}$
$dA = -PdV - TdS + \sum_i \mu_i dn_i$	$\mu_i = \left(\frac{\partial A}{\partial n_i}\right)_{V,T,n_{j\neq i}}$
$dG = VdP - SdT + \sum_i \mu_i dn_i$	$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_{j\neq i}}$

The last definition, in which the chemical potential is defined as the partial molar Gibbs function, is the most commonly used, and perhaps the most useful (Equation 9.3.1). As the partial most Gibbs function, it is easy to show that:

$$d\mu = VdP - SdT$$

where V is the molar volume, and S is the molar entropy. Using this expression, it is easy to show that:

$$\left(\frac{\partial \mu}{\partial P}\right)_T = V$$

and so at constant temperature:

$$\int_{\mu^o}^{\mu} d\mu = \int_{P^o}^{P} V\, dP \tag{9.3.2}$$

So that for a substance for which the molar volume is fairly independent of pressure at constant temperature (i. e., κ_T is very small), therefore Equation 9.3.2 becomes:

$$\int_{\mu^o}^{\mu} d\mu = V \int_{P^o}^{P} dP$$

$$\mu - \mu^o = V(P - P^o)$$

or:

$$\mu = \mu^o + V(P - P^o)$$

Where P^o is the standard state pressure (1 bar) and μ^o is the chemical potential at the standard pressure. If the substance is highly compressible (such as a gas) the pressure dependence of the molar volume is needed to complete the integral. If the substance is an ideal gas:

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

So at constant temperature, Equation 9.3.2 then becomes:

$$\int_{\mu^o}^{\mu} d\mu = RTint_{P^o}^{P} \frac{dP}{P} \tag{9.3.3}$$

or:

$$\mu = \mu^o + RT \ln\left(\frac{P}{P^o}\right)$$

A lot of chemistry takes place in solution and therefore this topic is of prime interest for chemistry.

9.3.1: Thermodynamic potentials of solutions

The Gibbs free energy of an ideal gas depends logarithmically on pressure:

$$G = G^o + RT \ln \frac{P}{P^o}$$

$P^{\ominus}$ is *is often dropped out of the formula.* and we write:

$$G = G^o + RT \ln P$$

> Notice however that although P and P/P^o have the same numerical value, the dimensions are different. P usually has dimensions of bar, but P/P^o is *dimensionless*.

If we have a gas mixture we can hold the same logarithmic argument for each partial pressure as the gases do not notice each other. We do need to take into account the number of moles of each and work with (partial) molar values, i.e. the thermodynamic potential:

$$\mu_j = \mu_j^o + RT \ln \frac{P_j}{P^o} \tag{9.3.4}$$

If we are dealing with an equilibrium over an ideal liquid solution the situation in the gas phase gives us a probe for the situation in the liquid. The equilibrium must hold for each of *all* components j (say two in binary mixture). That means that for each of them the thermodynamic potential in the liquid and in the gas must be equal:

$$\mu_j^{sln} = \mu_j^{gas}$$

for all j. Consider what happens to a pure component, e.g. $j = 1$ in equilibrium with its vapor. We can write:

$$\mu_1^{pure\ liq} = \mu_1^{pure\ vapor} = \mu_1^o + RT \ln \frac{P_1^*}{P^o}$$

The asterisk in P_1^* denotes the equilibrium vapor pressure of pure component 1 and we will use that to indicate the thermodynamic potential of pure compounds too:

$$\mu_1^{*liq} = \mu_1^o + RT \ln \frac{P_1^*}{P^o} \tag{9.3.5}$$

Combining Equations 9.3.5 and 9.3.4 we find a relationship between the solution and the pure liquid:

$$\mu_j^{sln} = \mu_j^* + RT \ln \frac{P_j}{P_j^*}$$

Notice that the *gas* and its pressure is used to link the mixture and the pure compound.

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9.4: Ideal Solutions obey Raoult's Law

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.

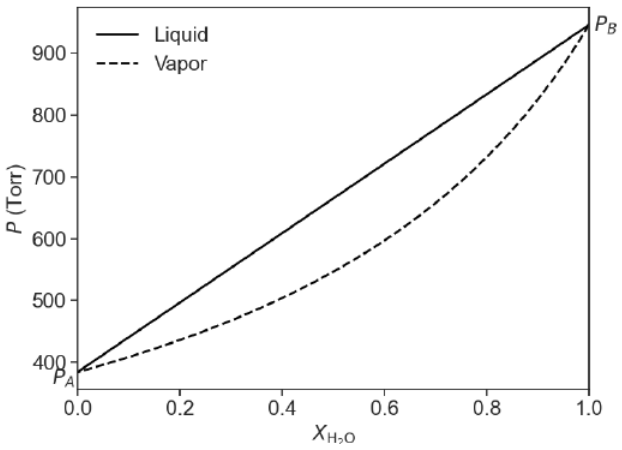


Figure 24.4.1: The composition of the liquid phase (solid line) and the vapor phase (dashed lined) as a function of mole fraction according to Raoult's law. The solution is a mixture of water and ethanol. P_A is the vapor pressure of pure water and P_B is the vapor pressure of pure ethanol at 75 °C

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.

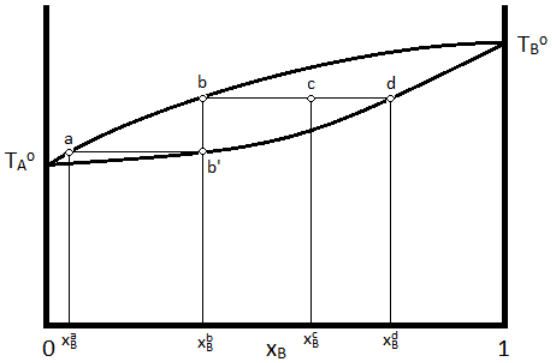


Figure 24.4.2: A typical temperature vs. composition diagram.

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.

9.4.1: 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.

9.4.2: 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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9.5: Most Solutions are Not Ideal

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).

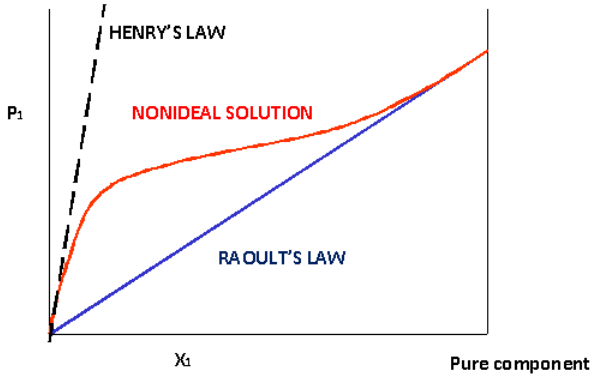


Figure 24.5.1 : Vapor pressure above an ideal and a non-ideal solution

> 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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9.6: 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 **9.6.1**.

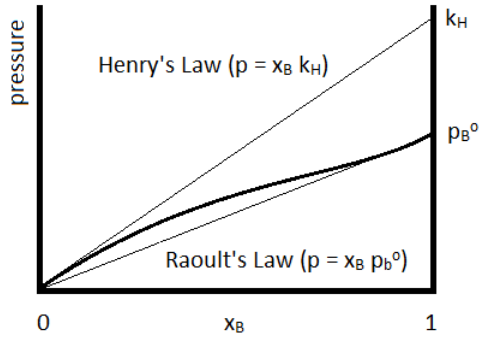


Figure **9.6.1**: The relationship between Raoult's Law and Henry's Law for a binary mixture.

Henry's Law is depicted by the upper straight line and Raoult's Law by the lower.

Example 9.6.1: 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

$$k_H = 1.67\times10^9\,Pa$$

9.6.1: Azeotropes

An azeotrope is defined as the common composition of vapor and liquid when they have the same composition.

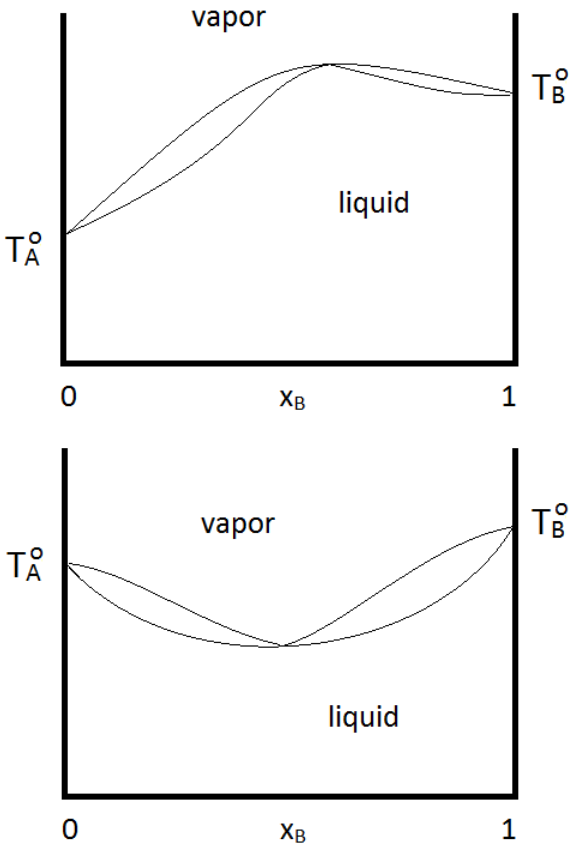


Figure **9.6.2**: Phase diagrams for (left) a maximum boiling point azeotrope and (right) Ta maximum boiling point azeotrope.

Azeotropes can be either maximum boiling or minimum boiling, as show in Figure **9.6.2;**. 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 **9.6.2;**:

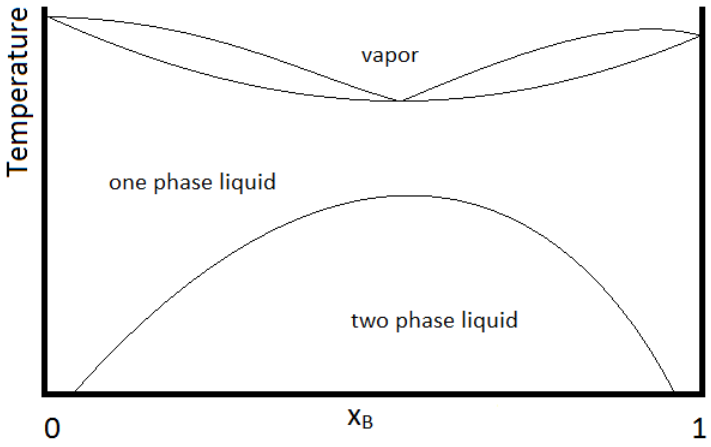
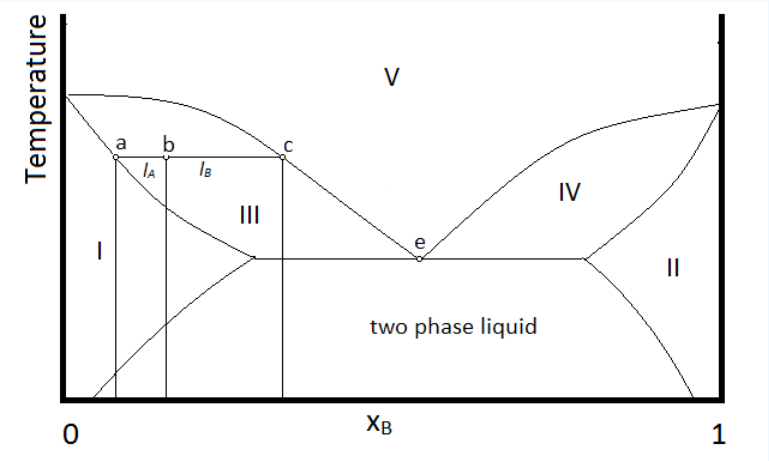


Figure **9.6.3**: *Phase diagram for a binary solution with the boiling point of a minimum boiling azeotrope that is higher that when components are miscible (single phase).*

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 **9.6.3**.

Example 9.6.1:

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.

9.6.1.1: Gibbs-Duhem and Henry's law

What happens when Raoult does *not* hold over the whole range? Recall that in a gas:

$$\mu_j = \mu_j^o + RT \ln \frac{P_j}{P^o} \tag{9.6.1}$$

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

$$\frac{x_1}{x_1} = x_2\frac{\partial \ln P_2}{\partial x_2}$$

$$1 = x_2\frac{\partial \ln P_2}{\partial x_2}$$

$$\frac{1}{x_2} = \frac{\partial \ln P_2}{\partial x_2} \tag{9.6.2}$$

We can integrate Equation 9.6.2 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.)

9.6.2: 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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9.7: Activities of Nonideal Solutions

The bulk of the discussion in this chapter dealt with ideal solutions. However, real solutions will deviate from this kind of behavior. So much as in the case of gases, where fugacity was introduced to allow us to use the ideal models, **activity** is used to allow for the deviation of real solutes from limiting ideal behavior. The activity of a solute is related to its concentration by

$$a_B = \gamma \frac{m_B}{m^o}$$

where γ is the **activity coefficient**, m_B is the molaliy of the solute, and m^o is unit molality. The activity coefficient is unitless in this definition, and so the activity itself is also unitless. Furthermore, the activity coefficient approaches unity as the molality of the solute approaches zero, insuring that dilute solutions behave ideally. The use of activity to describe the solute allows us to use the simple model for chemical potential by inserting the activity of a solute in place of its mole fraction:

$$\mu_B = \mu_B^o + RT \ln a_B$$

The problem that then remains is the measurement of the activity coefficients themselves, which may depend on temperature, pressure, and even concentration.

9.7.1: Activity Coefficients for Ionic Solutes

For an ionic substance that dissociates upon dissolving

$$MX(s) \rightarrow M^+(aq) + X^-(aq)$$

the chemical potential of the cation can be denoted μ_+ and that of the anion as μ_-. For a solution, the total molar Gibbs function of the solutes is given by

$$G = \mu_+ + \mu_-$$

where

$$\mu = \mu^* + RT \ln a$$

where \(\mu^*\) denotes the chemical potential of an ideal solution, and a is the activity of the solute. Substituting his into the above relationship yields

$$G = \mu_+^* + RT \ln a_+ + \mu_-^* + RT \ln a_-$$

Using a molal definition for the activity coefficient

$$a_i = \gamma_i m_i$$

The expression for the total molar Gibbs function of the solutes becomes

$$G = \mu_+^* + RT \ln \gamma_+ m_+ + \mu_-^* + RT \ln \gamma_- m_-$$

This expression can be rearranged to yield

$$G = \mu_+^* + \mu_-^* + RT \ln m_+ m_- + RT \ln \gamma_+ \gamma_-$$

where all of the deviation from ideal behavior comes from the last term. Unfortunately, it impossible to experimentally deconvolute the term into the specific contributions of the two ions. So instead, we use a geometric average to define the **mean activity coefficient**, $\gamma_\pm$.

$$\gamma_\pm = \sqrt{\gamma_+ \gamma_-}$$

For a substance that dissociates according to the general process

$$M_x X_y(s) \rightarrow xM^{y+}(aq) + yX^{x-}(aq)$$

the expression for the mean activity coefficient is given by

$$\gamma_\pm = (\gamma_+^x \gamma_-^y)^{1/x+y}$$

9.7.1.1: Debeye-Hückel Law

In 1923, Debeye and Hückel (Debye & Hückel, 1923) suggested a means of calculating the mean activity coefficients from experimental data. Briefly, they suggest that

$$\log_{10}\gamma_{\pm} = \frac{1.824 \times 10^6}{(\epsilon T)^{3/2}}|z_+ + z_-|\sqrt{I}$$

where ϵ is the dielectric constant of the solvent, T is the temperature in K, z_+ and z_- are the charges on the ions, and I is the **ionic strength** of the solution. I is given by

$$I = \frac{1}{2}\frac{m_+ z_+^2 + m_- z_-^2}{m^o}$$

For a solution in water at 25 ^oC,

As seen before activities are a way to account for deviation from ideal behavior while still keeping the formulism for the ideal case intact. For example in a ideal solution we have:

$$\mu^{sln} = \mu^* + RT\ln x_i$$

is replaced by

$$\mu^{sln} = \mu^* + RT\ln a_i$$

The relationship between a_i and x_i is often written using an activity coefficient γ:

$$a_i = \gamma_i x_i$$

9.7.2: Raoult versus Henry

Implicitly we have made use of Raoult's law here because we originally used

$$x_i = \frac{P_i}{P_i^*}$$

In the case of a solvent this makes sense because Raoult's law is still valid in the limiting case, but for the solute it would make more sense to use Henry's law as a basis for the definition of activity:

$$a_{solute,H} \equiv \frac{P_{solute}}{K_{x,H}}$$

This does mean that the μ^* now becomes a μ^{*Henry} because the extrapolation of the Henry law all the way to the other side of the diagram where $x_{solute} = 1$ points to a point that is not the equilibrium vapor pressure of this component. In fact it represents a virtual state of the system that cannot be realized. This however does not affect the usefulness of the convention.

9.7.3: Various concentration units

The subscript X was added to the K value because we are still using mole fractions. However Henry's law is often used with other concentration measures. The most important are:

- molarity
- molality
- mole fraction

Both the numerical values and the dimensions of K will differ depending on which concentration measure is used. In addition the pressure units can differ. For example for oxygen in water we have:

$K_{x,H}$= 4.259 10^4 atm

$K_{cp,H}$= 1.3 10^{-3} mol/lit.atm

$K_{pc,H}$= 769.23 lit.atm/mol

As you can see $K_{cp,H}$ is simply $1/K_{pc,H}$, both conventions are used..

Note that in this case a choice based on Raoult is really not feasible. At room temperature we are far above the critical point of oxygen which make the equilibrium vapor pressure a non-existent entity. Returning to activities we could use each of the versions of K as a basis for the activity definition. This means that when using activities it must be specified what scale we are using. Activities and Henry coefficients of dissolved gases in water (both fresh and salt) are quite important in geochemistry, environmental chemistry etc.

9.7.4: Non-volatile solutes

A special case arises if the vapor pressure of a solute is negligible. For example if we dissolve sucrose in water. In that case we can still use the Henry based definition

$$a_{solute,H} \equiv \frac{P_{solute}}{K_{x,H}}$$

Even though both K and P will be exceedingly small their ratio is still finite. However how do we determine either?

The answer lies in the solvent. Even if the vapor pressure of sucrose is immeasurably small, the water vapor pressure above the solution can be measured. The Gibbs-Duhem equation can then be used to translate one into the other. We can use Raoult Law to define the activity of the solvent:

$$a_1 = \frac{P_1}{P_1^*}$$

We can measure the pressures as a function of the solute concentrations. At low concentrations

$$\ln a_1 \ln x - 1 \approx -x - 2$$

At higher concentrations we will get deviations, we can write:

$$\ln \frac{P_1}{P_1^*} = \ln a_1 \approx -x_2 \varphi$$

The 'fudge factor' φ is known as the *osmotic coefficient* and can thus be determined as a function of the solute concentration from the pressure data. What we are really interested in is a_2, not a_1:

$$a_2 = \gamma_2 x_2$$

Using Gibbs-Duhem we can convert φ into γ_2. Usually this is done in terms of molalities rather than mole fractions and it leads to this integral:

$$\ln \gamma_{2,m} = \varphi - 1 + \int_{m'=0}^{m} \frac{\varphi - 1}{m'} dm'$$

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9.8: Activities are Calculated with Respect to Standard States

Need to define a new variable. The thermodynamic activity, a, is the effective concentration of a species in a mixture. It is a dimensionless quantity that are calculated with respect to standard states. For a gas, this would be related to the fugacity and for a solution, to the concentration. The activity for a real gas:

$$a_i = \frac{f_i}{P^\circ} = \frac{\phi_i P_i}{P^\circ} = \frac{\phi_i (y_i P)}{P^\circ}$$

For systems where we treat the gases as ideal:

$$\phi_i = 1$$

$$a_i = \frac{P_i}{P^\circ} = y_i \frac{P}{P^\circ}$$

The activity for a solution:

$$a_i = \gamma i \frac{[A]}{1\ \underline{M}}$$

General chemistry and organic chemistry use ideal reactants where $\gamma_i = 1$:

$$a_i = \frac{[A]}{1\ \underline{M}}$$

The activity for a solid or liquid:

$$a_i = 1$$

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9.9: Gibbs Energy of Mixing of Binary Solutions in Terms of the Activity Coefficient

9.9.0.1: Activity and activity coefficients

In the ideal case, we have seen that the thermodynamic potential for species i can be written as:

$$\mu_i^{sln} = \mu_i^o + RT \ln x_i = \mu_2^o + RT \ln \left(\frac{P_i}{P^o} \right)$$

One approach to non-ideality is to simply ***redefine*** the problem and say:

$$\mu_i^{sln} \equiv \mu_i^o + RT \ln a_i$$

≡ indicates this is actually a definition. The newly defined variable a_2 is known as the **activity**. Alternatively we can define it as:

$$[a_i] \equiv \frac{P_i}{P^o}$$

As at high enough values of the mole fraction we know that we can still apply Raoult law. So a_i must approach x_i in this limit, but for other concentrations this will no longer hold. Often this is expressed in terms of an ***activity coefficient*** γ:

$$[a_i] = \gamma_i x_i$$

For high values of x_i, γ_i will approach unity. If we model the non-ideality with a Margules function we see that:

$$P_i = x_i P^o f_{Mar}$$

$$[a_i] = \left[\frac{P_i}{P^0} \right] = \left[\frac{x_i P^0 f_{Mar}}{P^0} \right] = [x_i f_{Mar}]$$

The activity coefficient and the Margules function are the same thing in this description.

9.9.0.1: Regular solutions

A special and simplest case of a Margules function is the case where all but one Margules parameters (a) can be neglected. Such a system is called a ***regular solution***. In this case, we can write:

$$a_1 = x_1 e^{a x_2^2}$$

We can use Gibbs-Duhem to show that this *implies*:

$$a_2 = x_2 e^{a x_1^2}$$

Gibbs free energy of regular solutions

Consider the change in Gibbs free energy when we mix two components to form a regular solution:

$$\Delta G_{mix} = n_1 \mu_1^{sln} + n_2 \mu_2^{sln} - (n_1 \mu_1^* + n_2 \mu_2^*)$$

Dividing by the total number of moles, we get:

$$\Delta_{mix} G = x_1 \mu_1^{sln} + x_2 \mu_2^{sln} - (x_1 \mu_1^* + x_2 \mu_2^*)$$

Using:

$$\mu_i^{sln} \equiv \mu_i^* + RT \ln a_i$$

and:

$$[a_i] = \gamma_i x_i$$

We get:

$$\frac{\Delta_{mix} G}{RT} = x_1 \ln x_1 + x_2 \ln x_2 + x_1 \ln \gamma_1 + x_2 \ln \gamma_2$$

For a regular solution:

$$\ln \gamma_1 = \ln f_{Mar} = a x_2^2$$

$$\ln \gamma_2 = \ln f_{Mar} = a x_1^2$$

This gives:

$$\begin{aligned} \frac{\Delta_{mix} G}{RT} &= x_1 \ln x_1 + x_2 \ln x_2 + x_1 a x_2^2 + x_2 a x_1^2 \\ &= x_1 \ln x_1 + x_2 \ln x_2 + a[x_1 + x_2] x_1 x_2 \\ &= x_1 \ln x_1 + x_2 \ln x_2 + a x_1 x_2 \end{aligned}$$

Since:

$$x_1 + x_2 = 1$$

In this expression we see that we have an additional term to the entropy of mixing term we had seen before. Its coefficient a is dimensionless but represents the fact that the (strong!) interactions between the molecules are different depending on who is the neighbor. In general. a can be written as W/RT, where W represents an energy (enthalpy) that brings the difference in interaction energies into account. W does not depend strongly on temperature. We could look at W as the difference in average interaction energies:

$$W = 2U_{12} - U_{11} - U_{22}$$

Rearranging we get:

$$\frac{\Delta_{mix} G}{W} = \frac{RT}{W}[x_1 \ln X_1 + x_2 \ln x_2] + x_1 x_2$$

The two terms will ***compete*** as a function of temperature. The mixing entropy will be more important at high temperatures, the interaction enthalpy at low temperatures. The entropy term has a *minimum* at x_1=0.5, the enthalpy term a *maximum* if W is positive. So, one tends to favor mixing, the other segregation and we will get a compromise between the two. Depending on the value of RT/W (read: temperature), we can either get one or two minima. This means that at low temperatures there will be a solubility limit of 1 into 2 and *vice versa*. At higher temperatures the two components can mix completely. At the transition between these two regimes we will have ***critical or consolute point***.

Notice that even though we used the vapor pressures of the gas to develop our theory, they are conspicuously absent from the final result. The same thing we said about melting points hold true here. Because we are dealing with the miscibility behavior of two condensed phases, the outcome should not depend very strongly on the total pressure of our experiment.

Although in regular solutions the consolute point is predicted to be a maximum in temperature, we can find them as minima as well in practice. The nicotine-water system even has two consolute points, an upper and a lower one. When heating up a mixture of these we first observe mixing, then segregation and then mixing again. Obviously this behavior is far more complicated than we can describe with just one Margules parameter.

9.9.0.0.1: Partial molar volumes

What we said above about volumes simply being additive in the ideal case is no longer true here.

$$\left(\frac{\partial \Delta G_{mix}}{\partial P}\right)_T = \Delta V_{\text{regular}}$$

$$\left(\frac{\partial \Delta H_{mix} + RT(n_1 \ln [x_1] + n_2 \ln [x_2])}{\partial P}\right)_T = \Delta V_{\text{mix}}$$

$$\left(\frac{\partial \Delta H_{mix}}{\partial P}\right)_T = \Delta V_{\text{mix}}$$

In general the enthalpy of mixing does depend on pressure as it is related to the interactions between the molecules in solution. (W depends on the distance between them). This means that partial molar volumes now become a function of composition and volume is no longer simply additive.

9.9.1: Real solutions

Notice that the curves are *symmetrical* around $x = 0.5$. This implies that it is as easy (or not) dissolving A into B as vice versa. In many cases this is not realistic. Many systems diverge more seriously from ideal behavior that the regular one. Up to a point we can model that by adding more terms to the Margules function. For example, adding a β-term undoes the symmetry (see example 24-7). However, many systems are so non-ideal that the Margules expression become unwieldy with too many parameters.

9.9.2: Boiling non-ideal solutions

9.9.2.1: Azeotropes

For ideal solutions we have seen that there is a lense shaped two-phase region between the gas and the liquid phase. For non-ideal systems the two-phase region can attain different shapes. In many cases there is either a minimum or a maximum. As such a point the phase gap closes to a point that is known as an *azeotrope*. It represents a composition of the liquid that boils *congruently*. That means that the vapor and the liquid have the same composition for a change. Azeotropes impose an important limitation unto distillation: they represent the end point of a distillation beyond which we can not purify by this method.

9.9.2.2: Eutectics

Another point to be made is that in the diagram with the consolute point we are assuming the pressure to be constant. If we lower the pressure this would affect the boiling points strongly: the whole gas-liquid gap would come down in temperature (see animation). The mixing behavior is only weakly affected. (The reason is that one involves the volume term of the gas, the other only of the liquid(s)). At lower pressures it is possible therefore that the consolute point is *above* the gas-liquid gap. In other words: the mixtures will boil before they get a chance to mix. The boiling points will be lower there than for the pure compounds. There will be a composition for which the boiling point is at a minimum and where the mixture boils congruently (i.e. to a vapor with the same (overall) composition).

The mutual solubility limits increase as temperature increases, just as happens in the critical mixing case, but that due to the competition from the vapor phase this process comes to an end at the eutectic temperature. At this temperature one liquid boils always completely, the other one in part. At the eutectic composition they both boil away simultaneously.

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9.E: Solutions I- Liquid-Liquid Solutions (Exercises)

TBA

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10.12: Activities are Important for Ionic Species
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10.1: Equilibrium Results when Gibbs Energy is Minimized

Many important chemical reactions -if not *most*- are performed in *solution* rather than between solids or gases. Solid state reactions are often very slow and not all chemical species can be put in the vapor phase because they decompose before evaporating.

Often we are not concerned with the temporal aspects of a reaction. That can be technologically very important but it is the domain of *kinetics* - a different branch of Physical Chemistry - rather than classical thermodynamics.. The latter is more concerned with the endpoint. This is the thermodynamically speaking the (stable) equilibrium, but chemically it can either represent a *completed* reaction or a *chemical equilibrium*.

Unfortunately, of the three main aggregation states: gas – liquid – solid, the structure of liquids is least understood and one of the most complex liquids is also one of the most extensively used ones: water. It is vital to many branches of chemistry varying from geochemistry to environmental chemistry to biochemistry. We shall make just a small inroad into its complexity.

10.1.1: Extent of reaction

To describe the progress of a reaction we define the **extent of reaction**. It is usually denoted by the Greek letter ξ.

Consider a generic reaction:

$$v_A A + v_B B \rightleftharpoons v_Y Y + v_Z Z$$

Using stoichiometry we can define the extent by considering how the number of moles (or molar amounts) of each species changes during the reaction:

reactants

- $n_A = n_{A,0} - v_A \xi$
- $n_B = n_{B,0} - v_B \xi$

products

- $n_Y = n_{Y,0} + v_Y \xi$
- $n_Z = n_{Z,0} + v_Z \xi$

The dimension of ξ is [mol] because the stoichiometric coefficients v_i are dimensionless integers. If the reaction goes to completion for one of the reactants -the *limiting reactant*- $n_{A \text{ or } B}$=n_{limiting} will go to zero. If we start with $n_{limiting} = v_{limiting}$ moles, the value of ξ starts at 0 (no products) and goes to 1 at completion (limiting reactant depleted). When approaching an equilibrium ξ will not go beyond ξ_{eq}.

10.1.2: Measuring ξ

The extent of reaction is what is the central subject of reaction kinetics. Its value is typically measured as a function of time indirectly by measuring a quantity q that is *linearly dependent* on ξ(t):

$$q(\xi) = a\xi + b$$

Consider the situation at the extremes $\xi = 0$ and $\xi = 1$:

$$q_0 = a.0 + b = b$$

$$q_1 = a.1 + b = a + b$$

$$q_1 - q_0 = a$$

Thus, ξ can be found from

$$\frac{q(t) - q0}{q_1 - q_0} = \frac{q(t) - b}{a}$$

The nature of q can vary widely from UV/Vis absorption, conductivity, gravimetric to caloric data.

In practice, q_0 at $\xi = 0$ is often hard to observe because it takes time to mix the reactants, particularly in solutions, and q_1 at ξ=1 may never be reached if the reaction goes to equilibrium. Nevertheless the values of a and b can often be found from the available data by fitting techniques.

In (equilibrium, static) thermodynamics we are only concerned with the endpoint:

- $\xi = 1$: the reaction runs to completion
- $\xi = \xi_{eq}$: the react ion goes to a state of chemical equilibrium

10.1.3: Thermodynamic Potentials

As we have seen we can write any change in the Gibbs free energy due to changes in the molar amounts of the species involved in the reaction (at T, P constant) as:

$$dG = \sum \frac{\partial G}{\partial n_i} dn_i = \sum \mu_i dn_i$$

where μ is the *thermodynamic potential*, often called *chemical potential* when dealing with reactions. From the definition of ξ we can see by differentiation that

- $dn_A = -v_A d\xi$
- $dn_B = -v_A d\xi$
- $dn_Y = v_Y d\xi$
- $dn_Z = v_Z d\xi$

This allows us to *unify the changes* in the molar amount of all the species into *one single variable* $d\xi$. We get:

$$dG = \left[\sum -v_{i,reactants}\mu_{i,reactants} + \sum +v_{i,products}\mu_{j,products}\right] d\xi$$

or

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,P} = -\sum v_{i,r}\mu_{i,r} + \sum v_{i,p}\mu_{j,p}$$

This quantity is also written as:

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

This quantity gives the change in Gibbs free energy for the reaction (as written!!) for $\Delta\xi$=1 mole. (Units are [J/mol] therefore). This is the change in Gibbs energy (the slope of G vs ξ) when the extent of reaction changes by one mole with a fixed composition. Equilibrium results when Gibbs energy is at a minimum with respect to the extent of reaction.

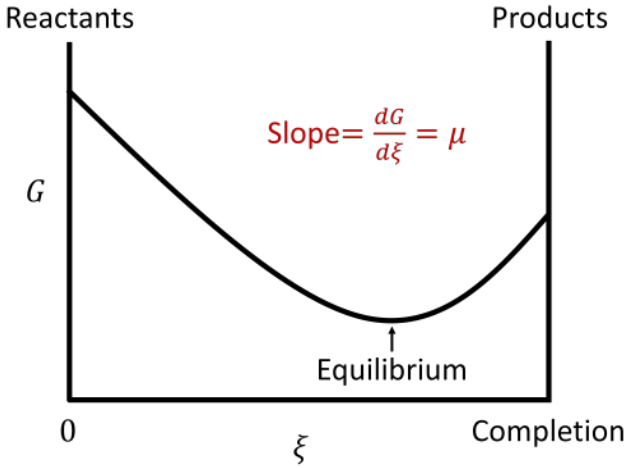


Figure 1. Gibbs energy plotted as a function of the extent of reaction. Equilibrium results when the Gibbs energy is minimized.

10.1.4: Gas Reactions

Let us assume that our reaction is entirely between gas species and that the gas is sufficiently dilute that we can use the ideal gas law. Then we can write for each species:

$$\mu_i = \mu_i^o + RT \ln \frac{P_i}{P_i^o}$$

We can then split up the $\Delta_r G$ expression in two parts:

$$\Delta_r G = \Delta_r G^o + RT \ln Q$$

The standard potentials:

$$\Delta_r G^o = -\sum v_{i,r}\, \mu_{i,r}^o + \sum v_{i,p} \mu_{j,p}^o$$

and the logarithmic terms:

$$RT \ln Q = -v_A RT \ln \left(\frac{P_A}{P_A^o} \right) - v_B RT \ln \left(\frac{P_B}{P_B^o} \right) + v_Y RT \ln \left(\frac{P_Y}{P_Y^o} \right) + v_Z RT \ln \left(\frac{P_Z}{P_Z^o} \right)$$

We can combine all the logarithmic terms into Q, called the ***reaction quotient***. The stoichiometric coefficients become exponents and the reactants' factors will be 'upside down' compared to the products, because of the properties of logarithms:

$$a \ln x = \ln x^a$$

$$-a \ln x = \ln \left(\frac{1}{x^a} \right)$$

We have kept the standard pressures P_i^o in the expression, but often they are omitted. They are usually all 1 bar, but in principle we could choose 1 bar for A 1 Torr for B an 1 psi for the products. It creates a valid (though ridiculous) definition of what $^\ominus$ stands for. (Of course the value of $\Delta_r G^o$ does *depend* on that choice!).

We could write

$$RT \ln Q = RT \ln \frac{Q_P}{Q^o}$$

Q^o is typically unity in magnitude but it *cancels the dimensions* of Q_P. That means that Q and Q_P are equal in magnitude and we can get Q from Q_P by simply dropping the dimensions. Q is dimensionless but Q_P usually is not. Often this fine distinction is simply not made and Q^o is *omitted*, we get:

$$\Delta_r G = \Delta_r G^o + RT \ln \frac{P_Y^{v_Y} P_Z^{v_Z}}{P_A^{v_A} P_B^{v_B}}$$

Notice the difference between $\Delta_r G$ which denotes the conditions (e.g. pressures) of *your reaction* and $\Delta_r G^o$ denotes standard conditions.

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10.2: An Equilibrium Constant is a Function of Temperature Only

Consider a generic reaction:

$$v_A A + v_B B \rightleftharpoons v_Y Y + v_Z Z$$

When the reaction reaches equilibrium, the Gibbs energy of reaction, $\Delta_r G$, goes to zero. In this case, the reaction quotient, Q, is usually rewritten as the **equilibrium constant**, K, and we get:

$$\Delta_r G = \Delta_r G^o + RT \ln K = 0$$

$$\Delta_r G^o = -RT \ln K$$

where

$$K = \frac{P_{eq,Y}^{vY} P_{eq,Z}^{vZ}}{P_{eq,A}^{vA} P_{eq,B}^{vB}}$$

> **Note**
>
> As you see $\Delta_r G^o$ is ***not*** zero, because the standard state does ***not*** represent an equilibrium state (typically).

We can calculate the temperature dependence of K. Rather than look at:

$$\left(\frac{\partial K}{\partial T}\right)_P$$

We will look at:

$$\left(\frac{\partial \ln K}{\partial T}\right)_P$$

Starting with Gibbs energy:

$$\Delta_r G^\circ = -RT \ln K$$

$$\therefore \ln K = -\frac{\Delta r G^\circ}{RT}$$

$$\left(\frac{\partial \ln K}{\partial T}\right)_P = -\frac{1}{R}\left[\frac{\partial (\Delta_r G^\circ / T)}{\partial T}\right]_P$$

We need to take the Gibbs-Helmholtz equation:

$$\Delta \bar{H} = -T^2 \left[\frac{\partial (\Delta \bar{G}/T)}{\partial T}\right]_P$$

We can also write it as:

$$\left[\frac{\partial \left(\Delta \bar{G}/T\right)}{\partial T}\right]_P = -\frac{\Delta \bar{H}}{T^2}$$

Plugging the Gibbs-Helmholtz equation into our earlier equation, we obtain the Van't Hoff equation:

$$\left(\frac{\partial \ln K}{\partial T}\right)_P = \frac{\Delta_r H^\circ}{RT^2}$$

The temperature dependence of the equilibrium constant depends on enthalpy of reaction. Rearranging:

$$d(\ln K) = \frac{\Delta_r H^\circ(T)}{RT^2} dT$$

This is the Van't Hoff equation. We can use it to find K at other temperatures. Assuming enthalpy is independent of temperature, the integrated form becomes:

$$\ln \frac{K(T_2)}{K(T_1)} = -\frac{\Delta_r H^\circ}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

10.2.1: Le Chatelier's Principle

In the ideal gas reaction case, K **only** depends on temperature, T, (just like U) not on the total pressure, P. This leads to the well-known principle of Le Chatelier. Consider a gas reaction like:

\[A \rightleftharpoons B + C \nonumber \nonumber \]

e.g.

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

In pressures, the equilibrium constant becomes:

$$K = \frac{P_B P_C}{P_A}$$

If initially n_A =1 we have at an extent ξ:

n_A = 1- ξ

n_B= ξ

n_C= ξ

n_{Total} = 1+ ξ

The partial pressures are given by Dalton's law:

P_A= [1- ξ /1+ ξ] P

P_B [ξ / 1+ ξ] P

P_C [ξ /1+ ξ] P

The equilibrium constant becomes:

$$K = P\frac{\xi_{eq}^2}{1-\xi_{eq}^2}$$

Even though the total pressure, P, does occur in this equation, K is *not* dependent on P. If the total pressure is changed (e.g. by compression of the gas) the value of ξ_{eq} will change (the equilibrium shifts) in response. It will go to the side with the fewer molecules. This fact is known as le Chatelier's principle

If the system is not ideal we will also get a Chatelier shift, but the value of K may change a little because the value of the activity coefficients (or fugacity) is a little dependent on the pressure too. In solution the same thing holds. In ideal solutions K is only T dependent, but as we saw these systems are rare. Particularly in ionic solutions equilibrium constants will be effected by other things than just temperature, e.g. changes in the ionic strength and we need to find the activity coefficients to make any predictions.

Example

Consider the reaction of ammonia decomposition:

$$2NH_3\,(g) \leftrightharpoons N_2\,(g) + 3H_2\,(g)$$

$$\Delta_f H^\circ(NH_3, g) = -45.90\ \text{kJ/mol}$$

The reaction is initially at equilibrium. For each of the stresses, use your General Chemistry knowledge to decide if equilibrium will be unaffected, or if it will shift towards reactants or products.

Process	Shifts towards
Isothermal removal of H_2 gas	
Isothermal addition of N_2 gas	
Isothermal decrease of container volume	
Isothermal and isochoric addition of argon gas	
Isobaric increase of temperature	

Write the equilibrium constant expression for the above chemical reaction in terms of gas-phase mole fractions.

10.2.2: Concentration

The gas law contains a hidden definition of concentration:

$$PV = nRT$$

$$P = \left(\frac{n}{V}\right) RT$$

$$P = cRT$$

$$c = \frac{P}{RT} \tag{10.2.1}$$

Here c stands for the molar amount per unit volume or ***molarity***. For gaseous mixtures we do not use this fact much, but it provides the link to the more important liquid solution as a reaction medium. We can rewrite the equilibrium constant as

$$K = \frac{c_{eq,Y}^{v_Y} c_{eq,Z}^{v_Z}}{c_{eq,A}^{v_A} c_{eq,B}^{v_B}} \tag{10.2.2}$$

However, c (Equation 10.2.1) is substituted into K (Equation 10.2.2), then not all the factors of RT cancel. The missing term g. ln[RT] depends on the stoichiometric coefficients:

$$g = v_Y + v_Z - v_A - v_B$$

The term is generally *incorporated* in $\Delta_r G^\circ$ so that the latter now refers to a new standard state of 1 mole per liter of each species rather than 1 bar of each (or so).

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10.3: Standard Gibbs Energies of Formation Can Be Used to Calculate Equilibrium Constants

10.3.1:

The relation $K = e^{-\frac{\Delta_r G^\circ}{RT}}$ gives us a way to evaluate the thermodynamic equilibrium constant K of a reaction at a given temperature from the value of the standard molar reaction Gibbs energy $\Delta_r G^\circ$ at that temperature. If we know the value of $\Delta_r G^\circ$, we can calculate the value of K.

One method is to calculate $\Delta_r G^\circ$ from values of the **standard molar Gibbs energy of formation** $\Delta_f G^\circ$ of each reactant and product. These values are the standard molar reaction Gibbs energies for the formation reactions of the substances. To relate $\Delta_f G^\circ$ to measurable quantities, we make the substitution $\mu_i = H_i - TS_i$ (Eq. 9.2.46) in $\Delta_r G = \sum_i \nu_i \mu_i$ to give $\Delta_r G = \sum_i \nu_i H_i - T\sum_i \nu_i S_i$, or

$$\Delta_r G = \Delta_r H - T\Delta_r S \tag{11.8.20}$$

When we apply this equation to a reaction with each reactant and product in its standard state, it becomes

$$\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ \tag{11.8.21}$$

where the standard molar reaction entropy is given by

$$\Delta_r S^\circ = \sum_i \nu_i S_i^\circ \tag{11.8.22}$$

If the reaction is the *formation* reaction of a substance, we have

$$\Delta_f G^\circ = \Delta_f H^\circ - T\sum_i \nu_i S_i^\circ \tag{11.8.23}$$

where the sum over i is for the reactants and product of the formation reaction. We can evaluate the standard molar Gibbs energy of formation of a substance, then, from its standard molar enthalpy of formation and the standard molar entropies of the reactants and product.

Extensive tables are available of values of $\Delta_f G^\circ$ for substances and ions. An abbreviated version at the single temperature $298.15\,\mathrm{K}$ is given in Appendix H. For a reaction of interest, the tabulated values enable us to evaluate $\Delta_r G^\circ$, and then K, from the expression (analogous to Hess's law)

$$\Delta_r G^\circ = \sum_i \nu_i \Delta_f G^\circ(i) \tag{11.8.24}$$

The sum over i is for the reactants and products of the reaction of interest.

Recall that the standard molar enthalpies of formation needed in Eq. 11.8.23 can be evaluated by calorimetric methods (Sec. 11.3.2). The absolute molar entropy values S_i° come from heat capacity data or statistical mechanical theory by methods discussed in Sec. 6.2. Thus, it is entirely feasible to use nothing but calorimetry to evaluate an equilibrium constant, a goal sought by thermodynamicists during the first half of the 20th century. (Another method, for a reaction that can be carried out reversibly in a galvanic cell, is described in Sec. 14.3.3.)

For *ions in aqueous solution*, the values of S_m° and $\Delta_f G^\circ$ found in Appendix H are based on the reference values $S_m^\circ = 0$ and $\Delta_f G^\circ = 0$ for H^+(aq) at all temperatures, similar to the convention for $\Delta_f H^\circ$ values discussed in Sec. 11.3.2. For a reaction with aqueous ions as reactants or products, these values correctly give $\Delta_r S^\circ$ using Eq. 11.8.22, or $\Delta_r G^\circ$ using Eq. 11.8.24.

Note that the values of S_m° in Appendix H for some ions, unlike the values for substances, are *negative*; this simply means that the standard molar entropies of these ions are less than that of H^+(aq).

The relation of Eq. 11.8.23 does not apply to an ion, because we cannot write a formation reaction for a single ion. Instead, the relation between $\Delta_f G^\circ$, $\Delta_f H^\circ$ and S_m° is more complicated.

Consider first a hypothetical reaction in which hydrogen ions and one or more elements form H_2 and a cation M^{z+} with charge number z_+:

$$z_+\mathrm{H^+(aq)} + \text{elements} \rightarrow (z_+/2)\mathrm{H_2(g)} + \mathrm{M^{z+}(aq)}$$

For this reaction, using the convention that $\Delta_f H^\circ$, S°_m, and $\Delta_f G^\circ$ are zero for the aqueous H^+ ion and the fact that $\Delta_f H^\circ$ and $\Delta_f G^\circ$ are zero for the elements, we can write the following expressions for standard molar reaction quantities:

$$\Delta_r H^\circ = \Delta_f H^\circ(\mathrm{M^{z+}}) \tag{11.8.25}$$

$$\Delta_r S^\circ = (z_+/2)S^\circ_m(\mathrm{H_2}) + S^\circ_m(\mathrm{M^{z+}}) - \sum_{\text{elements}} S^\circ_i \tag{11.8.26}$$

$$\Delta_r G^\circ = \Delta_f G^\circ(\mathrm{M^{z+}}) \tag{11.8.27}$$

Then, from $\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ$, we find

$$\Delta_f G^\circ(\mathrm{M^{z+}}) = \Delta_f H^\circ(\mathrm{M^{z+}}) \quad - T\left[S^\circ_m(\mathrm{M^{z+}}) - \sum_{\text{elements}} S^\circ_i + (z_+/2)S^\circ_m(\mathrm{H_2})\right] \tag{11.8.28}$$

For example, the standard molar Gibbs energy of the aqueous mercury(I) ion is found from

$$\Delta_f G^\circ(\mathrm{Hg_2{}^{2+}}) = \Delta_f H^\circ(\mathrm{Hg_2{}^{2+}}) - TS^\circ_m(\mathrm{Hg_2{}^{2+}}) + 2TS^\circ_m(\mathrm{Hg}) - \tfrac{2}{2}TS^\circ_m(\mathrm{H_2}) \tag{11.8.29}$$

For an anion $\mathrm{X^{z-}}$ with negative charge number z_-, using the hypothetical reaction

$$|z_-/2|\mathrm{H_2(g)} + \text{elements} \rightarrow |z_-|\mathrm{H^+(aq)} + \mathrm{X^{z-}(aq)}$$

we find by the same method

$$\Delta_f G^\circ(\mathrm{X^{z-}}) = \Delta_f H^\circ(\mathrm{X^{z-}}) - T\left[S^\circ_m(\mathrm{X^{z-}}) - \sum_{\text{elements}} S^\circ_i - |z_-/2|S^\circ_m(\mathrm{H_2})\right] \tag{11.8.30}$$

For example, the calculation for the nitrate ion is

$$\begin{aligned}&\Delta_f G^\circ(\mathrm{NO_3{}^-}) \\ &= \Delta_f H^\circ(\mathrm{NO_3{}^-}) - TS^\circ_m(\mathrm{NO_3{}^-}) + \tfrac{1}{2}TS^\circ_m(\mathrm{N_2}) + \tfrac{3}{2}TS^\circ_m(\mathrm{O_2}) + \tfrac{1}{2}TS^\circ_m(\mathrm{H_2})\end{aligned} \tag{11.8.31}$$

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10.4: Gibbs Energy of a Reaction vs. Extent of Reaction is a Minimum at Equilibrium

As discussed in Section 26.4, we defined the extent of the reaction (ξ) as a quantitative measure of how far along the reaction has evolved. For simple reactions like $\mathbf{A} \rightleftharpoons \mathbf{B}$, the extent of reaction is easy to define and is simply the number of moles of **A** that has been converted to **B**. Since $d\xi$ has the same value as dn, we can write that

$$\begin{aligned} dG &= \mu_A dn_A + \mu_B dn_B \\ &= -\mu_A d\xi + \mu_B d\xi. \end{aligned}$$

The minus sign comes from the fact that when the reaction goes in the left to right direction, the amount of **A** is decreasing, while the amount of **B** is increasing. Looking at these equations, it is reasonable to suggest that:

$$\left(\frac{\partial G}{\partial \xi}\right)_{PT} = \mu_B - \mu_A$$

This is the slope of the free energy with respect to the extent of the reaction. This relationship will have a region where the sign is negative, one point where the value is zero and a region where the value is positive (Figure **10.4.1**). If we look at a plot of G as a function of ξ, we can see that the point where is the minimum of the curve:

$$\left(\frac{\partial G}{\partial \xi}\right)_{PT} = 0$$

This is the point where μ_A and μ_B are the same. On one side of the minimum, the slope is negative and on the other side, the slope is positive. In both cases, the reaction is spontaneous (i.e, $dG < 0$) as long as the reaction is evolving towards the minimum, which will be called the **equilibrium position**. Hence, all reactions spontaneously move towards equilibrium; the immediate question is what value of ξ corresponds to the equilibrium position of a reaction?

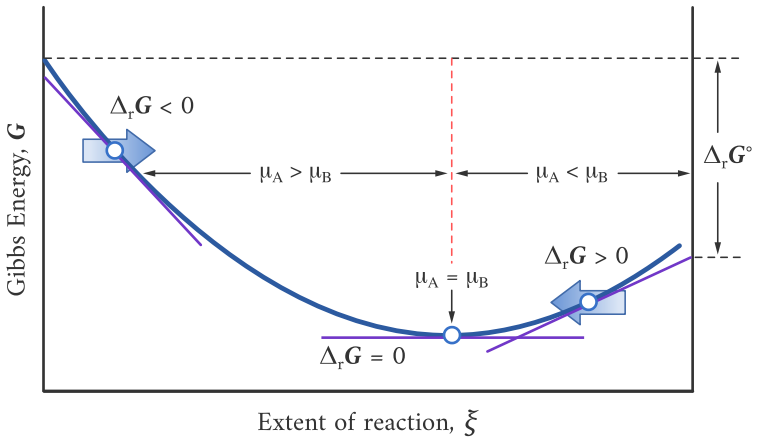


Figure **10.4.1**: Reactive Gibbs Energy and Equilibria. (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

Terminology

- A reaction for which $\Delta_r G < 0$ is called **exergonic**.
- A reaction for which $\Delta_r G > 0$ is called **endergonic**.
- $\Delta_r G < 0$, the forward reaction is spontaneous.
- $\Delta_r G > 0$, the reverse reaction is spontaneous.
- $\Delta_r G = 0$, the reaction is at equilibrium.

10.4.1: Ideal Gas Equilibrium

To understand how we can find the minimum and what the Gibbs free energy of a reaction depends on, let's first start with a reaction that converts one ideal gas into another.

$$\mathbf{A} \rightleftharpoons \mathbf{B}$$

Let's assume the reaction enthalpy is zero and hence the only thing that determines what the ratio of product to reactant should be is the entropy term (the mixing term), which is the most favorable when the mixture is half and half.

$$\Delta G_{\text{mix}} = nRT\left(\chi_A \ln \chi_A + \chi_B \ln \chi_B\right) \tag{10.4.1}$$

Remember that the Gibbs free energy of mixing is not a molar quantity and depends on n (unlike the reaction Gibbs free energy). Also, the Gibbs free energy of mixing is defined relative to pure **A** and **B**. The free energy of mixing in Equation 10.4.1 is at a minimum when the amounts of **A** equal **B**.

Thus, if we have a reaction $\mathbf{A} \rightleftharpoons \mathbf{B}$ and there is no enthalpy term (and no change in the inherent entropy of A vs. B), we would expect the system to have the minimum Gibbs free energy when the mole fraction of **A** and **B** are each 0.5.

Think about it

If **A** can form **B** and **B** can form **A** and there is no other forces involved (no heat/enthalpy) that would favor one product over the other, probability would just state that eventually you will have statistically the same amount of both A and B present -- this is the lowest free energy state. (This, of course, will not be true if the enthalpy for the reaction is not zero or if **A** and **B** have different inherent entropies). Usually there are additional terms for the reaction.

Lets work through this for an ideal gas reaction:

$$\begin{aligned}\Delta_r G &= \mu_B - \mu_A \\ &= \mu_B^o + RT\ln\frac{P_B}{P^\theta} - \mu_A^o - RT\ln\frac{P_A}{P^\theta} \\ &= \mu_B^o - \mu_A^o + RT\ln\frac{P_B}{P_A}\end{aligned}$$

What we normally do at this point is to give the first two terms a special name. Since it is the difference between the chemical potentials at standard conditions, we refer to it as the Gibbs free energy of reaction at standard conditions or the **standard Gibbs free energy of reaction**.

$$\begin{aligned}\Delta_r G^o &= \mu_B^o - \mu_A^o \\ \Delta_r G &= \Delta_r G^o + RT\ln\frac{P_B}{P_A}\end{aligned} \tag{10.4.2}$$

There are two parts to Equation 10.4.2. The first term ($\Delta_r G^o$) is the Gibbs free energy for converting one mole of **A** to **B** under standard conditions (1 bar of both **A** and **B**). The second term is the mixing term that is minimized when the amounts of A and B are equal to one another (Figure 10.4.2). The first term you look up in a reference book and is specific for a specific reaction. The second term is calculated knowing the partial pressures of **A** and **B** in the gas.

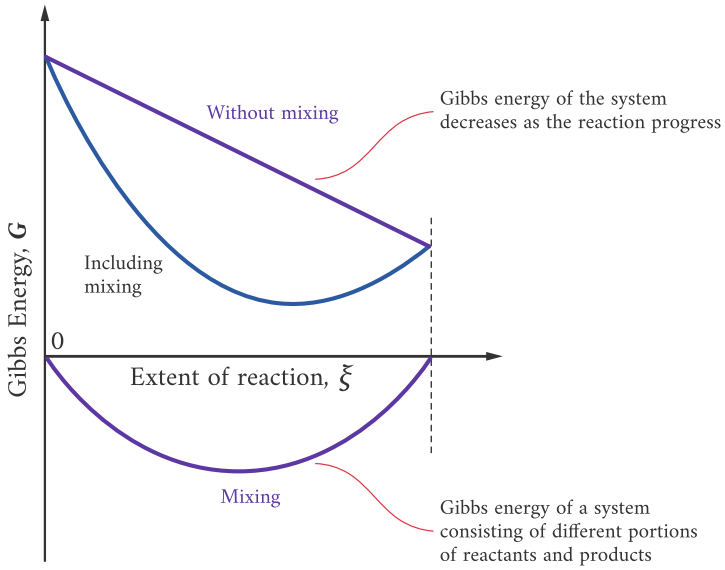


Figure **10.4.2**: Molecular interpretation of the minimum in the reaction Gibbs energy Gibbs energy of the system decreases as the reaction progress Gibbs energy of a system consisting of different portions of reactants and products. (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

Now the minimum absolute Gibbs free energy will occur at the bottom of the curve where the slope is zero. Thus, the lowest free energy will occur when the reaction free energy (i.e., the slope of that curve in Figure **10.4.1**) is equal to zero. The chemical potentials of **A** and **B** are equal.

$$\mu_A = \mu_B$$

At this point, the reaction will neither go forwards or backwards and we call this equilibrium. Hence, at equilibrium:

$$\begin{aligned}\Delta_r G &= \Delta_r G^o + RT \ln \frac{P_B}{P_A} \\ &= 0\end{aligned}$$

and the specific ratio of P_A and P_B necessary to ensure $\Delta_r G = 0$ is characteristic of the reaction and is called the **equilibrium constant** for that reaction.

$$K_{eq} = \frac{P_B}{P_A}$$

We can now relate thermodynamic quantities to concentrations of molecules at equilibrium. We can also see that at equilibrium:

$$\begin{aligned}0 &= \Delta_r G^o + RT \ln K_{eq} \\ \Delta_r G^o &= -RT \ln K_{eq} \\ K_{eq} &= e^{-\frac{\Delta_r G^o}{RT}}\end{aligned}$$

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10.5: Reaction Quotient and Equilibrium Constant Ratio Determines Reaction Direction

The Gibbs free energy function was constructed to be able to predict which changes could occur spontaneously. If we start with a set of initial concentrations we can write them in a reaction quotient

$$\Delta_r G = \Delta_r G^o + RT \ln Q$$

if we subtract the equilibrium version of this expression:

$$0 = \Delta_r G^o + RT \ln K$$

we get

$$\Delta_r G = RT \ln \left(\frac{Q}{K} \right)$$

That gives us the sign of $\Delta_r G$. If this is negative the reaction will spontaneously proceed from left to right as written, if positive it will run in reverse. In both case the value of Q will change until $Q = K$ and equilibrium has been reached.

The main difference between K and Q is that K describes a reaction that is at equilibrium, whereas Q describes a reaction that is not at equilibrium. To determine Q, the concentrations of the reactants and products must be known. For a given general chemical equation:

$$aA + bB \rightleftharpoons cC + dD \tag{10.5.1}$$

the Q equation is written by multiplying the activities for the species of the products and dividing by the activities of the reactants. If any component in the reaction has a coefficient, indicated above with lower case letters, the concentration is raised to the power of the coefficient. Q for the above equation is therefore:

$$Q = \frac{[C]^c[D]^d}{[A]^a[B]^b} \tag{10.5.2}$$

Note

A comparison of Q with K indicates which way the reaction shifts and which side of the reaction is favored:

- If $Q > K$, then the reaction favors the reactants. This means that in the Q equation, the ratio of the numerator (the concentration or pressure of the products) to the denominator (the concentration or pressure of the reactants) is larger than that for K, indicating that more products are present than there would be at equilibrium. Because reactions always tend toward equilibrium (Le Châtelier's Principle), the reaction produces more reactants from the excess products, therefore causing the system to shift to the **LEFT.** This allows the system to reach equilibrium.
- If $Q < K$, then the reaction favors the products. The ratio of products to reactants is less than that for the system at equilibrium—the concentration or the pressure of the reactants is greater than the concentration or pressure of the products. Because the reaction tends toward reach equilibrium, the system shifts to the **RIGHT** to make more products.
- If $Q = K$, then the reaction is already at equilibrium. There is no tendency to form more reactants or more products at this point. No side is favored and no shift occurs.

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10.6: The Sign of ΔG and not ΔG° Determines the Direction of Reaction Spontaneity

It is important to distinguish between the Gibbs energy of reaction, $\Delta_r G$ and the standard state Gibbs energy of reaction, $\Delta_r G°$. The ° refers to standard state conditions. That is, each reactant and product has a partial pressure of 1 bar if a gas, a concentration of 1 M if a solution, and they are all unmixed from each other. Such idealized conditions, while convenient for serving as a reference state, do not actually represent real reaction conditions. Consider the reaction of nitrogen with hydrogen to form ammonia:

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

$$\Delta_r G° = -32.9\ \frac{\mathrm{kJ}}{\mathrm{mol\ K}}$$

If the reaction was run under standard state conditions (1 bar partial pressure of each gas), the reaction would shift towards the products since $\Delta_r G° < 0$. That is, the partial pressures of N_2 and O_2 will decrease and the partial pressure of NH_3 will increase until equilibrium is reached. The Gibbs energy of reaction is dependent on the composition:

$$\Delta_r G = \Delta_r G° + RT \ln Q = \Delta_r G° + RT \ln \left(\frac{P_{\mathrm{NH_3}}^2}{P_{\mathrm{N_2}} P_{\mathrm{H_2}}^3} \right)$$

At equilibrium, the minimum Gibbs energy of reaction will be reached:

$$\Delta_r G = 0\ \frac{\mathrm{kJ}}{\mathrm{mol\ K}}$$

And the reaction quotient will equal the equilibrium constant:

$$Q = K$$

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10.7: The van 't Hoff Equation

We can use Gibbs-Helmholtz to get the temperature dependence of K

$$\left(\frac{\partial[\Delta G^o/T]}{\partial T}\right)_P = \frac{-\Delta H^o}{T^2}$$

At equilibrium, we can equate ΔG^o to $-RT\ln K$ so we get:

$$\left(\frac{\partial[\ln K]}{\partial T}\right)_P = \frac{\Delta H^o}{RT^2}$$

We see that whether K increases or decreases with temperature is linked to whether the reaction enthalpy is positive or negative. If temperature is changed little enough that ΔH^o can be considered constant, we can translate a K value at one temperature into another by integrating the above expression, we get a similar derivation as with melting point depression:

$$\ln\frac{K(T_2)}{K(T_1)} = \frac{-\Delta H^o}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

If more precision is required we could correct for the temperature changes of ΔH^o by using heat capacity data.

> *How K increases or decreases with temperature is linked to whether the reaction enthalpy is positive or negative.*

The expression for K is a rather sensitive function of temperature given its exponential dependence on the difference of stoichiometric coefficients One way to see the sensitive temperature dependence of equilibrium constants is to recall that

$$K = e^{-\Delta_r G^o/RT} \tag{10.7.1}$$

However, since under constant pressure and temperature

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

Equation 10.7.1 becomes

$$K = e^{-\Delta H^o/RT} e^{\Delta S^o/R} \tag{10.7.2}$$

Taking the natural log of both sides, we obtain a linear relation between $\ln K$and the standard enthalpies and entropies:

$$\ln K = -\frac{\Delta H^o}{R}\frac{1}{T} + \frac{\Delta S^o}{R} \tag{10.7.3}$$

which is known as the van 't Hoff equation. It shows that a plot of $\ln K$ vs. $1/T$ should be a line with slope $-\Delta_r H^o/R$ and intercept $\Delta_r S^o/R$.

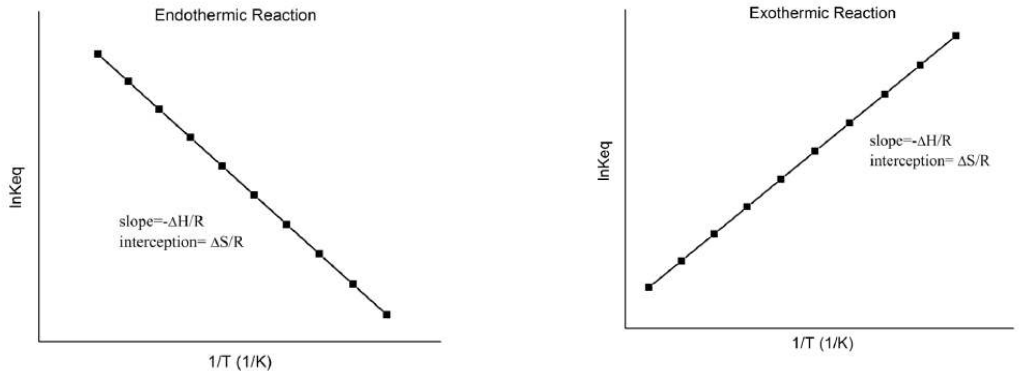


Figure 26.7.1 : Endothermic Reaction (left) and Exothermic Reaction van 't Hoff Plots (right). Figures used with permission of Wikipedia

Hence, these quantities can be determined from the $\ln K$ vs. $1/T$ data without doing calorimetry. Of course, the main assumption here is that $\Delta_r H^o$ and $\Delta_r S^o$ are only very weakly dependent on T, which is usually valid.

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10.8: Equilibrium Constants in Terms of Partition Functions

Consider the general gas phase chemical reaction represented by

$$\nu_A A + \nu_B B \rightleftharpoons \nu_C C + \nu_D D \tag{10.8.1}$$

where A, B, C and D are the reactants and products of the reaction, and ν_A is the stoichiometric coefficient of chemical A, ν_B is the stoichiometric coefficient of chemical B, and so on. Each of the gases involved in the reaction will eventually reach an equilibrium concentration when the forward and reverse reaction rates become equal. The distribution of reactants to products at the equilibrium point is represented by the equilibrium constant (K_c):

$$K_c = \frac{[C]^{\nu_C}[D]^{\nu_D}}{[A]^{\nu_A}[B]^{\nu_B}}$$

If the system is not at equilibrium, a shift in the number of reactants and products will occur to lower the overall energy of the system. The difference in the energy of the system at this non-equilibrated point and the energy of the system at equilibrium for any particular species is termed chemical potential. When both temperature and volume are constant for both points aforementioned, the chemical potential μ of species i is expressed by the equation

$$\mu_i = \left(\frac{\partial A}{\partial N_i}\right)_{T,V,N_{j\neq 1}} \tag{10.8.2}$$

where A is the Helmholtz energy, and N_i is the number of molecules of species i. The Helmholtz energy can be determined as a function of the total partition function, Q:

$$A = -k_B T \ln Q$$

where k_B is the Boltzmann constant and T is the temperature of the system. The total partition function is given by

$$Q = \frac{q_i(V,T)^{Ni}}{N_i!}$$

where q_i is the molecular partition function of chemical species i. Substituting the molecular partition function into the equation for Helmholtz energy yields:

$$A = -k_B T \ln\left(\frac{q_i(V,T)^{N_i}}{N_i!}\right)$$

and then further substituting this equation into the definition of chemical potential (Equation 10.8.2) yields:

$$\mu_i = \left(\frac{\partial - k_B T \ln\left(\frac{q_i(V,T)^{Ni}}{N_i!}\right)}{\partial N_i}\right)_{T,V,N_{j\neq 1}}$$

rearranging this equation the following derivative can be set-up:

$$\mu_i = -k_B T\left[\left(\frac{\partial N_i \ln\left(q_i(V,T)\right)}{\partial N_i}\right) - \left(\frac{\partial \ln\left(N_i!\right)}{\partial N_i}\right)\right]_{T,V,N_{j\neq 1}}$$

From this point Sterling's approximation

$$\ln N! = N \ln N - N$$

can be substituted into the derivative to yield:

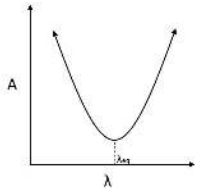
$$\mu_i = -k_B T\left[\left(\frac{\partial N_i \ln\left(q_i(V,T)\right)}{\partial N_i}\right) - \left(\frac{\partial \left(N_i \ln N_i - N_i\right)}{\partial N_i}\right)\right]_{T,V,N_{j\neq 1}}$$

From here the derivative can be rearranged and solved:

$$\begin{aligned}\mu_i &= -k_B T \\ &\quad \left[\ln\left(q_i(V,T)\right)\frac{\partial N_i}{\partial N_i} + N_i\frac{\partial \ln\left(q_i(V,T)\right)}{\partial N_i} - \ln\left(N_i\right)\frac{\partial N_i}{\partial N_i} - N_i\frac{\partial \ln\left(N_i\right)}{\partial N_i}\right. \\ &\quad \left. + \frac{\partial N_i}{\partial N_i}\right]_{T,V,N_{j\neq 1}} \\ &= -k_B T\left(\ln\left(q_i(V,T)\right) + 0 - \ln\left(N_i\right) - N_i\frac{1}{N_i} + 1\right) \\ &= -k_B T(\ln\left(q_i(V,T)\right) - \ln\left(N_i\right)) \\ &= -k_B T \ln\left(\frac{q_i(V,T)}{N_i}\right) \end{aligned} \tag{10.8.3}$$

A variable, λ, is then defined such that $dN_j = \nu_j d\lambda$, where j = A, B, C or D and ν_j is taken to be positive for products and negative for reactants. A change in λ therefore corresponds to a change in the concentrations of the reactants and products. Thus, at equilibrium,

$$\left(\frac{\partial A}{\partial \lambda}\right)_{T,V} = 0$$



Helmholtz Energy with respect to Equilibrium Shifts

From Classical thermodynamics, the total differential of A is:

$$dA = -SdT - pdV + \sum_j \mu_j dN_j$$

For a reaction at a fixed volume and temperature (such as in the canonical ensemble), dT and dV equal 0. Therefore,

$$\begin{aligned} dA &= \sum_j \mu_j dN_j \\ &= \sum_j \mu_j \nu_j d\lambda \\ &= d\lambda \sum_j \mu_j \nu_j \end{aligned}$$

with

$$\sum_j \mu_j \nu_j = 0$$

Substituting the expanded form of chemical potential (Equation 10.8.3):

$$\begin{aligned} -k_B T \sum_j \ln\left(\frac{q_i}{N_i}\right)\nu_j &= 0 \\ \sum_j \ln\left(\frac{q_i}{N_i}\right)\nu_j &= 0 \\ \sum_j \nu_j[\ln(q_j) - \ln(N_j)] &= 0 \end{aligned}$$

For the reaction in Equation 10.8.1:

$$\begin{aligned}&[\nu_C \ln(q_C) - \nu_C \ln(N_C)] + [\nu_D \ln(q_D) - \nu_D \ln(N_D)] \\ &- [\nu_A \ln(q_A) - \nu_A \ln(N_A)] - [\nu_B \ln(q_B) - \nu_B \ln(N_B)] = 0\end{aligned}$$

This equation simplifies to

$$\frac{(q_C)^{\nu_C}(q_D)^{\nu_D}}{(q_A)^{\nu_A}(q_B)^{\nu_B}} = \frac{(N_C)^{\nu_C}(N_D)^{\nu_D}}{(N_A)^{\nu_A}(N_B)^{\nu_B}}$$

By dividing all terms by volume, and noting the relationship $\frac{N_A}{V} = \frac{\#molecules}{volume} = \rho_A = [A]$ where ρ is referred to a number density, the following equation is obtained:

$$K_c = \frac{\rho_C^{\nu_C}\rho_D^{\nu_D}}{\rho_A^{\nu_A}\rho_B^{\nu_B}} = \frac{(q_C/V)^{\nu_C}(q_D/V)^{\nu_D}}{(q_A/V)^{\nu_A}(q_B/V)^{\nu_B}} \tag{10.8.4}$$

Hence, knowledge of the molecular partition function for all species in the reaction will ensure the calculation of the equilibrium constant.

Example 10.8.1: Reacting Diatomic Molecules

Calculate the equilibrium constant (K_c) for the reaction of $\mathbf{H_2\,(g)}$ and $\mathbf{Cl_2\,(g)}$ at 650 K.

$$\mathbf{H_2\,(g) + Cl_2\,(g) \rightleftharpoons 2\,HCl\,(g)}$$

Solution

We will use Equation 10.8.4 that uses Molecular Partition Functions to evaluate K_c.

$$K_c(T) = \frac{\left(\frac{q_{HCl}}{V}\right)^2}{\left(\frac{q_{H_2}}{V}\right)\left(\frac{q_{Cl_2}}{V}\right)} \tag{10.8.5}$$

This equation is expanded into the rotational, vibrational, translational and electronic molecular partition functions of each species.

$$K_c(T) = \frac{\left(\frac{q_{\text{trans HCl}}q_{rot\text{HCl}}q_{vib\text{HCl}}q_{elec\text{HCl}}}{V}\right)^2}{\left(\frac{q_{\text{trans}H_2}q_{\text{rot }H_2}q_{vib\text{H}_2}q_{elec\text{H}_2}}{V}\right)\left(\frac{q_{\text{trans}Cl_2}q_{\text{rot }Cl_2}q_{vib\text{Cl}_2}q_{elec\text{Cl}_2}}{V}\right)}$$

A simple problem solving strategy for finding equilibrium constants via statistical mechanics is to separate the equation into the molecular partition functions of each of the reactant and product species, solve for each one, and recombine them to arrive at a final answer (e.g., for **HCl**.

$$\frac{q_{HCl}}{V} = \underbrace{\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}}_{\text{translation}} \times \underbrace{\frac{2k_BT\mu r_e^2}{\sigma\hbar^2}}_{\text{rotation}} \times \underbrace{\frac{1}{1-\exp\left(\frac{-h\nu}{k_BT}\right)}}_{\text{vibration}} \times \underbrace{g_1 \exp\left(\frac{D_0}{k_BT}\right)}_{\text{electronic}}$$

To simplify the calculations of molecular partition functions, the characteristic temperature of rotation (Θ_r) and vibration (Θ_ν) are used.

$$\frac{q_{HCl}}{V} = \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} \times \frac{T}{\sigma\Theta_r} \times \frac{1}{1-\exp\left(\frac{-\Theta_\nu}{T}\right)} \times g_1 \exp\left(\frac{D_0}{RT}\right) \tag{10.8.6}$$

These values are constants that incorporate the physical constants found in the rotational and vibrational partition functions of the molecules. Tabulated values of Θ_r and Θ_ν for select molecules can be found here.

Species	Θ_ν (K)	Θ_r (K)	D_0 (kJ mol^{-1})
$\mathbf{Cl_2\,(g)}$	6125	0.351	239.0
$\mathbf{H_2\,(g)}$	808	87.6	431.9
$\mathbf{HCl\,(g)}$	4303	15.2	427.7

We need to evaluate Equation 10.8.6 for each species then then evaluate Equation 10.8.5 directly.

For $\mathbf{HCl}$:

$$\frac{q_{HCl}}{V} = \left(\frac{2\pi\left(2.1957\times10^{-24}\ \text{kg}\right)\left(1.38065\times10^{-23}\text{JK}^{-1}\right)(650K)}{\left(6.62607\times10^{-34}\text{Js}\right)^2}\right)^{3/2} \times \frac{650\ \text{K}}{(1)(15.2\ \text{K})} \times \frac{1}{1-\exp\left(\frac{-4303\ \text{K}}{650\ \text{K}}\right)} \times (1)\exp\left(\frac{427,700\text{Jmol}^{-1}}{(8.3145\,\text{J K mol}^{-1})(650\ \text{K})}\right)$$

$$\frac{q_{HCl}}{V} = \left(1.4975\times10^{35}\ \text{m}^{-3}\right)(42.76)(1.0013)\left(2.3419\times10^{34}\right)$$

For $\mathbf{H_2}$:

$$\frac{q_{H_2}}{V} = \left(\frac{2\pi\left(1.2140\times10^{-25}\ \text{kg}\right)\left(1.38065\times10^{-23}\text{JK}^{-1}\right)(650\ \text{K})}{\left(6.62607\times10^{-34}\text{Js}\right)^2}\right)^{3/2} \times \frac{650\ \text{K}}{(2)(87.6\ \text{K})} \times \frac{1}{1-\exp\left(\frac{-808\ \text{K}}{650\ \text{K}}\right)} \times (1)\exp\left(\frac{431,900\text{Jmol}^{-1}}{(8.3145\ \text{J Kmol}^{-1})(650\ \text{K})}\right)$$

$$\frac{q_{H_2}}{V} = \left(1.9468\times10^{33}\ \text{m}^{-3}\right)(3.71)(1.41)\left(5.0942\times10^{34}\right)$$

For $\mathbf{Cl_2}$:

$$\frac{q_{Cl_2}}{V} = \left(\frac{2\pi\left(4.2700\times10^{-24}\ \text{kg}\right)\left(1.38065\times10^{-23}\text{JK}^{-1}\right)(650K)}{\left(6.62607\times10^{-34}\text{Js}^2\right.}\right)^{3/2} \times \frac{650\ \text{K}}{(2)(0.351\ \text{K})} \times \frac{1}{1-\exp\left(\frac{-6125\ \text{K}}{650\ \text{K}}\right)} \times (1)\exp\left(\frac{239,000\text{Jmol}^{-1}}{(8.3145\ \text{J K mol}^{-1})(650\ \text{K})}\right)$$

$$\frac{q_{Cl_2}}{V} = \left(5.4839\times10^{35}\ \text{m}^{-3}\right)(925.9)(1.00)\left(1.606\times10^{19}\right)$$

Combining the terms from each species, the following expression is obtained:

$$\begin{aligned} K_c &= \frac{\left(1.9468\times10^{33}\ \text{m}^{-3}\right)^2}{\left(1.9468\times10^{33}\ \text{m}^{-3}\right)\left(5.4839\times10^{35}\ \text{m}^{-3}\right)} \times \frac{(42.76)^2}{(3.71)(925.9)} \times \frac{(1.0013)^2}{(1.41)(1.00)} \times \frac{\left(2.3419\times10^{34}\right)^2}{\left(1.606\times10^{19}\right)\left(5.0942\times10^{34}\right)} \\ &= (0.003550)(0.1333)(0.711)\left(6.7037\times10^{14}\right) \\ &= \left(2.26\times10^{11}\right) \end{aligned}$$

At 650 K, the reaction between $\mathbf{H_2}\,(\mathbf{g})$ and $\mathbf{Cl_2}\,(\mathbf{g})$ proceeds spontaneously towards the products. From a statistical mechanics point of view, the product $\mathbf{HCl}\,(\mathbf{g})$ molecule has more states accessible to it than the reactant species. The spontaneity of this reaction is largely due to the electronic partition function: two very strong H—Cl bonds are formed at the expense of a very strong H—H bond and a relatively weak Cl—Cl bond.

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10.9: Molecular Partition Functions and Related Thermodynamic Data Are Extensively Tabulated

Real molecules can be significantly more complicated than the simple models that we often use to approximate them. To obtain a high degree of accuracy, calculations include complex corrections that can significantly decrease the efficiency of the calculations. For this reason, numerical tables of partition functions and other thermodynamical data are extensively tabulated. By placing these data in tables, they become readily accessible. The tables include experimental data combined with theoretical calculations that represent a collection of thermodynamic properties of substances.

The tabulated thermochemical properties of a substance are often given in JANAF (joint, army, navy, air force) tables. NIST contains are a large database of JANAF tables for many substances. Consider the JANAF table for methane (CH_4). The table contains the constant pressure heat capacity (C_P), standard state entropy ($S°$), standard state Gibbs energy ($G°$), standard state enthalpy ($H°$), standard state enthalpy of formation ($\Delta_f H°$), standard state Gibbs energy of formation ($\Delta_f H°$), equilibrium constant of formation expressed as a log value ($\log(K_f)$). $G°$ and $H°$ are expressed relative to the standard molar enthalpy at 298.15 K, $H°(298.15\ \text{K})$.

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10.10: Real Gases Are Expressed in Terms of Partial Fugacities

The relationship for chemical potential

$$\mu = \mu^o + RT \ln\left(\frac{p}{p^o}\right)$$

was derived assuming **ideal gas** behavior. But for real gases that deviate widely from ideal behavior, the expression has only limited applicability. In order to use the simple expression on real gases, a "fudge" factor is introduced called **fugacity**. Using fugacity instead of pressure, the chemical potential expression becomes

$$\mu = \mu^o + RT \ln\left(\frac{f}{f^o}\right)$$

where f is the fugacity. Fugacity is related to pressure, but contains all of the deviations from ideality within it. To see how it is related to pressure, consider that a change in chemical potential for a single component system can be expressed as

$$d\mu - V dp - S dT$$

and so

$$\left(\frac{\partial \mu}{\partial p}\right)_T = V \tag{10.10.1}$$

Differentiating the expression for chemical potential above with respect to pressure at constant volume results in

$$\left(\frac{\partial \mu}{\partial p}\right)_T = \left\{\frac{\partial}{\partial p}\left[\mu^o + RT \ln\left(\frac{f}{f^o}\right)\right]\right\}$$

which simplifies to

$$\left(\frac{\partial \mu}{\partial p}\right)_T = RT\left[\frac{\partial \ln(f)}{\partial p}\right]_T = V$$

Multiplying both sides by p/RT gives

$$\left[\frac{\partial \ln(f)}{\partial p}\right]_T = \frac{pV}{RT} = Z$$

where Z is the compression factor as discussed previously. Now, we can use the expression above to obtain the **fugacity coefficient** γ, as defined by

$$f = \gamma p$$

Taking the natural logarithm of both sides yields

$$\ln f = \ln \gamma + \ln p$$

or

$$\ln \gamma = \ln f - \ln p$$

Using some calculus and substitutions from above,

$$\int \left(\frac{\partial \ln \gamma}{\partial p}\right)_T dp = \int \left(\frac{\partial \ln f}{\partial p} - \frac{\partial \ln p}{\partial p}\right)_T dp$$

$$= \int \left(\frac{Z}{\partial p} - \frac{1}{\partial p}\right)_T dp$$

Finally, integrating from 0 to p yields

$$\ln \gamma = \int_0^p \left(\frac{Z-1}{p}\right)_T dp$$

If the gas behaves ideally, $\gamma = 1$. In general, this will be the limiting value as $p \rightarrow 0$ since all gases behave ideal as the pressure approaches 0. The advantage to using the fugacity in this manner is that it allows one to use the expression

$$\mu = \mu^o + RT \ln \left(\frac{f}{f^o} \right)$$

to calculate the chemical potential, insuring that Equation 10.10.1 holds even for gases that deviate from ideal behavior!

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10.11: Thermodynamic Equilibrium Constants Are Expressed in Terms of Activities

The above is a general principle that can be extended to other concentration units and to liquid solutions, ideal or not. In non-ideal systems we could replace

$$\mu_i = \mu_i^{\ominus} + RT\ln P_i/P_i^{\ominus}$$

by:

$$\mu_i = \mu_i^{\ominus} + RT\ln a_i$$

and follow the same procedure as above. In stead of an expression for K involving pressures or concentrations it now read in ***activities***:

$$K=[a_{eq,Y}{}^{\nu_Y} a_{eq,Z}{}^{\nu_Z} / a_{eq,A}{}^{\nu_A} a_{eq,B}{}^{\nu_B}]$$

For each species we could write the activity as:

$$a_i = \gamma_i c_i / c_i^{\ominus}$$

Here $c_i^{\ominus}$ is unity in whatever concentration measure we wish to choose. Again its function is to cancel the dimension of c_i.

With this split in three factors we can write K as three factors as well:

$$K = K_\gamma K_c / K_{c^{\ominus}}$$

$$K_\gamma = [\gamma_{eq,Y}{}^{\nu_Y} \gamma_{eq,Z}{}^{\nu_Z} / \gamma_{eq,A}{}^{\nu_A} \gamma_{eq,B}{}^{\nu_B}]$$

$$K_c = [c_{eq,Y}{}^{\nu_Y} c_{eq,Z}{}^{\nu_Z} / c_{eq,A}{}^{\nu_A} c_{eq,B}{}^{\nu_B}]$$

$$K_{c^{\ominus}} = [c_{c^{\ominus}}{}^{\nu_Y} c_{c^{\ominus}}{}^{\nu_Z} / c_{c^{\ominus}}{}^{\nu_A} c_{c^{\ominus}}{}^{\nu_B}]$$

The last factor is unity, it cancels the dimensions of K_c and is often *omitted*. The factor K_γ is unity *if the solution is ideal*. Obviously, for ionic solutions that is seldom the case.

10.11.1: activities of pure condensed phases

Sometimes one of the reactants or products is a pure solid (precipitate) or liquid (more solvent e.g.). What activity should we assign in such a case?

We start by choosing a suitable standard state, say the pure compound at 1 bar and temperature of interest, we then have:

$$\mu = \mu^{\ominus}$$

but also:

$$\mu = \mu^{\ominus} + RT\ln a$$

So a=1 at standard conditions

Any change can be written as

$$d\mu = RTd\ln a$$

We can study the pressure dependence by considering:

$$\partial \mu / \partial P |_T = V_{\text{partial molar}} \; (V_{bar})$$

For a solid or liquid V_{bar} is a relatively small and constant value. Thus we can write:

$d\mu = V_{bar}dP$

$RTdlna = V_{bar}dP$

$dlna = V_{bar}dP/RT$

Upon integration to a different pressure P' we find

$lna' = (P'-1)\ V_{bar}/RT$

S&McQ
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Example 26-12 shows that for graphite the activity is only 1.01 at 100 bars, so the activity is *not* very pressure dependent. Mostly if pure condensed compounds are involved in reactions the activity can taken as **unity**.

This is also in line with what we said previously about the solvent following Raoult's law. In the limit of the solvent going to pure solvent we have that its P goes to P*. As the activity is defined as P/P* this converges to unity. If a reaction produces more solvent molecules we can usually consider their activity equal to one in very good approximation for dilute solutions, even if they are already non-ideal.

The fact that a=1 for pure condensed phases has an important consequence for reactions (in general: processes) that only involve such phases. If all activities are unity, Q=1 and lnQ=0 which means that $\Delta_rG = \Delta_rG^{\ominus} + 0$. Thus Δ_rG can only be zero -i.e. an equilibrium achieved- ***if*** $\Delta_rG^{\ominus}$ happens to be zero, which is generally not the case. In fact there can only be an equilbrium at one specific temperature:

$\Delta_rG^{\ominus} = 0$

$\Delta_rH^{\ominus}-T\Delta_rS^{\ominus}$

$T_{equilibrium} = \Delta_rH^{\ominus}/\Delta_rS^{\ominus}$

If the process is the transformation from a solid to a liquid this is the well-known *melting point*. At temperature other than 0^oC only one phase can exist: either ice or water. If the other is present, that is an unstable condition and it will transform *entirely* to the stable form. In other words the process will go to completion, *not* equilbirium. Only *at* 0^oC can the two coexist in equilibrium. This holds for all melting points but it also holds for e.g. a solid-solid chemical reactions only producing, say, another solid.

Another way of expressing the above is to say that in order to have equilibrium at a *series* of temperatures, one needs at least one species involved for which activity depends on composition, e.g. a dilute solute or a gas.

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10.12: Activities are Important for Ionic Species

10.12.0.1: Weak electrolytes

We have seen that strong electrolytes are non-ideal even at tiny concentrations and that even the Debye-Hückel theory only allowed us to work at very small concentrations of strong electrolytes. The same problems are encountered with weak electrolytes but they are compounded by the equilibrium that is inherent to their solutions. Take acetic acid as in household vinegar:

$$HAc + H_2O \rightleftharpoons Ac^- + H_3O^+$$

We can write the equilibrium constant as:

$$K = \frac{a_{Ac^-} a_{H_3O^+}}{a_{HAc} a_{H_2O}}$$

As

$$a_{H2O} = 1$$

$$K = \frac{a_{Ac^-} a_{H_3O^+}}{a_{HAc}}$$

At an initial concentration of say 0.1 mol/l the activity coefficient for HAc (being a *neutral* species) is essentially one, but for the other species we should write:

$$(a_{Ac^-} a_{H_3O^+}) = [Ac^-][H_3O^+]\gamma_{\pm}^2$$

The value of $\gamma_{\pm}^2$ is *not* unity and this will affect the equilibrium. In first approximation we will ignore that fact and write:

$$K = \frac{[Ac^-][H_3O^+]}{[HAc]} = 1.74 \times 10^{-5}$$

(We can either write [mol.l] as dimensions or drop them, depending on whether we are talking about K or K_c)

At equilibrium we would get:

$$K = \frac{x^2}{0.1 - x} = 1.74 \times 10^{-5}$$

which yields

$$x = 1.31 \times 10^{-3} mol/l$$

We can now use Debye-Hückel theory to estimate the means ionic activity coefficient but the concentrations are already to high for that. Instead we will use one of its extensions:

$$\ln \gamma_{\pm} = -1.173 |z_+ z_-| \frac{\sqrt{I}}{1 + \sqrt{I}}$$

The ionic strength is ½ ($[Ac^-]+[H_3O^+]$) =x

Although we do not know x precisely the value we have is at least a starting point. We can use it to calculate a first approximation for $\gamma_{\pm}^2$. We find a value of 0.921. We then divide the value of K by this value and recalculate x. It changes from x=1.31 10^{-3} mol/l to x=1.365 10^{-3} mol/l. Now we can repeat this process until the value of x does not change appreciably anymore (*converges*). This process is called ***iteration***. The final value is about x=1.37 10^{-3} mol/l.

As can be seen the non-ideality does change the values from the ones you would have calculated before entering this course, but the difference is not staggering, at least if no other solutes are present.

Question: does the equilibrium change if we add 0.5 mol/l NaCl to the solution?

10.12.1: Solubility products

For solubility products the differences can be more important. Take BaF_2 in water K= 1.7 10^{-6}.

$$K = \gamma_{\pm}^3 [Ba^{2+}][F^-]2$$

Let's start by assuming ideality and say that $\gamma_{\pm}^3$=1 and say that :$[Ba^{2+}]$=x

$$[F^-] = 2x$$

Thus K= x $(4x^2)$ so x= 7.52 10^{-3} mol/lit

The ionic strength is

$$I = \frac{1}{2}(+2)^2 x + (-1)^2 x = 3x$$

The extended Debye-Hückel theory gives $\gamma_{\pm}$ =0.736 this raises x to 0.0102. Repeating the process a few times we find x=0.011. This means an increase of about 30% due to non-ideal behavior for this sparingly soluble salt. Again the presence of other solutes may induce larger effects because they add to the ionic strength.

? Exercise

Even pure water contains OH^- and H_3O^+ ions. The K for this equilibrium is 10^{-14}. How does the pH change if we add 0.5 m/lit of a strong electrolyte M^{2+} X^{2-}? CH 431/Lecture 17/answer2

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10.13: Homework Problems

In the mid 1920's the German physicist Werner Heisenberg showed that if we try to locate an electron within a region Δx; e.g. by scattering light from it, some momentum is transferred to the electron, and it is not possible to determine exactly how much momentum is transferred, even in principle. Heisenberg showed that consequently there is a relationship between the uncertainty in position Δx and the uncertainty in momentum Δp.

$$\Delta p \Delta x \geq \frac{\hbar}{2} \tag{10.13.1}$$

You can see from Equation 10.13.1 that as Δp approaches 0, Δx must approach ∞, which is the case of the free particle discussed previously.

This uncertainty principle, which also is discussed in Chapter 4, is a consequence of the wave property of matter. A wave has some finite extent in space and generally is not localized at a point. Consequently there usually is significant uncertainty in the position of a quantum particle in space. Activity 1 at the end of this chapter illustrates that a reduction in the spatial extent of a wavefunction to reduce the uncertainty in the position of a particle increases the uncertainty in the momentum of the particle. This illustration is based on the ideas described in the next section.

? Exercise 10.13.1

Compare the minimum uncertainty in the positions of a baseball (mass = 140 gm) and an electron, each with a speed of 91.3 miles per hour, which is characteristic of a reasonable fastball, if the standard deviation in the measurement of the speed is 0.1 mile per hour. Also compare the wavelengths associated with these two particles. Identify the insights that you gain from these comparisons.

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CHAPTER OVERVIEW

11: Chemical Kinetics I - Rate Laws

11.1: The Time Dependence of a Chemical Reaction is Described by a Rate Law

11.2: Rate Laws Must Be Determined Experimentally

11.3: First-Order Reactions Show an Exponential Decay of Reactant Concentration with Time

11.4: Different Rate Laws Predict Different Kinetics

11.5: Reactions can also be Reversible

11.6: The Rate Constants of a Reversible Reaction Can Be Determined Using Relaxation Techniques

11.7: Rate Constants Are Usually Strongly Temperature Dependent

11.8: Transition-State Theory Can Be Used to Estimate Reaction Rate Constants

11.E: Chemical Kinetics I - Rate Laws (Exercises)

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11.1: The Time Dependence of a Chemical Reaction is Described by a Rate Law

11.1.1: The Reaction Rate

The rate of a chemical reaction (or the **reaction rate**) can be defined by the time needed for a change in concentration to occur. But there is a problem in that this allows for the definition to be made based on concentration changes for either the reactants or the products. Plus, due to stoichiometric concerns, the rates at which the concentrations are generally different! Toward this end, the following convention is used.

For a general reaction

$$aA + bB \rightarrow cC + dD$$

the reaction rate can be defined by any of the ratios

$$\text{rate} = -\frac{1}{a}\frac{\Delta[A]}{dt} = -\frac{1}{b}\frac{\Delta[B]}{dt} = +\frac{1}{c}\frac{\Delta[C]}{dt} = +\frac{1}{d}\frac{\Delta[D]}{dt}$$

Or for infinitesimal time intervals

$$\text{rate} = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[C]}{dt} = +\frac{1}{c}\frac{d[C]}{dt} = +\frac{1}{d}\frac{d[D]}{dt}$$

Example 11.1.1:

Under a certain set of conditions, the rate of the reaction

$$\mathrm{N_2 + 3\,H_2 \rightarrow 2\,NH_3}$$

the reaction rate is $6.0 \times 10^{-4}\ M/s$. Calculate the time-rate of change for the concentrations of N_2, H_2, and NH_3.

Solution:

Due to the stoichiometry of the reaction,

$$\text{rate} = -\frac{d[N_2]}{dt} = -\frac{1}{3}\frac{d[H_2]}{dt} = +\frac{1}{2}\frac{d[NH_3]}{dt}$$

so

$$\frac{d[N_2]}{dt} = -6.0 \times 10^{-4}\ M/s$$
$$\frac{d[H_2]}{dt} = -2.0 \times 10^{-4}\ M/s$$
$$\frac{d[NH_3]}{dt} = 3.0 \times 10^{-4}\ M/s$$

Note: The time derivatives for the reactants are negative because the reactant concentrations are decreasing, and those of products are positive since the concentrations of products increase as the reaction progresses.

11.1.2: The Rate Law

As shown above, the rate of the reaction can be followed experimentally by measuring the rate of the loss of a reactant or the rate of the production of a product. The rate of the reaction is often related to the concentration of some or all of the chemical species present at a given time. An equation called the *rate law* is used to show this relationship. The rate law **cannot** be predicted by looking at the balanced chemical reaction but must be determined by experiment. For example, the rate law for the reaction

$$\mathrm{Cl_2\,(g) + CO\,(g) \longrightarrow Cl_2CO\,(g)}$$

was experimentally determined to be

$$\text{rate} = k[Cl_2]^{3/2}[CO]$$

In this equation, k is the rate constant, and $[Cl_2]$ and $[CO]$ are the molar concentrations of Cl_2 and of CO. Each exponent is called the *order* of the given species. Thus, the rate law is second order in Cl_2 and first order in CO. The sum of the individual reactant orders is called the **reaction order**. This reaction has a reaction order of two and a half.

In the next section, we will discuss methods to experimentally determine the rate law.

11.1.3: Contributors and Attributions

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- Tom Neils (Grand Rapids Community College)

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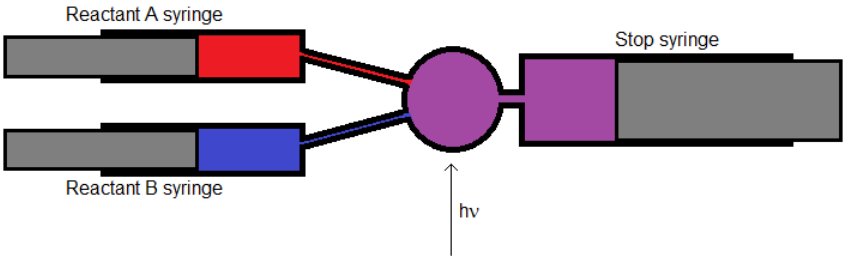
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11.2: Rate Laws Must Be Determined Experimentally

There are several methods that can be used to measure chemical reactions rates. A common method is to use spectrophotometry to monitor the concentration of a species that will absorb light. If it is possible, it is preferable to measure the appearance of a product rather than the disappearance of a reactant, due to the low background interference of the measurement. However, high-quality kinetic data can be obtained either way.

11.2.1: The Stopped-Flow Method

The **stopped-flow method** involves using flow control (which can be provided by syringes or other valves) to control the flow of reactants into a mixing chamber where the reaction takes place. The reaction mixture can then be probed spectrophotometrically. Stopped-flow methods are commonly used in physical chemistry laboratory courses (Progodich, 2014).



Some methods depend on measuring the initial rate of a reaction, which can be subject to a great deal of experimental uncertainty due to fluctuations in instrumentation or conditions. Other methods require a broad range of time and concentration data. These methods tend to produce more reliable results as they can make use of the broad range of data to smooth over random fluctuations that may affect measurements. Both approaches (initial rates and full concentration profile data methods) will be discussed below.

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11.3: First-Order Reactions Show an Exponential Decay of Reactant Concentration with Time

A first order rate law would take the form

$$\frac{d[A]}{dt} = k[A]$$

Again, separating the variables by placing all of the concentration terms on the left and all of the time terms on the right yields

$$\frac{d[A]}{[A]} = -k\,dt$$

This expression is also easily integrated as before

$$\int_{[A]=0}^{[A]} \frac{d[A]}{[A]} = -k \int_{t=0}^{t=t} dt$$

Noting that

$$\frac{dx}{x} = d(\ln x)$$

The form of the integrated rate law becomes

$$\ln[A] - \ln[A]_o = kt$$

or

$$\ln[A] = \ln[A]_o - kt \tag{11.3.1}$$

This form implies that a plot of the natural logarithm of the concentration is a linear function of the time. And so a plot of ln[A] as a function of time should produce a linear plot, the slope of which is -k, and the intercept of which is $\ln[A]_0$.

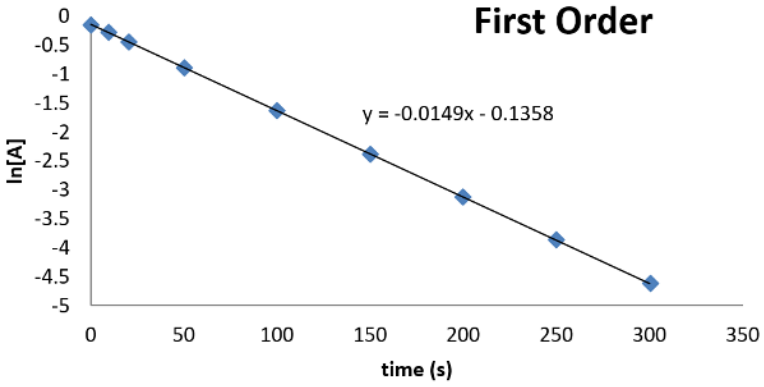
Example 11.3.1:

Consider the following kinetic data. Use a graph to demonstrate that the data are consistent with first order kinetics. Also, if the data are first order, determine the value of the rate constant for the reaction.

Time (s)	0	10	20	50	100	150	200	250	300
[A] (M)	0.873	0.752	0.648	0.414	0.196	0.093	0.044	0.021	0.010

Solution

The plot looks as follows:



From this plot, it can be seen that the rate constant is 0.0149 s^{-1}. The concentration at time $t = 0$ can also be inferred from the intercept.

It should also be noted that the integrated rate law (Equation **11.3.1**) can be expressed in exponential form:

$$[A] = [A]_o e^{-kt}$$

Because of this functional form, 1st order kinetics are sometimes referred to as exponential decay kinetics. Many processes, including radioactive decay of nuclides follow this type of rate law.

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11.4: Different Rate Laws Predict Different Kinetics

Difference rate laws predict different kinetics

11.4.1: Zero-order Kinetics

If the reaction follows a zeroth order rate law, it can be expressed in terms of the time-rate of change of [A] (which will be negative since A is a reactant):

$$-\frac{d[A]}{dt} = k$$

In this case, it is straightforward to separate the variables. Placing time variables on the right and [A] on the left

$$d[A] = -k\,dt$$

In this form, it is easy to integrate. If the concentration of A is $[A]_0$ at time t = 0, and the concentration of A is [A] at some arbitrary time later, the form of the integral is

$$\int_{[A]_o}^{[A]} d[A] = -k\int_{t_o}^{t} dt$$

which yields

$$[A] - [A]_o = -kt$$

or

$$[A] = [A]_o - kt$$

This suggests that a plot of concentration as a function of time will produce a straight line, the slope of which is –k, and the intercept of which is $[A]_0$. If such a plot is linear, then the data are consistent with 0^{th} order kinetics. If they are not, other possibilities must be considered.

11.4.2: Second Order Kinetics

If the reaction follows a second order rate law, the some methodology can be employed. The rate can be written as

$$-\frac{d[A]}{dt} = k[A]^2 \tag{11.4.1}$$

The separation of concentration and time terms (this time keeping the negative sign on the left for convenience) yields

$$-\frac{d[A]}{[A]^2} = k\,dt$$

The integration then becomes

$$-\int_{[A]_o}^{[A]} \frac{d[A]}{[A]^2} = \int_{t=0}^{t} k\,dt \tag{11.4.2}$$

And noting that

$$-\frac{dx}{x^2} = d\left(\frac{1}{x}\right)$$

the result of integration Equation 11.4.2 is

$$\frac{1}{[A]} - \frac{1}{[A]_o} = kt$$

or

$$\frac{1}{[A]} = \frac{1}{[A]_o} + kt$$

And so a plot of $1/[A]$ as a function of time should produce a linear plot, the slope of which is k, and the intercept of which is $1/[A]_0$.

Other 2nd order rate laws are a little bit trickier to integrate, as the integration depends on the actual stoichiometry of the reaction being investigated. For example, for a reaction of the type

$$A + B \rightarrow P$$

That has rate laws given by

$$-\frac{d[A]}{dt} = k[A][B]$$

and

$$-\frac{d[B]}{dt} = k[A][B]$$

the integration will depend on the decrease of [A] and [B] (which will be related by the stoichiometry) which can be expressed in terms the concentration of the product [P].

$$[A] = [A]_o - [P] \tag{11.4.3}$$

and

$$[B] = [B]_o - [P] \tag{11.4.4}$$

The concentration dependence on A and B can then be eliminated if the rate law is expressed in terms of the production of the product.

$$\frac{d[P]}{dt} = k[A][B] \tag{11.4.5}$$

Substituting the relationships for $[A]$ and $[B]$ (Equations 11.4.3 and 11.4.4) into the rate law expression (Equation 11.4.5) yields

$$\frac{d[P]}{dt} = k([A]_o - [P])([B] = [B]_o - [P]) \tag{11.4.6}$$

Separation of concentration and time variables results in

$$\frac{d[P]}{([A]_o - [P])([B] = [B]_o - [P])} = k\,dt$$

Noting that at time $t = 0$, $[P] = 0$, the integrated form of the rate law can be generated by solving the integral

$$\int_{[A]_o}^{[A]} \frac{d[P]}{([A]_o - [P])([B]_o - [P])} = \int_{t=0}^{t} k\,dt$$

Consulting a table of integrals reveals that for $a \neq b$[1],

$$\int \frac{dx}{(a-x)(b-x)} = \frac{1}{b-a}\ln\left(\frac{b-x}{a-x}\right)$$

Applying the definite integral (as long as $[A]_0 \neq [B]_0$) results in

$$\frac{1}{[B]_0 - [A]_0}\ln\left(\frac{[B]_0 - [P]}{[A]_0 - [P]}\right)\Bigg|_0^{[A]} = k\,t\Big|_0^t$$

$$\frac{1}{[B]_0 - [A]_0}\ln\left(\frac{[B]_0 - [P]}{[A]_0 - [P]}\right) - \frac{1}{[B]_0 - [A]_0}\ln\left(\frac{[B]_0}{[A]_0}\right) = k\,t \tag{11.4.7}$$

Substituting Equations 11.4.3 and 11.4.4 into Equation 11.4.7 and simplifying (combining the natural logarithm terms) yields

$$\frac{1}{[B]_0 - [A]_0}\ln\left(\frac{[B][A]_o}{[A][B]_o}\right) = kt$$

For this rate law, a plot of $\ln([B]/[A])$ as a function of time will produce a straight line, the slope of which is

$$m = ([B]_0 - [A]_0)k.$$

In the limit at $[A]_0 = [B]_0$, then $[A] = [B]$ at all times, due to the stoichiometry of the reaction. As such, the rate law becomes

$$\text{rate} = k[A]^2$$

and integrate direct like in Equation 11.4.1 and the integrated rate law is (as before)

$$\frac{1}{[A]} = \frac{1}{[A]_o} + kt$$

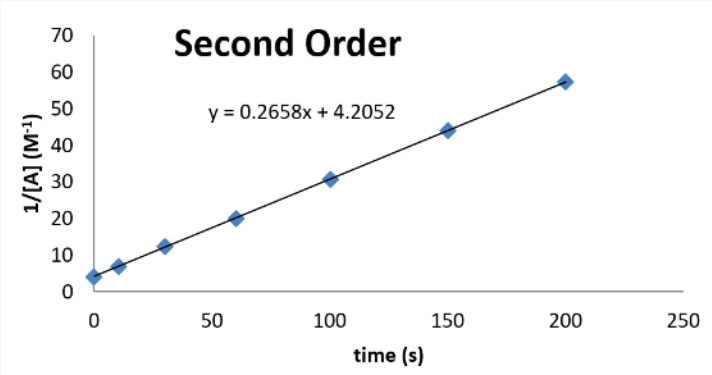
Example 11.4.2: Confirming Second Order Kinetics

Consider the following kinetic data. Use a graph to demonstrate that the data are consistent with second order kinetics. Also, if the data are second order, determine the value of the rate constant for the reaction.

time (s)	0	10	30	60	100	150	200
[A] (M)	0.238	0.161	0.098	0.062	0.041	0.029	0.023

Solution

The plot looks as follows:



From this plot, it can be seen that the rate constant is 0.2658 M^{-1} s^{-1}. The concentration at time $t = 0$ can also be inferred from the intercept.

---

[1] This integral form can be generated by using the method of partial fractions. See (House, 2007) for a full derivation.

Example 11.4.3

Dinitrogen pentoxide (N_2O_5) decomposes to NO_2 and O_2 at relatively low temperatures in the following reaction:

$$2N_2O_5\,(soln) \rightarrow 4NO_2\,(soln) + O_2\,(g)$$

This reaction is carried out in a CCl_4 solution at 45°C. The concentrations of N_2O_5 as a function of time are listed in the following table, together with the natural logarithms and reciprocal N_2O_5 concentrations. Plot a graph of the concentration versus *t*, ln concentration versus *t*, and 1/concentration versus *t* and then determine the rate law and calculate the rate constant.

Time (s)	$[N_2O_5]$ (M)	$\ln[N_2O_5]$	$1/[N_2O_5]$ (M^{-1})
0	0.0365	−3.310	27.4
600	0.0274	−3.597	36.5
1200	0.0206	−3.882	48.5
1800	0.0157	−4.154	63.7
2400	0.0117	−4.448	85.5
3000	0.00860	−4.756	116
3600	0.00640	−5.051	156

Given: balanced chemical equation, reaction times, and concentrations

Asked for: graph of data, rate law, and rate constant

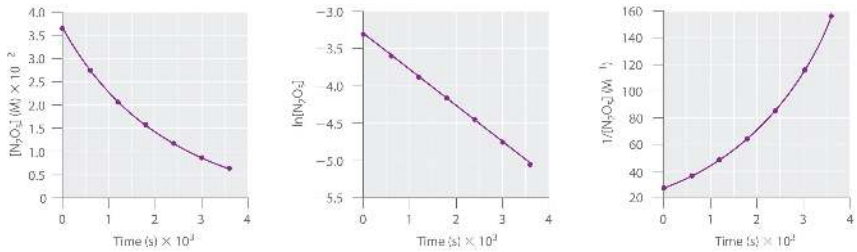
Strategy:

A Use the data in the table to separately plot concentration, the natural logarithm of the concentration, and the reciprocal of the concentration (the vertical axis) versus time (the horizontal axis). Compare the graphs with those in Figure 13.4.2 to determine the reaction order.

B Write the rate law for the reaction. Using the appropriate data from the table and the linear graph corresponding to the rate law for the reaction, calculate the slope of the plotted line to obtain the rate constant for the reaction.

Solution:

A Here are plots of $[N_2O_5]$ versus t, $\ln[N_2O_5]$ versus t, and $1/[N_2O_5]$ versus t:



The plot of $\ln[N_2O_5]$ versus t gives a straight line, whereas the plots of $[N_2O_5]$ versus t and $1/[N_2O_5]$ versus t do not. This means that the decomposition of N_2O_5 is first order in $[N_2O_5]$.

B The rate law for the reaction is therefore

$$rate = k\,[N_2O_5]$$

Calculating the rate constant is straightforward because we know that the slope of the plot of ln[A] versus t for a first-order reaction is $-k$. We can calculate the slope using any two points that lie on the line in the plot of $\ln[N_2O_5]$ versus t. Using the points for t = 0 and 3000 s,

$$slope = \frac{ln\,[N_2O_5]_{3000} - ln\,[N_2O_5]_0}{3000\ s - 0\ s} = \frac{[-4.756] - [-3.310]}{3000\ s} = 4.820 \times 10^{-4}\ s^{-1}$$

Thus $k = 4.820 \times 10^{-4}\ s^{-1}$.

11.4.3: Contributors

- Anonymous

Modified by Joshua Halpern (Howard University), Scott Sinex, and Scott Johnson (PGCC)

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11.5: Reactions can also be Reversible

Reversible and irreversible reactions are prevalent in nature and are responsible for reactions such as the breakdown of ammonia.

11.5.1: Introduction

It was believed that all chemical reactions were irreversible until 1803, when French chemist Claude Louis Berthollet introduced the concept of reversible reactions. Initially he observed that sodium carbonate and calcium chloride react to yield calcium carbonate and sodium chloride; however, after observing sodium carbonate formation around the edges of salt lakes, he realized that large amount of salts in the evaporating water reacted with calcium carbonate to form sodium carbonate, indicating that the reverse reaction was occurring.

Chemical reactions are represented by chemical equations. These equations typically have a unidirectional arrow ($\rightarrow$) to represent irreversible reactions. Other chemical equations may have a bidirectional harpoons ($\rightleftharpoons$) that represent reversible reactions (not to be confused with the double arrows $\leftrightarrow$ used to indicate resonance structures). To review the fundamentals of chemical reactions, click here: Chemical Reactions

11.5.2: Irreversible Reactions

A fundamental concept of chemistry is that chemical reactions occurred when reactants reacted with each other to form products. These unidirectional reactions are known as irreversible reactions, reactions in which the reactants convert to products and where the products *cannot* convert back to the reactants. These reactions are essentially like baking. The ingredients, acting as the reactants, are mixed and baked together to form a cake, which acts as the product. This cake cannot be converted back to the reactants (the eggs, flour, etc.), just as the products in an irreversible reaction cannot convert back into the reactants.

An example of an irreversible reaction is combustion. Combustion involves burning an organic compound—such as a hydrocarbon—and oxygen to produce carbon dioxide and water. Because water and carbon dioxide are stable, they do not react with each other to form the reactants. Combustion reactions take the following form:

$$C_xH_y + O_2 \rightarrow CO_2 + H_2O \tag{11.5.1}$$

11.5.3: Reversible Reactions

In reversible reactions, the reactants and products are never fully consumed; they are each constantly reacting and being produced. A reversible reaction can take the following summarized form:

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C + D \tag{11.5.2}$$

This reversible reaction can be broken into two reactions.

Reaction 1:

$$A + B \xrightarrow{k_1} C + D \tag{11.5.3}$$

Reaction 2:

$$C + D \xrightarrow{k_{-1}} A + B \tag{11.5.4}$$

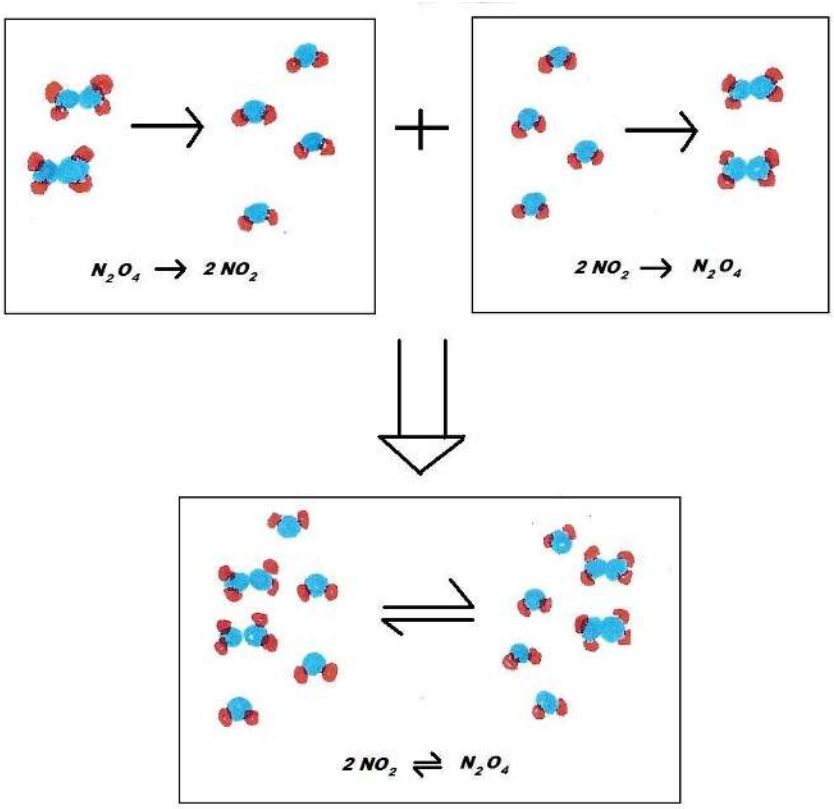
These two reactions are occurring ***simultaneously***, which means that the reactants are reacting to yield the products, as the products are reacting to produce the reactants. Collisions of the reacting molecules cause chemical reactions in a closed system. After products are formed, the bonds between these products are broken when the molecules collide with each other, producing sufficient energy needed to break the bonds of the product and reactant molecules.

Below is an example of the summarized form of a reversible reaction and a breakdown of the reversible reaction $N_2O_4 \leftrightarrow 2NO_2$

Reaction 1 and Reaction 2 happen at the same time because they are in a closed system.

Blue: Nitrogen Red: Oxygen

Reaction 1 Reaction 2



Imagine a ballroom. Let reactant A be 10 girls and reactant B be 10 boys. As each girl and boy goes to the dance floor, they pair up to become a product. Once five girls and five boys are on the dance floor, one of the five pairs breaks up and moves to the sidelines, becoming reactants again. As this pair leaves the dance floor, another boy and girl on the sidelines pair up to form a product once more. This process continues over and over again, representing a reversible reaction.

Unlike irreversible reactions, reversible reactions lead to equilibrium: in reversible reactions, the reaction proceeds in both directions whereas in irreversible reactions the reaction proceeds in only one direction. To learn more about this phenomenon, click here: Chemical Equilibrium

If the reactants are formed at the same rate as the products, a dynamic equilibrium exists. For example, if a water tank is being filled with water at the same rate as water is leaving the tank (through a hypothetical hole), the amount of water remaining in the tank remains consistent.

11.5.4: Connection to Biology

There are four binding sites on a hemoglobin protein. Hemoglobin molecules can either bind to carbon dioxide or oxygen. As blood travels through the alveoli of the lungs, hemoglobin molecules pick up oxygen-rich molecules and bind to the oxygen. As the hemoglobin travels through the rest of the body, it drops off oxygen at the capillaries for the organ system to use oxygen. After expelling the oxygen, it picks up carbon dioxide. Because this process is constantly carried out through the body, there are always hemoglobin molecules picking or expelling oxygen and other hemoglobin molecules that are picking up or expelling carbon dioxide. Therefore, the hemoglobin molecules, oxygen, and carbon dioxide are reactants while the hemoglobin molecules with oxygen or carbon dioxide bound to them are the products. In this closed system, some reactants convert into products as some products are changing into reactants, making it similar to a reversible reaction.

11.5.5: Contributors and Attributions

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11.6: The Rate Constants of a Reversible Reaction Can Be Determined Using Relaxation Techniques

The traditional experimental methods described above all assume the possibility of following the reaction after its components have combined into a homogeneous mixture of known concentrations. But what can be done if the time required to complete the mixing process is comparable to or greater than the time needed for the reaction to run to completion?

11.6.1: Flow methods

Flow instruments are a rapid mixing devices used to study the chemical kinetics of fast reactions in solution. There are different flavors that can be implement depending on the nature of the reaction as discussed below.

11.6.1.1: Continuous Flow Approach

For reactions that take place in milliseconds, the standard approach since the 1950s has been to employ a flow technique of some kind. An early example was used to study fast gas-phase reactions in which one of the reactants is a free radical such as OH that can be produced by an intense microwave discharge acting on a suitable source gas mixture. This gas, along with the other reactant being investigated, is made to flow through a narrow tube at a known velocity.

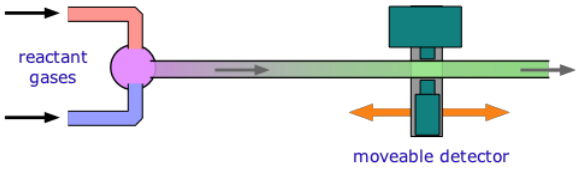


Figure **11.6.1**: A continuous flow fast kinetic system.

If the distance between the point at which the reaction is initiated and the product detector is known, then the time interval can be found from the flow rate. By varying this distance, the time required to obtain the maximum yield can then be determined. Although this method is very simple in principle, it can be complicated in practice.

11.6.1.2: Stopped Flow Approach

Owing to the rather large volumes required, continuous flow method is more practical for the study of gas-phase reactions than for solutions, for which the stopped-flow method described below is generally preferred. These are by far the most common means of studying fast solution-phase reactions over time intervals of down to a fraction of a millisecond. The use of reasonably simple devices is now practical even in student laboratory experiments. These techniques make it possible to follow not only changes in the concentrations of reactants and products, but also the buildup and decay of reaction intermediates.

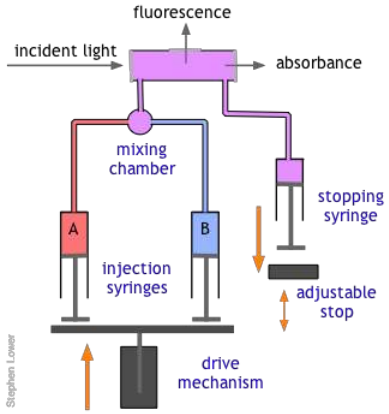


Figure **11.6.2**: A stop flow fast kinetic system.

The basic stopped-flow apparatus consists of two or more coupled syringes that rapidly inject the reactants into a small mixing chamber and then through an observation cell that can be coupled to instruments that measure absorption, fluorescence, light scattering, or other optical or electrical properties of the solution. As the solution flows through the cell, it empties into a stopping syringe that, when filled, strikes a backstop that abruptly stops the flow. The volume that the stopping syringe can accept is

adjusted so that the mixture in the cell has just become uniform and has reached a steady state; at this point, recording of the cell measurement begins and its change is followed.

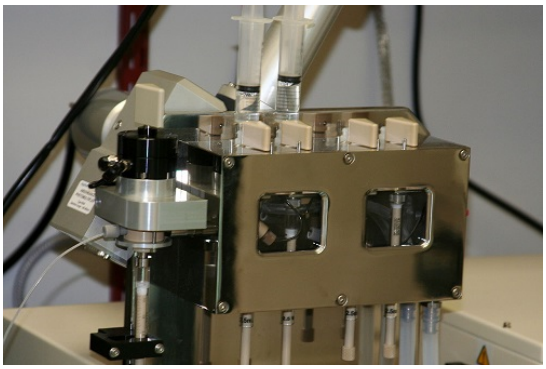


Figure **11.6.3**: Stop-flow equipment at a biochemistry research laboratory for measuring rapid reactions and properties such as enzyme kinetics. from Wladimir Labeikovsky.

11.6.1.3: Quenched Flow Approach

In a quenched-flow instrument, the reaction is stopped after a certain amount of time has passed after mixing. The stopping of the reaction is called quenching and it can be achieved by various means, for example by mixing with another solution, which stops the reaction (chemical quenching), quickly lowering the temperature (freeze quenching) or even by exposing the sample to light of a certain wavelength (optical quenching).

Of course, there are many reactions that cannot be followed by changes in light absorption or other physical properties that are conveniently monitored. In such cases, it is often practical to *quench* (stop) the reaction after a desired interval by adding an appropriate quenching agent. For example, an enzyme-catalyzed reaction can be stopped by adding an acid, base, or salt solution that denatures (destroys the activity of) the protein enzyme. Once the reaction has been stopped, the mixture is withdrawn and analyzed in an appropriate manner.

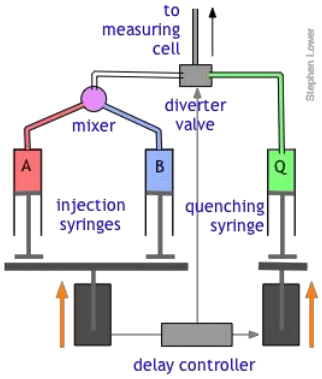


Figure **11.6.4**: A quench flow fast kinetic system.

The quenched-flow technique works something like the stopped-flow method described above, with a slightly altered plumbing arrangement. The reactants A and B are mixed and fed directly through the diverter valve to the measuring cell, which is not shown in this diagram. After a set interval that can vary from a few milliseconds to 200 sec or more, the controller activates the quenching syringe and diverter valve, flooding the cell with the quenching solution.

11.6.2: Relaxation Methods

To investigate reactions that are complete in less than a millisecond, one can start with a pre-mixed sample in which one of active reactants is generated *in situ*. Alternatively, a rapid change in pressure or temperature can alter the composition of a reaction that has already achieved equilibrium.

11.6.2.1: Flash Photolysis

Many reactions are known which do not take place without light of wavelength sufficiently short to supply the activation energy needed to break a bond, often leading to the creation of a highly reactive radical. A good example is the combination of gaseous Cl_2 with H_2, which proceeds explosively when the system is illuminated with visible light. In *flash photolysis*, a short pulse of light is used to initiate a reaction whose progress can be observed by optical or other means.

Photolysis refers to the use of light to decompose a molecule into simpler units, often ions or free radicals. In contrast to *thermolysis* (decomposition induced by high temperature), photolysis is able to inject energy into a molecule almost instantaneously and can be much "cleaner," meaning that there are fewer side reactions that often lead to complex mixtures of products. Photolysis can also be highly *specific*; the wavelength of the light that triggers the reaction can often be adjusted to activate one particular kind of molecule without affecting others that might be present.

Norrish and Porter

All this had been known for a very long time, but until the mid-1940's there was no practical way of studying the kinetics of the reactions involving the highly reactive species produced by photolysis. In 1945, Ronald Norrish of Cambridge University and his graduate student George Porter conceived the idea of using a short-duration flash lamp to generate gas-phase CH_2 radicals, and then following the progress of the reaction of these radicals with other species by means of absorption spectroscopy.

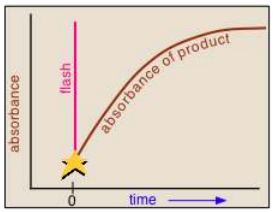


Figure **11.6.5**: Basic principle of a flash-photolysis relaxation experiment where an excitation pulse purturbed a system at equilibrium and the subsequent dynamics are resolved in time.

In a flash photolysis experiment, recording of the absorbance of the sample cell contents is timed to follow the flash by an interval that can be varied in order to capture the effects produced by the product or intermediate as it is formed or decays. Norrish and Porter shared the 1967 Nobel Prize in Chemistry for this work.

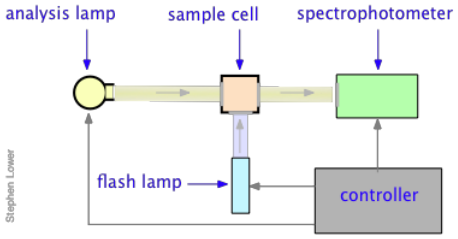


Figure **11.6.6**: A flash-photolysis relaxation experiment

Many reactions, especially those that take place in solution, occur too rapidly to follow by flow techniques, and can therefore only be observed when they are already at equilibrium. The classical examples of such reactions are two of the fastest ones ever observed, the dissociation of water

$$2H_2O \rightarrow H_3O^+ + OH^- \tag{11.6.1}$$

and the formation of the triiodide ion in aqueous solution

$$I^- + I_2 \rightarrow I_3^- \tag{11.6.2}$$

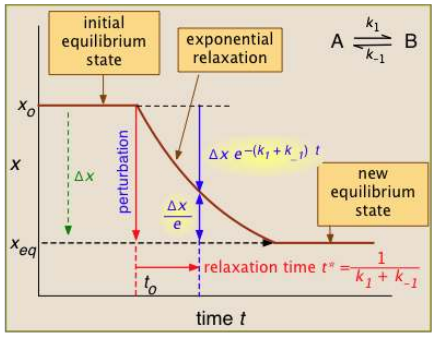
Reactions of these kinds could not be studied until the mid-1950s when techniques were developed to shift the equilibrium by imposing an abrupt physical change on the system.

11.6.2.2: Temperature Jumps

The rate constants of reversible reactions can be measured using a relaxation method. In this method, the concentrations of reactants and products are allowed to achieve equilibrium at a specific temperature. Once equilibrium has been achieved, the temperature is rapidly changed, and then the time needed to achieve the new equilibrium concentrations of reactants and products is measured. For example, if the reaction

$$\mathbf{A} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathbf{B} \tag{11.6.3}$$

is endothermic, then according to the Le Chatelier principle, subjecting the system to a rapid jump in temperature will shift the equilibrium state to one in which the product B has a higher concentration. The composition of the system will than begin to shift toward the new equilibrium composition at a rate determined by the kinetics of the process.



For the general case illustrated here, the quantity "*x*" being plotted is a measurable quantity such as light absorption or electrical conductivity that varies linearly with the composition of the system. **In a first-order process**, *x* will vary with time according to

$$x_t = x_o e^{-kt} \tag{11.6.4}$$

After the abrupt perturbation at time t_o, the relaxation time t^* is defined as the half-time for the return to equilibrium — that is, as the time required for x_o to decrease by \(\Delta x/e = \Delta x/2.718\). The derivation of t^* and the relations highlighted in yellow can be found in most standard kinetics textbooks. Temperature jumps are likely most commonly used.

The rate law for the reversible reaction in Equation 11.6.3 can be written as

$$\frac{d\,[\mathrm{B}]}{dt} = k_1\,[\mathrm{A}] - k_{-1}\,[\mathrm{B}] \tag{11.6.5}$$

Consider a system comprising **A** and **B** that is allowed to achieve equilibrium concentrations at a temperature, T_1. After equilibrium is achieved, the temperature of the system is instantaneously lowered to T_2 and the system is allowed to achieve new equilibrium concentrations of **A** and **B**, $[\mathrm{A}]_{\mathrm{eq},2}$ and $[\mathrm{B}]_{\mathrm{eq},2}$. During the transition time from the first equilibrium state to the second equilibrium state, we can write the instantaneous concentration of **A** as

$$[\mathrm{A}] = [\mathrm{B}]_{\mathrm{eq},1} - [\mathrm{B}] \tag{11.6.6}$$

The rate of change of species **B** can then be written as

$$\frac{d\,[\mathrm{B}]}{dt} = k_1\left([\mathrm{B}]_{\mathrm{eq},1} - [\mathrm{B}]\right) - k_{-1}\,[\mathrm{B}] = k_1\,[\mathrm{B}]_{\mathrm{eq},1} - (k_1 + k_{-1})\,[\mathrm{B}] \tag{11.6.7}$$

At equilibrium, $d\,[\mathrm{B}]\,/dt = 0$ and $[\mathrm{B}] = [\mathrm{B}]_{\mathrm{eq},2}$, allowing us to write

$$k_1\,[\mathrm{B}]_{\mathrm{eq},1} = (k_1 + k_{-1})\,[\mathrm{B}]_{\mathrm{eq},2} \tag{11.6.8}$$

Using the above equation, we can rewrite the rate equation as

$$\frac{d\mathrm{B}}{\left([\mathrm{B}]_{\mathrm{eq},2} - [\mathrm{B}]\right)} = (k_1 + k_{-1})\,dt \tag{11.6.9}$$

Integrating yields

$$-\ln\left([\mathrm{B}]-[\mathrm{B}]_{\mathrm{eq},2}\right)=-\left(k_1+k_{-1}\right)t+C \tag{11.6.10}$$

We can rearrange the above equation in terms of $\mathbf{B}$

$$[\mathrm{B}]=Ce^{-(k_1+k_{-1})t}+[\mathrm{B}]_{\mathrm{eq},2} \tag{11.6.11}$$

At $t=0$, $[\mathrm{B}]=[\mathrm{B}]_{\mathrm{eq},1}$, so $C=[\mathrm{B}]_{\mathrm{eq},1}-[\mathrm{B}]_{\mathrm{eq},2}$. Plugging the the value of C, we arrive at

$$[\mathrm{B}]-[\mathrm{B}]_{\mathrm{eq},2}=\left([\mathrm{B}]_{\mathrm{eq},1}-[\mathrm{B}]_{\mathrm{eq},2}\right)e^{-(k_1+k_{-1})t} \tag{11.6.12}$$

which can also be expressed as

$$\Delta[\mathrm{B}]=\Delta[\mathrm{B}]_0\,e^{-(k_1+k_{-1})t}=\Delta[\mathrm{B}]_0\,e^{-t/\tau} \tag{11.6.13}$$

where $\Delta[\mathrm{B}]$ is the difference in the concentration of $\mathbf{B}$ from the final equilibrium concentration after the perturbation, and τ is the *relaxation time*. A plot of $\ln\left(\Delta[\mathrm{B}]/\Delta[\mathrm{B}]_0\right)$ versus t will be linear with a slope of $-(k_1+k_{-1})$, where k_1 and k_{-1} are the rate constants at temperature, T_2.

11.6.3: Contributors and Attributions

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11.7: Rate Constants Are Usually Strongly Temperature Dependent

In general, increases in temperature increase the rates of chemical reactions. It is easy to see why, since most chemical reactions depend on molecular collisions. And as we discussed in Chapter 2, the frequency with which molecules collide increases with increased temperature. But also, the kinetic energy of the molecules increases, which should increase the probability that a collision event will lead to a reaction. An empirical model was proposed by Arrhenius to account for this phenomenon. The **Arrhenius model** (Arrhenius, 1889) can be expressed as

$$k = Ae^{-E_a/RT}$$

Although the model is empirical, some of the parameters can be interpreted in terms of the energy profile of the reaction. E_a, for example, is the **activation energy**, which represents the energy barrier that must be overcome in a collision to lead to a reaction.

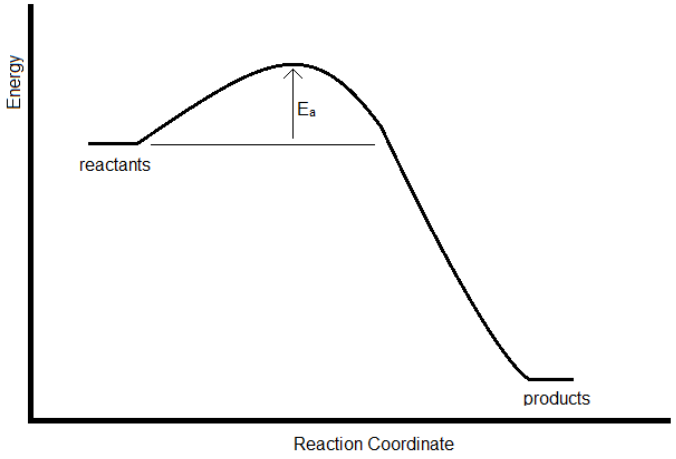


Figure 11.9.1: Reaction profile for an elementary sttep over an activated barrier of height E_a.

If the rate constant for a reaction is measure at two temperatures, the activation energy can be determined by taking the ratio. This leads to the following expression for the Arrhenius model:

$$\ln\left(\frac{k_1}{k_2}\right) = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{11.7.1}$$

Example 11.7.1:

For a given reaction, the rate constant doubles when the temperature is increased form 25 °C to 35 °C. What is the Arrhenius activation energy for this reaction?

Solution

The energy of activation can be calculated from the Arrhenius Equation (Equation 11.7.1).

$$\ln\left(\frac{2k_1}{k_1}\right) = -\frac{E_a}{8.314\,\frac{J}{mol\,K}}\left(\frac{1}{308\,K} - \frac{1}{298\,K}\right)$$

From this reaction:

$$E_a = 52.9\,kJ/mol$$

Preferably, however, the rate constant is measured at several temperatures, and then the activation energy can be determined using all of the measurements, by fitting them to the expression

$$\ln(k) = -\frac{E_a}{RT} + \ln(A)$$

This can be done graphically by plotting the natural logarithm of the rate constant as a function of $1/T$ (with the temperature measured in K). The result should be a straight line (for a well-behaved reaction!) with a slope of $-E_a/R$.

There are some theoretical models (such as collision theory and transition state theory) which suggest the form of the Arrhenius model, but the model itself is purely empirical. A general feature, however, of the theoretical approaches is to interpret the activation energy as an energy barrier which a reaction must overcome in order to lead to a chemical reaction.

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11.8: Transition-State Theory Can Be Used to Estimate Reaction Rate Constants

11.8.1: Transition State Theory

In Figure 28.8.1 , the point at which we evaluate or measure E_a serves as a dividing line (also called a *dividing surface*) between reactants and products. At this point, we do not have $\mathbf{A}+\mathbf{B}$, and we do not have $\mathbf{C}$. Rather, what we have is an activated complex of some kind called a *transition state* between reactants and products. The value of the reaction coordinate at the transition state is denoted $q^{\ddagger}$. Recall our notation $\mathbf{x}$ for the complete set of coordinates and momenta of all of the atoms in the system. Generally, the reaction coordinate q is a function $q(\mathbf{x})$ of all of the coordinates and momenta, although typically, $q(\mathbf{x})$ is a function of a subset of the coordinates and, possibly, the momenta.

As an example, let us consider two atoms $\mathbf{A}$ and $\mathbf{B}$ undergoing a collision. An appropriate reaction coordinate could simply be the distance r between $\mathbf{A}$ and $\mathbf{B}$. This distance is a function of the positions $\mathbf{r}_{\mathbf{A}}$ and $\mathbf{r}_{\mathbf{B}}$ of the two atoms, in that

$$q = r = |\mathbf{r}_{\mathbf{A}} - \mathbf{r}_{\mathbf{B}}| \tag{11.8.1}$$

When $\mathbf{A}$ and $\mathbf{B}$ are molecules, such as proteins, $q(\mathbf{x})$ is a much more complicated function of $\mathbf{x}$.

Now, recall that the mechanical energy $\mathcal{E}(\mathbf{x})$ is given by

$$\mathcal{E}(\mathbf{x}) = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m_1} + U(\mathbf{r}_1, \ldots, \mathbf{r}_N) \tag{11.8.2}$$

and is a sum of kinetic and potential energies. Transition state theory assumes the following:

1. The system is classical, and the time dependence of the coordinates and momenta is determined by Newton's laws of motion
$$m_i \ddot{\mathbf{r}}_i = \mathbf{F}_i \tag{11.8.3}$$
2. We start a trajectory obeying this equation of motion with an initial condition $\mathbf{x}$ that makes $q(\mathbf{x}) = q^{\ddagger}$ and such that $\dot{q}(\mathbf{x}) > 0$ so that the reaction coordinate proceeds initial to the right, i.e., toward products.
3. We follow the motion $\mathbf{x}_t$ of the coordinates and momenta in time starting from this initial condition $\mathbf{x}$, which gives us a unique function $\mathbf{x}_t(\mathbf{x})$.
4. If $q(\mathbf{x}_t(\mathbf{x})) > q^{\ddagger}$ at time t, then the trajectory is designated as "reactive" and contributes to the reaction rate.

Define a function $\theta(y)$, which is 1 if $y \geq 0$ and 0 if $y < 0$. The function $\theta(y)$ is known as a *step function*.

We now define a *flux* of reactive trajectories $k(t)$ using statistical mechanics

$$k(t) = \frac{1}{hQ_r} \int_{q(\mathbf{x})=q^{\ddagger}} d\mathbf{x}\, e^{-\beta\mathcal{E}(\mathbf{x})} |\dot{q}(\mathbf{x})| \, \theta\left(q(\mathbf{x}_t(\mathbf{x})) - q^{\ddagger}\right) \tag{11.8.4}$$

where h is Planck's constant. Here Q_r is the partition function of the reactants

$$Q_r = \int d\mathbf{x}\, e^{-\beta\mathcal{E}(\mathbf{x})} \theta\left(q^{\ddagger} - q(\mathbf{x})\right) \tag{11.8.5}$$

The meaning of Equation 11.8.4 is an ensemble average over a canonical ensemble of the product $|\dot{q}(\mathbf{x})|$ and $\theta\left(q(\mathbf{x}_t(\mathbf{x})) - q^{\ddagger}\right)$. The first factor in this product $|\dot{q}(\mathbf{x})|$ forces the initial velocity of the reaction coordinate to be positive, i.e., toward products, and the step function $\theta\left(q(\mathbf{x}_t(\mathbf{x})) - q^{\ddagger}\right)$ requires that the trajectory of $q(\mathbf{x}_t(\mathbf{x}))$ be reactive, otherwise, the step function will give no contribution to the flux. The function $k(t)$ in Equation 11.8.4 is known as the *reactive flux*. In the definition of Q_r the step function $\theta\left(q^{\ddagger} - q(\mathbf{x})\right)$ measures the total number of microscopic states on the reactive side of the energy profile.

A plot of some examples of reactive flux functions $k(t)$ is shown in Figure 28.8.2 . These functions are discussed in greater detail in *J. Chem. Phys.* **95**, 5809 (1991). These examples all show that $k(t)$ decays at first but then finally reaches a plateau value. This plateau value is taken to be the true rate of the reaction under the assumption that eventually, all trajectories that will become reactive will have done so after a sufficiently long time. Thus,

$$k = \lim_{t\to\infty} k(t) \tag{11.8.6}$$

gives the true rate constant. On the other hand, a common approximation is to take the value $k(0)$ as an estimate of the rate constant, and this is known as the transition *state theory approximation* to k, i.e.,

$$k^{(\mathrm{TST})} = k(0) \tag{11.8.7}$$

$$= \frac{1}{Q_r} \int_{q(\mathbf{x})=q^\ddagger} d\mathbf{x}\, e^{-\beta \mathcal{E}(\mathbf{x})} \left|\dot{q}(\mathbf{x})\right| \theta\left(q(\mathbf{x}) - q^\ddagger\right) \tag{11.8.8}$$

However, note that since we require $\dot{q}(\mathbf{x})$ to initially be toward products, then by definition, at $t = 0$, $q(\mathbf{x}) \geq q^\ddagger$, and the step function in the above expression is redundant. In addition, if $\dot{q}(\mathbf{x})$ only depends on momenta (or velocities) and not actually on coordinates, which will be true if $q(\mathbf{x})$ is not curvilinear (and is true for some curvilinear coordinates $q(\mathbf{x})$), and if $q(\mathbf{x})$ only depends on coordinates, then Equation ??? reduces to

$$k^{(\mathrm{TST})} = \frac{1}{hQ_r} \int d\mathbf{x}_\mathbf{p} e^{-\beta \sum_{i=1}^N \mathbf{p}_i^2/2m_i} \left|\dot{q}(\mathbf{p}_1, \ldots, \mathbf{p}_N)\right| \int_{q(\mathbf{r}_1,\ldots,\mathbf{r}_N)=q^\ddagger} d\mathbf{x}_\mathbf{r} e^{-\beta U(\mathbf{r}_1,\ldots,\mathbf{r}_N)} \tag{11.8.9}$$

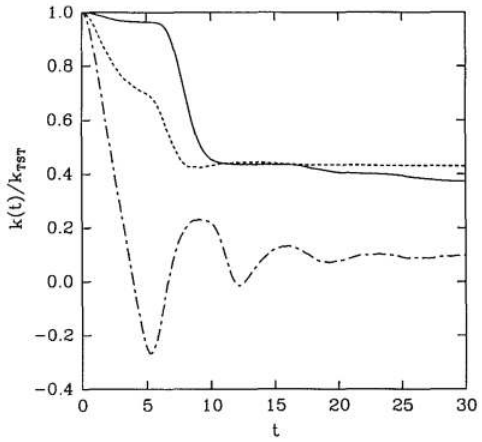


Figure 28.8.2 : Examples of the reactive flux $k(t)$.

The integral

$$Z^\ddagger = \int_{q(\mathbf{r}_1,\ldots,\mathbf{r}_N)=q^\ddagger} d\mathbf{x}_\mathbf{r} e^{-\beta U(\mathbf{r}_1,\ldots,\mathbf{r}_N)}$$

counts the number of microscopic states consistent with the condition $q(\mathbf{r}_1, \ldots, \mathbf{r}_N) = q^\ddagger$ and is, therefore, a kind of partition function, and is denoted $Q^\ddagger$. On the other hand, because it is a partition function, we can derive a free energy $\Delta F^\ddagger$ from it

$$F^\ddagger \propto -k_B T \ln Z^\ddagger \tag{11.8.10}$$

Similarly, if we divide Q_r into its ideal-gas and configurational contributions

$$Q_r = Q_r^{(\mathrm{ideal})} Z_r \tag{11.8.11}$$

then we can take

$$Z_r = e^{-\beta F_r} \tag{11.8.12}$$

where F_r is the free energy of the reactants. Finally, setting $\dot{q} = p/\mu$, where μ is the associated mass, and p is the corresponding momentum of the reaction coordinate, then, canceling most of the momentum integrals between the numerator and $Q_r^{(\mathrm{ideal})}$, the momentum integral we need is

$$\int_0^\infty e^{-\beta p^2/2\mu} \frac{p}{\mu} = k_B T \tag{11.8.13}$$

which gives the final expression for the transition state theory rate constant

$$k^{(\mathrm{TST})} = \frac{k_B T}{h} e^{-\beta(F^\ddagger - F_r)} = \frac{k_B T}{h} e^{-\beta \Delta F^\ddagger} \tag{11.8.14}$$

Figure 28.8.2 actually shows $k(t)/k^{(TST)}$, which must start at 1. As the figure shows, in addition, for $t > 0$, $k(t) < k^{(TST)}$. Hence, $k^{(TST)}$ is always an upper bound to the true rate constant. Transition state theory assumes that any trajectory that initially moves toward products will be a reactive trajectory. For this reason, it overestimates the reaction rate. In reality, trajectories can cross the dividing surface several or many times before eventually proceeding either toward products *or* back toward reactants.

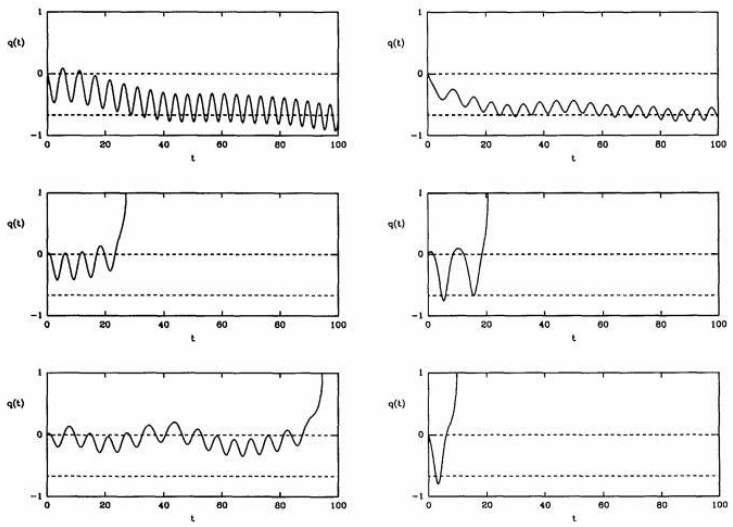


Figure 28.8.3 : Examples of the trajectories in a typical system, some of which are reactive but some of which return to reactants.

Figure 28.8.3 shows that one can obtain trajectories of both types. Here, the dividing surface lies at $q = 0$. Left, toward $q = -1$ is the reactant side, and right, toward $q = 1$ is the product side. Because some trajectories return to reactants and never become products, the true rate is always less than $k^{(TST)}$, and we can write

$$k = \kappa k^{(TST)} \tag{11.8.15}$$

where the factor $\kappa < 1$ is known as the *transmission factor*. This factor accounts for multiple recrossings of the dividing surface and the fact that some trajectories do not become reactive ones.

Contributors and Attributions

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11.E: Chemical Kinetics I - Rate Laws (Exercises)

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CHAPTER OVERVIEW

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12.1: A Mechanism is a Sequence of Elementary Reactions

The mechanism of a reaction is a series of steps leading from the starting materials to the products. After each step, an intermediate is formed. The intermediate is short-lived, because it quickly undergoes another step to form the next intermediate. These simple steps are called elementary reactions. Because an overall reaction is composed of a series of elementary reaction, the overall rate of the reaction is somehow dependent on the rates of those smaller reactions. But how are the two related? Let's look at two cases. We'll keep it simple and both cases will be two-step reactions.

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12.2: The Principle of Detailed Balance

The principle of **detailed balance** is formulated for kinetic systems which are decomposed into elementary processes (collisions, or steps, or elementary reactions): *At equilibrium, each elementary process should be equilibrated by its reverse process.* Lewis put forward this general principle in 1925:

> *Corresponding to every individual process there is a reverse process, and in a state of equilibrium the average rate of every process is equal to the average rate of its reverse process.*[1]

According to Ter Haar, [2] the essence of the detailed balance is:

> *...at equilibrium the number of processes destroying situation* $\boldsymbol{A}$ *and creating situation* $\boldsymbol{B}$ *will be equal to the number of processes producing* $\boldsymbol{A}$ *and destroying* $\boldsymbol{B}$

The principle of detailed balance was explicitly introduced for collisions by Ludwig Boltzmann. In 1872, he proved his H-theorem using this principle. The arguments in favor of this property are founded upon microscopic reversibility. In 1901, R. Wegscheider introduced the principle of detailed balance for chemical kinetics. In particular, he demonstrated that the irreversible cycles

$$A \to B \to C ... Y \to Z \tag{12.2.1}$$

are impossible and found explicitly the relations between kinetic constants that follow from the principle of detailed balance. This system is more accurately described thusly:

$$A \rightleftharpoons B \rightleftharpoons C ... Y \rightleftharpoons Z \tag{12.2.2}$$

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12.3: Multiple Mechanisms are often Indistinguishable

The great value of chemical kinetics is that it can give us insights into the actual reaction pathways (mechanisms) that reactants take to form the products of reactions. Analyzing a reaction mechanism to determine the type of rate law that is consistent (or not consistent) with the specific mechanism can give us significant insight. For example, the reaction

$$A + B \rightarrow C$$

might be proposed to follow one of two mechanistic pathways:

$$\underbrace{A + A \xrightarrow{k_1} A_2}_{\text{step 1}}$$

$$\underbrace{A_2 + B \xrightarrow{k_2} C}_{\text{step 2}}$$

or

$$\underbrace{A \xrightarrow{k_1} A^*}_{\text{step 1}}$$

$$\underbrace{A^* + B \xrightarrow{k_2} C}_{\text{step 2}}$$

The first rate law will predict that the reaction should be second order in A, whereas the second mechanism predicts that it should be first order in A (in the limit that the steady state approximation, discussed in the following sections, can be applied to A_2 and A^*). Based on the observed rate law being first or second order in A, one can rule out one of the rate laws. Unfortunately, this kind of analysis cannot confirm a specific mechanism. Other evidence is needed to draw such conclusions, such as the spectroscopic observation of a particular reaction intermediate that can only be formed by a specific mechanism.

In order analyze mechanisms and predict rate laws, we need to build a toolbox of methods and techniques that are useful in certain limits. The next few sections will discuss this kind of analysis, specifically focusing on

- the **Rate Determining Step** approximation,
- the **Steady State** approximation, and
- the **Equilibrium** approximation.

Each type of approximation is important in certain limits, and they are oftentimes used in conjunction with one another to predict the final forms of rate laws.

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12.4: The Steady-State Approximation

One of the most commonly used and most attractive approximations is the **steady state approximation**. This approximation can be applied to the rate of change of concentration of a highly reactive (short lived) intermediate that holds a constant value over a long period of time. The advantage here is that for such an intermediate (I),

$$\frac{d[I]}{dt} = 0$$

So long as one can write an expression for the rate of change of the concentration of the intermediate I, the steady state approximation allows one to solve for its constant concentration. For example, if the reaction

$$A + B \rightarrow C \tag{12.4.1}$$

is proposed to follow the mechanism

$$A + A \xrightarrow{k_1} A_2 \tag{12.4.2}$$

$$A_2 + B \xrightarrow{k_2} C + A \tag{12.4.3}$$

The time-rate of change of the concentration of the intermediate A_2 can be written as

$$\frac{d[A_2]}{dt} = k_1[A]^2 - k_2[A_2][B]$$

In the limit that the steady state approximation can be applied to A_2

$$\frac{d[A_2]}{dt} = k_1[A]^2 - k_2[A_2][B] \approx 0$$

or

$$[A_2] \approx \frac{k_1[A]^2}{k_2[B]}$$

So if the rate of the overall reaction is expressed as the rate of formation of the product C,

$$\frac{d[C]}{dt} = k_2[A_2][B]$$

the above expression for $[A_2]$ can be substituted

$$\frac{d[C]}{dt} = k_2\left(\frac{k_1[A]^2}{k_2[B]}\right)[B]$$

of

$$\frac{d[C]}{dt} = k_1[A]^2$$

and the reaction is predicted to be second order in $[A]$.

Alternatively, if the mechanism for Equation 12.4.1 is proposed to be

$$A \xrightarrow{k_1} A^* \tag{12.4.4}$$

$$A^* + B \xrightarrow{k_2} C \tag{12.4.5}$$

then the rate of change of the concentration of A^* is

$$\frac{[A^*]}{dt} = k_1[A] - k_2[A^*][B]$$

And if the steady state approximation holds, then

$$[A^*] \approx \frac{k_1[A]}{k_2[B]}$$

So the rate of production of C is

$$\frac{d[C]}{dt} = k_2[A^*][B] \tag{12.4.6}$$

$$= \cancel{k_2}\left(\frac{k_1[A]}{\cancel{k_2}\cancel{[B]}}\right)\cancel{[B]} \tag{12.4.7}$$

or

$$\frac{d[C]}{dt} = k_1[A]$$

and the rate law is predicted to be first order in A. In this manner, the plausibility of either of the two reaction mechanisms is easily deduced by comparing the predicted rate law to that which is observed. If the prediction cannot be reconciled with observation, then the scientific method eliminates that mechanism from consideration.

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12.5: Rate Laws Do Not Imply Unique Mechanism

Because a proposed mechanism can only be valid if it is consistent with the rate law found experimentally, the rate law plays a central role in the investigation of chemical reaction mechanisms. The discussion above introduces the problems and methods associated with collecting rate data and with finding an empirical rate law that fits experimental concentration-*versus*-time data. We turn now to finding the rate laws that are consistent with a particular proposed mechanism. For simplicity, we consider reactions in closed constant-volume systems.

In principle, numerical integration can be used to predict the concentration at any time of each of the species in any proposed reaction mechanism. This prediction can be compared to experimental observations to see whether they are consistent with the proposed mechanism. To do the numerical integration, it is necessary to know the initial concentrations of all of the chemical species and to know, or assume, values of all of the rate constants. The initial concentrations are known from the procedure used to initiate the reaction. However, the rate constants must be determined by some iterative procedure in which initial estimates of the rate constants are used to predict concentration-*versus*-time data that can be compared to the experimental results to produce refined estimates.

In practice, we tailor our choice of reaction conditions so that we can use various approximations to test whether a proposed mechanism can explain the data. We now consider the most generally useful of these approximations.

In this discussion, we assume that the overall reaction goes to completion; that is, at equilibrium the concentration of the reactant whose concentration is limiting has become essentially zero. If the overall reaction involves more than one elementary step, then an intermediate compound is involved. A valid mechanism must include this intermediate, and more than one differential equation may be needed to characterize the time rate of change of all of the species involved in the reaction. We focus on conditions and approximations under which the rate of appearance of the final products in a multi-step reaction mechanism can be described by a single differential equation, the rate law.

We examine the application of these approximations to a particular reaction mechanism. When we understand the application of these approximations to this mechanism, the ways in which they can be used in other situations are clear.

Consider the following sequence of elementary steps

$$\mathrm{A} + \mathrm{B} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{C} \xrightarrow{k_3} \mathrm{D}$$

whose kinetics are described by the following simultaneous differential equations:

$$\frac{d[A]}{dt} = \frac{d[B]}{dt} = -k_1[A][B] + k_2[C]$$

$$\frac{d[C]}{dt} = k_1[A][B] - k_2[C] - k_3[C]$$

$$\frac{d[D]}{dt} = k_3[C]$$

The general analytical solution for this system of coupled differential equations can be obtained, but it is rather complex, because $[C]$ increases early in the reaction, passes through a maximum, and then decreases at long times. In principle, experimental data could be fit to these equations. The numerical approach requires that we select values for k_1, k_2, k_3, $[A]_0$, $[B]_0$, $[C]_0$, and $[D]_0$, and then numerically integrate to get $[A]$, $[B]$, $[C]$, and $[D]$ as functions of time. In principle, we could refine our estimates of k_1, k_2, and k_3 by comparing the calculated values of one or more concentrations to the experimental ones. In practice, the approximate treatments we consider next are more expedient.

When we begin a kinetic study, we normally have a working hypothesis about the reaction mechanism, and we design our experiments to simplify the differential equations that apply to it. For the present example, we will assume that we always arrange the experiment so that $[C]_0 = 0$ and $[D]_0 = 0$. In consequence, at all times:

$$[A]_0 = [A] + [C] + [D]\,.$$

Also, we restrict our considerations to experiments in which $[B]_0 \gg [A]_0$. This exemplifies the use of **flooding**. The practical effect is that the concentration of B remains effectively constant at its initial value throughout the entire reaction, which simplifies the

differential equations significantly. In the present instance, setting $[B]_0 \gg [A]_0$ means that the rate-law term $k_1[A][B]$ can be replaced, to a good approximation, by $k_{obs}[A]$, where $k_{obs} = k_1[B]_0$.

Once we have decided upon the reaction conditions we are going to use, whether the resulting concentration-*versus*-time data can be described by a single differential equation depends on the relative magnitudes of the rate constants in the several steps of the overall reaction. Particular combinations of relationships that lead to simplifications are often referred to by particular names; we talk about a combination that has a ***rate-determining step***, or one that involves a ***prior equilibrium***, or one in which a ***steady-state approximation*** is applicable. To see what we mean by these terms, let us consider some particular relationships that can exist among the rate constants in the mechanism above.

12.5.1: Case I

Suppose that $k_1[A][B] \gg k_2[C]$ and $k_3 \gg k_2$. We often describe this situation by saying, rather imprecisely, that the reaction to convert C to D is very fast and that the reaction to convert C back to A and B is very slow—compared to the reaction that forms C from A and B. When C is produced in these circumstances, it is converted to D so rapidly that we never observe a significant concentration of C in the reaction mixture. The formation of a molecule of C is tantamount to the formation of a molecule of D, and the reaction produces D at essentially the same rate that it consumes A or B. We say that the first step, $A + B \rightarrow C$, is the rate-determining step in the reaction. We have

$$-\frac{d[A]}{dt} = -\frac{d[B]}{dt} \approx \frac{d[D]}{dt}$$

The assumption that $k_1[A][B] \gg k_2[C]$ means that we can neglect the smaller term in the equation for $d[A]/dt$, giving the approximation

$$\frac{d[A]}{dt} = \frac{d[B]}{dt} = -\frac{d[D]}{dt} = -k_1[A][B]$$

Letting $[D] = x$ and recognizing that our assumptions make $[C] \approx 0$, the mass-balance condition, $[A]_0 = [A] + [C] + [D]$, becomes $[A] = [A]_0 - x$. Choosing $[B]_0 \gg [A]_0$ means that $k_1[B] \approx k_1[B]_0 = k_{I,obs}$. The rate equation becomes first-order:

$$\frac{dx}{dt} = k_{I,obs}\,([A]_0 - x)$$

Since $k_{I,obs}$ is not strictly constant, it is a pseudo-first-order rate constant. The disappearance of A is said to follow a pseudo-first-order rate equation.

The concept of a rate-determining step step is an **approximation**. In general, the consequence we have in mind when we invoke this approximation is that no intermediate species can accumulate to a significant concentration if it is produced by the rate-determining step or by a step that occurs after the rate-determining step. We do not intend to exclude the accumulation of a species that is at equilibrium with another product. Thus, in the mechanism

$$\mathrm{A} \xrightarrow{k} \mathrm{B} \rightleftharpoons \mathrm{C}$$

we suppose that the conversion of A to B is rate-determining and that the interconversion of B and C is so rapid that their concentrations always satisfy the equilibrium relationship

$$K = \frac{[C]}{[B]}.$$

For the purpose at hand, we do not consider B to be an intermediate; B is a product that happens to be at equilibrium with the co-product, C.

12.5.2: Case II

Suppose that $k_1[A][B] \gg k_3[C]$. In this case $A + B \rightarrow C$ is fast compared to the rate at which C is converted to D, and we say that $C \rightarrow D$ is the rate-determining step. We can now distinguish three sub-cases depending upon the way $[C]$ behaves during the course of the reaction.

Case IIa: Suppose that $k_1[A][B] \gg k_3[C]$ and $k_3 \gg k_2$. Then $A + B \rightarrow C$ is rapid and essentially quantitative. That is, within a short time of initiating the reaction, all of the stoichiometrically limiting reactant is converted to C. Letting $[D] = x$ and recognizing that our assumptions make $[A] \approx 0$, the mass-balance condition,

$$[A]_0 = [A] + [C] + [D]$$

becomes

$$[C] = [A]_0 - x.$$

After a short time, the rate at which D is formed becomes

$$\frac{d[D]}{dt} = k_3[C]$$

or

$$\frac{dx}{dt} = k_3([A]_0 - x)$$

The disappearance of C and the formation of D follow a first-order rate law.

Case IIb: If the forward and reverse reactions in the first elementary process are rapid, then this process may be effectively at equilibrium during the entire time that D is being formed. (This is the case that $k_1[A][B] \gg k_3[C]$ and $k_2 \gg k_3$.) Then, throughout the course of the reaction, we have

$$K_{eq} = [C]/[A][B]$$

Letting $[D] = x$ and making the further assumption that $[A] \gg [C] \approx 0$ throughout the reaction, the mass-balance condition, $[A]_0 = [A] + [C] + [D]$, becomes $[A] = [A]_0 - x$. Substituting into the equilibrium-constant expression, we find

$$[C] = K_{eq}[B]_0\ ([A]_0 - x)$$

Substituting into $d[D]/dt = k_3[C]$ we have

$$\frac{dx}{dt} = k_3K_{eq}[B]_0\ ([A]_0 - x) = k_{IIa,obs}([A]_0 - x)$$

where $k_{IIa,obs} = k_3K_{eq}[B]_0$. The disappearance of A and the formation of D follow a pseudo-first-order rate equation. The pseudo-first-order rate constant is a composite quantity that is directly proportional to $[B]_0$.

Case IIc: If we suppose that the first step is effectively at equilibrium during the entire time that D is being produced (as in case IIb) but that $[C]$ is not negligibly small compared to $[A]$, we again have $K_{eq} = [C]/[A][B]$. With $[D] = x$, the mass-balance condition becomes $[A] = [A]_0 - [C] - x$. Eliminating $[A]$ between the mass-balance and equilibrium-constant equations gives

$$[C] = \frac{K_{eq}[B]_0([A]_0 - x)}{1 + K_{eq}[B]_0}$$

so that $d[D]/dt = k_3[C]$ becomes

$$\frac{dx}{dt} = \left(\frac{k_3K_{eq}[B]_0}{1 + K_{eq}[B]_0}\right)([A]_0 - x) = k_{IIc,obs}([A]_0 - x)$$

The formation of D follows a pseudo-first-order rate equation. (The disappearance of A is also pseudo-first-order, but the pseudo-first-order rate constant is different.) As in Case IIb, the pseudo-first-order rate constant, $k_{IIc,obs}$, is a composite quantity, but now its dependence on $[B]_0$ is more complex. The result for Case IIc reduces to that for Case IIb if $K_{eq}[B]_0 \ll 1$.

12.5.3: Case III

In the cases above, we have assumed that one or more reactions are intrinsically much slower than others are. The differential equations for this mechanism can also become much simpler if all three reactions proceed at similar rates, but do so in such a way that the concentration of the intermediate is always very small, $[C] \approx 0$. If the concentration of C is always very small, then we expect the graph of $[C]$ versus time to have a slope, $d[C]/dt$, that is approximately zero. In this case, we have

$$\frac{d[C]}{dt} = k_1[A][B] - k_2[C] - k_3[C] \approx 0$$

so that

$$[C] = \frac{k_1[A][B]}{k_2 + k_3}$$

With $[D] = x$, $d[D]/dt = k_3[C]$ becomes

$$\frac{dx}{dt} = \left(\frac{k_1 k_3 [B]_0}{k_2 + k_3}\right)([A]_0 - x) = k_{III,obs}([A]_0 - x)$$

As in the previous cases, the disappearance of A and the formation of D follow a pseudo-first-order rate equation. The pseudo-first-order rate constant is again a composite quantity, which depends on $[B]_0$ and the values of all of the rate constants.

Case III illustrates the ***steady-state approximation***, in which we assume that the concentration of an intermediate species is much smaller than the concentrations of other species that affect the reaction rate. Under these circumstances, we can be confident that the time-derivative of the intermediate's concentration is negligible compared to the reaction rate, so that it is a good approximation to set it equal to zero. The idea is simply that, if the concentration is always small, its time-derivative must also be small. If the graph of the intermediate's concentration versus time is always much lower than that of other participating species, then its slope will be much less.

Equating the time derivative of the steady-state intermediate's concentration to zero produces an algebraic expression that involves the intermediate's concentration. Solving this expression for the concentration of the steady-state intermediate makes it possible to greatly simplify the set of simultaneous differential equations that is predicted by the mechanism. When there are multiple intermediates to which the approximation is applicable, remarkable simplifications can result. This often happens when the mechanism involves free-radical intermediates.

The name "steady-state approximation" is traditional. When we use it, we do so on the understanding that the "state" which is approximately "steady" is the concentration of the intermediate, not the state of the system. Since a net reaction is occurring, the state of the system is distinctly not constant.

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12.6: The Lindemann Mechanism

The Lindemann mechanism, sometimes called the Lindemann-Hinshelwood mechanism, is a schematic reaction mechanism. Frederick Lindemann discovered the concept in 1921 and Cyril Hinshelwood developed it. It breaks down a stepwise reaction into two or more elementary steps, then it gives a rate constant for each elementary step. The rate law and rate equation for the entire reaction can be derived from this information. Lindemann mechanisms have been used to model gas phase decomposition reactions. Although the net formula for a decomposition may appear to be first-order (unimolecular) in the reactant, a Lindemann mechanism may show that the reaction is actually second-order (bimolecular).

A Lindemann mechanism typically includes an activated reaction intermediate, labeled A* (where A can be any element or compound). The activated intermediate is produced from the reactants only after a sufficient activation energy is applied. It then either deactivates from A* back to A, or reacts with another (dis)similar reagent to produce yet another reaction intermediate or the final product.

12.6.1: General Mechanism

The schematic reaction $A + M \rightarrow P$ is assumed to consist of two elementary steps:

STEP 1: Bimolecular activation of A

$$A + M \rightleftharpoons A^* + M \tag{12.6.1}$$

with

- forward activation reaction rate: k_1
- reverse deactivation reaction rate: k_{-1}

STEP 2: Unimolecular reaction of $A*$

$$A^* \xrightarrow{k_2} P \tag{12.6.2}$$

with

- forward reaction rate: k_2

Assuming that the concentration of intermediate A^* is held constant according to the quasi steady-state approximation, what is the rate of formation of product P?

Solution

First, find the rates of production and consumption of intermediate A^*. The rate of production of A^* in the first elementary step (Equation 12.6.1) and A^* is consumed both in the reverse first step and in the forward second step. The respective rates of consumption of A^* are:

$$\frac{d[A^*]}{dt} = \underset{\text{(forward first step)}}{k_1[A][M]} - \underset{\text{(reverse first step)}}{k_{-1}[A^*][M]} - \underset{\text{(forward second step)}}{k_2[A^*]} \tag{12.6.3}$$

According to the steady-state approximation,

$$\frac{d[A^*]}{dt} \approx 0 \tag{12.6.4}$$

Therefore the rate of production of A^* (first term in Equation 12.6.3) equals the rate of consumption (second and third terms in Equation 12.6.3):

$$k_1[A][M] = k_{-1}[A^*][M] + k_2[A^*] \tag{12.6.5}$$

Solving for $[A^*]$, it is found that

$$[A^*] = \frac{k_1[A][M]}{k_{-1}[M] + k_2} \tag{12.6.6}$$

The overall reaction rate is (Equation 12.6.2)

$$\frac{d[P]}{dt} = k_2[A^*] \tag{12.6.7}$$

Now, by substituting the calculated value for $[A^*]$ (Equation 12.6.6 into Equation 12.6.7), the overall reaction rate can be expressed in terms of the original reactants A and M as follows:

$$\frac{d[P]}{dt} = \frac{k_1 k_2 [A][M]}{k_{-1}[M] + k_2} \tag{12.6.8}$$

The rate law for the Lindemann mechanism is not a simple first or second order reaction. However, under certain conditions (discussed below), Equation 12.6.8 can be simplified.

Three Principles of the Lindemann Mechanism

1. Energy is transferred by collision (forward reaction of Equation 12.6.1)
2. There is a time delay Δt between collision and reaction (Equation 12.6.2)
3. Molecules may be de-activated by another collision during Δt (reverse reaction of Equation 12.6.1)

N_2O_5 Example 29.6.1 : Dissociation of

The decomposition of dinitrogen pentoxide to nitrogen dioxide and nitrogen trioxide

$$N_2O_5 \rightarrow NO_2 + NO_3$$

is postulated to take place via two elementary steps, which are similar in form to the schematic example given above:

1. $N_2O_5 + N_2O_5 \rightleftharpoons N_2O_5^* + N_2O_5$
2. $N_2O_5^* \rightarrow NO_2 + NO_3$

Using the quasi steady-state approximation soluioten (Equation 9) with $[M] = [N_2O_5]$, then rate equation is:

$$\text{Rate} = k_2[N_2O_5]^* = \frac{k_1 k_2 [N_2O_5]^2}{k_{-1}[N_2O_5] + k_2}$$

Experiment has shown that the rate is observed as first-order in the original concentration of N_2O_5 sometimes, and second order at other times.

- If $k_2 >> k_{-1}$, then the rate equation may be simplified by assuming that $k_{-1} \approx 0$. Then the rate equation is

  $$\text{Rate} = k_1[N_2O_5]^2$$

  which is *second order*.
- If $k_2 << k_{-1}$, then the rate equation may be simplified by assuming $k_2 \approx 0$. Then the rate equation is

  $$\text{Rate} = \frac{k_1 k_2 [N_2O_5]}{k_{-1}} = k_{obs}[N_2O_5]$$

  which is *first order* with

  $$k_{obs} = \frac{k_2 k_2}{k_{-1}}.$$

Exercise 29.6.1

The following first order rate constants for the gas phase decomposition of N_2O_5 have been obtained as a function of number density at 298 K.

$k_{obs}(s^{-1})$	7.81×10^{-3}	12.5×10^{-3}	15.6×10^{-3}
$[N_2O_5](mol/m^{-3})$	10	25	50

Confirm that these data are consistent with the Lindemann mechanism and derive a rate constant and a ratio of two rate constants for elementary reactions in the mechanism. What are the units of the two quantities.

12.6.2: Lindemann Mechanism

Consider the isomerization of methylisonitrile gas, CH_3NC, to acetonitrile gas, CH_3CN:

$$CH_3NC \xrightarrow{k} CH_3CN$$

If the isomerization is a unimolecular elementary reaction, we should expect to see 1^{st} order rate kinetics. Experimentally, however, 1^{st} order rate kinetics are only observed at high pressures. At low pressures, the reaction kinetics follow a 2^{nd} order rate law:

$$\frac{d\left[CH_3NC\right]}{dt} = -k\left[CH_3NC\right]^2 \tag{12.6.9}$$

To explain this observation, J.A. Christiansen and F.A. Lindemann proposed that gas molecules first need to be energized via intermolecular collisions before undergoing an isomerization reaction. The reaction mechanism can be expressed as the following two elementary reactions

$$\mathrm{A} + \mathrm{M} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{A}^* + \mathrm{M} \tag{12.6.10}$$

$$\mathrm{A}^* \xrightarrow{k_2} \mathrm{B} \tag{12.6.11}$$

where M can be a reactant molecule, a product molecule or another inert molecule present in the reactor. Assuming that the concentration of A^* is small, or $k_1 \ll k_2 + k_{-1}$, we can use a steady-state approximation to solve for the concentration profile of species B with time:

$$\frac{d\left[\mathrm{A}^*\right]}{dt} = k_1\left[\mathrm{A}\right]\left[\mathrm{M}\right] - k_{-1}\left[\mathrm{A}^*\right]_{ss}\left[\mathrm{M}\right] - k_2\left[\mathrm{A}^*\right]_{ss} \approx 0 \tag{12.6.12}$$

Solving for $[\mathrm{A}^*]$,

$$\left[\mathrm{A}^*\right] = \frac{k_1\left[\mathrm{M}\right]\left[\mathrm{A}\right]}{k_2 + k_{-1}\left[\mathrm{M}\right]} \tag{12.6.13}$$

The reaction rates of species A and B can be written as

$$-\frac{d\left[\mathrm{A}\right]}{dt} = \frac{d\left[\mathrm{B}\right]}{dt} = k_2\left[\mathrm{A}^*\right] = \frac{k_1 k_2\left[\mathrm{M}\right]\left[\mathrm{A}\right]}{k_2 + k_{-1}\left[\mathrm{M}\right]} = k_{\mathrm{obs}}\left[\mathrm{A}\right] \tag{12.6.14}$$

where

$$k_{\mathrm{obs}} = \frac{k_1 k_2\left[\mathrm{M}\right]}{k_2 + k_{-1}\left[\mathrm{M}\right]} \tag{12.6.15}$$

At high pressures, we can expect collisions to occur frequently, such that $k_{-1}\left[\mathrm{M}\right] \gg k_2$. Equation 12.6.14 then becomes

$$-\frac{d\left[\mathrm{A}\right]}{dt} = \frac{k_1 k_2}{k_{-1}}\left[\mathrm{A}\right] \tag{12.6.16}$$

which follows 1^{st} order rate kinetics.

At low pressures, we can expect collisions to occurs infrequently, such that $k_{-1}\left[\mathrm{M}\right] \ll k_2$. In this scenario, Equation 12.6.14 becomes

$$-\frac{d\left[\mathrm{A}\right]}{dt} = k_1\left[\mathrm{A}\right]\left[\mathrm{M}\right] \tag{12.6.17}$$

which follows second order rate kinetics, consistent with experimental observations.

12.6.3: References

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12.7: Some Reaction Mechanisms Involve Chain Reactions

A large number of reactions proceed through a series of steps that can collectively be classified as a **chain reaction**. The reactions contain steps that can be classified as

- **initiation step** – a step that creates the intermediates from stable species
- **propagation step** – a step that consumes an intermediate, but creates a new one
- **termination step** – a step that consumes intermediates without creating new ones

These types of reactions are very common when the intermediates involved are radicals. An example, is the reaction

$$H_2 + Br_2 \rightarrow 2HBr$$

The observed rate law for this reaction is

$$\text{rate} = \frac{k[H_2][Br_2]^{3/2}}{[Br_2] + k'[HBr]} \tag{12.7.1}$$

A proposed mechanism is

$$Br_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2Br^{\cdot} \tag{12.7.2}$$

$$2Br^{\cdot} + H_2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} HBr + H^{\cdot} \tag{12.7.3}$$

$$H^{\cdot} + Br_2 \xrightarrow{k_3} HBr + Br^{\cdot} \tag{12.7.4}$$

Based on this mechanism, the rate of change of concentrations for the intermediates ($H^{\cdot}$ and $Br^{\cdot}$) can be written, and the steady state approximation applied.

$$\frac{d[H^{\cdot}]}{dt} = k_2[Br^{\cdot}][H_2] - k_{-2}[HBr][H^{\cdot}] - k_3[H^{\cdot}][Br_2] = 0$$

$$\frac{d[Br^{\cdot}]}{dt} = 2k_1[Br_2] - 2k_{-1}[Br^{\cdot}]^2 - k_2[Br^{\cdot}][H_2] + k_{-2}[HBr][H^{\cdot}] + k_3[H^{\cdot}][Br_2] = 0$$

Adding these two expressions cancels the terms involving k_2, k_{-2}, and k_3. The result is

$$2k_1[Br_2] - 2k_{-1}[Br^{\cdot}]^2 = 0$$

Solving for $Br^{\cdot}$

$$Br^{\cdot} = \sqrt{\frac{k_1[Br_2]}{k_{-1}}}$$

This can be substituted into an expression for the $H^{\cdot}$ that is generated by solving the steady state expression for $d[H^{\cdot}]/dt$.

$$[H^{\cdot}] = \frac{k_2[Br^{\cdot}][H_2]}{k_{-2}[HBr] + k_3[Br_2]}$$

so

$$[H^{\cdot}] = \frac{k_2\sqrt{\frac{k_1[Br_2]}{k_{-1}}}[H_2]}{k_{-2}[HBr] + k_3[Br_2]}$$

Now, armed with expressions for $H^{\cdot}$ and $Br^{\cdot}$, we can substitute them into an expression for the rate of production of the product HBr:

$$\frac{d[HBr]}{dt} = k_2[Br^{\cdot}][H_2] + k_3[H^{\cdot}][Br_2] - k_{-2}[H^{\cdot}][HBr]$$

After substitution and simplification, the result is

$$\frac{d[HBr]}{dt} = \frac{2k_2\left(\frac{k_1}{k_{-1}}\right)^{1/2}[H_2][Br_2]^{1/2}}{1+\frac{k_{-1}}{k_3}\frac{[HBr]}{[Br_2]}}$$

Multiplying the top and bottom expressions on the right by $[Br_2]$ produces

$$\frac{d[HBr]}{dt} = \frac{2k_2\left(\frac{k_1}{k_{-1}}\right)^{1/2}[H_2][Br_2]^{3/2}}{[Br_2]+\frac{k_{-1}}{k_3}[HBr]}$$

which matches the form of the rate law found experimentally (Equation 12.7.1)! In this case,

$$k = 2k_2\sqrt{\frac{k_1}{k_{-1}}}$$

and

$$k' = \frac{k_{-2}}{k_3}$$

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12.8: A Catalyst Affects the Mechanism and Activation Energy

As can be seen from the Arrhenius equation, the magnitude of the activation energy, E_a, determines the value of the rate constant, k, at a given temperature and thus the overall reaction rate. Catalysts provide a means of reducing E_a and increasing the reaction rate. Catalysts are defined as substances that participate in a chemical reaction but are not changed or consumed. Instead they provide a new mechanism for a reaction to occur which has a lower activation energy than that of the reaction without the catalyst.

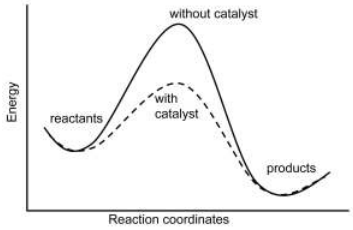


Figure 29.8.1 : Comparison of energy profiles with and without catalyst present.

Homogeneous catalysis refers to reactions in which the catalyst is in solution with at least one of the reactants whereas *heterogeneous catalysis* refers to reactions in which the catalyst is present in a different phase, usually as a solid, than the reactants. Figure 29.8.1 shows a comparison of energy profiles of a reaction in the absence and presence of a catalyst.

Consider a non-catalyzed elementary reaction

$$\mathrm{A} \xrightarrow{k} \mathrm{P}$$

which proceeds at rate k at a certain temperature. The reaction rate can be expressed as

$$\frac{d[\mathrm{A}]}{dt} = -k[\mathrm{A}]$$

In the presence of a catalyst C, we can write the reaction as

$$\mathrm{A} + \mathrm{C} \xrightarrow{k_{cat}} \mathrm{P} + \mathrm{C}$$

and the reaction rate as

$$\frac{d[\mathrm{A}]}{dt} = -k[\mathrm{A}] - k_{cat}[\mathrm{A}][\mathrm{C}]$$

where the first term represents the uncatalyzed reaction and the second term represents the catalyzed reaction. Because the reaction rate of the catalyzed reaction is often magnitudes larger than that of the uncatalyzed reaction (i.e. $k_{cat} \gg k$), the first term can often be ignored.

12.8.1: Example of Homogenous Catalysis: Acid Catalysis

A common example of homogeneous catalysts are acids and bases. For example, given an overall reaction is $\mathrm{S} \rightarrow \mathrm{P}$. If k is the rate, then

$$\frac{d[\mathrm{P}]}{dt} = k[\mathrm{S}]$$

The purpose of an enzyme is to enhance the rate of production of the product P. The equations of the acid-catalyzed reaction are

$$\mathrm{S} + \mathrm{A}H \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{S}H^+ + \mathrm{A}^- \tag{12.8.1}$$

$$\mathrm{S}H^+ + H_2O \xrightarrow{k_2} \mathrm{P} + H_3O^+ \tag{12.8.2}$$

$$H_3O^+ + \mathrm{A}^- \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \mathrm{A}H + H_2O \tag{12.8.3}$$

The full set of kinetic equations is

$$\frac{d[\mathrm{S}]}{dt} = -k_1[\mathrm{S}][\mathrm{A}H] + k_{-1}[\mathrm{S}H^+][\mathrm{A}^-] \tag{12.8.4}$$

$$\frac{d[\mathrm{A}H]}{dt} = -k_1[\mathrm{S}][\mathrm{A}H] + k_{-1}[\mathrm{S}H^+][\mathrm{A}^-] - k_{-3}[\mathrm{A}H] + k_3[H_3O^+][\mathrm{A}^-] \tag{12.8.5}$$

$$\frac{d[\mathrm{S}H^+]}{dt} = k_1[\mathrm{S}][\mathrm{A}H] - k_{-1}[\mathrm{S}H^+][\mathrm{A}^-] - k_2[\mathrm{S}H^+] \tag{12.8.6}$$

$$\frac{d[\mathrm{A}^-]}{dt} = k_1[\mathrm{S}][\mathrm{A}H] - k_{-1}[\mathrm{S}H^+][\mathrm{A}^-] - k_2[\mathrm{A}^-][H_3O^+] + k_{-3}[\mathrm{A}H] \tag{12.8.7}$$

$$\frac{d[\mathrm{P}]}{dt} = k_2[\mathrm{S}H^+] \tag{12.8.8}$$

$$\frac{d[H_3O^+]}{dt} = -k_2[\mathrm{S}H^+] - k_3[H_3O^+][\mathrm{A}^-] + k_{-3}[\mathrm{A}H] \tag{12.8.9}$$

We cannot easily solve these, as they are nonlinear. However, let us consider two cases $k_2 \gg k_{-1}[\mathrm{A}^-]$ and $k_2 \ll k_{-1}[\mathrm{A}^-]$. In both cases, $\mathrm{S}H^+$ is consumed quickly, and we can apply a steady-state approximation:

$$\frac{d[\mathrm{S}H^+]}{dt} = k_1[\mathrm{S}][\mathrm{A}H] - k_{-1}[\mathrm{A}^-][\mathrm{S}H^+] - k_2[\mathrm{S}H^+] = 0$$

Rearranging in terms of $\mathrm{S}H^+$ yields

$$[\mathrm{S}H^+] = \frac{k_1[\mathrm{S}][\mathrm{A}H]}{k_{-1}[\mathrm{A}^-] + k_2}$$

and the rate of production of P can be written as

$$\frac{d[\mathrm{P}]}{dt} = k_2[\mathrm{S}H^+] = \frac{k_1k_2[\mathrm{S}][\mathrm{A}H]}{k_{-1}[\mathrm{A}^-] + k_2}$$

In the case where $k_2 \gg k_{-1}[\mathrm{A}^-]$, Equation 29.8.17 can be written as

$$\frac{d[\mathrm{P}]}{dt} = k_1[\mathrm{S}][\mathrm{A}H]$$

which is known as a general acid-catalyzed reaction. On the other hand, if $k_2 \ll k_{-1}[\mathrm{A}^-]$, we can use an equilibrium approximation to write the rate of production of P as

$$\frac{d[\mathrm{P}]}{dt} = \frac{k_1k_2[\mathrm{S}][\mathrm{A}H]}{k_{-1}[\mathrm{A}^-]} = \frac{k_1k_2}{k_{-1}K}[\mathrm{S}][H^+]$$

where K is the acid dissociation constant:

$$K = \frac{[\mathrm{A}^-][H^+]}{[\mathrm{A}H]}$$

In this case, the reaction is hydrogen ion-catalyzed.

12.8.2: Example of Heterogeneous Catalysis: Surface Catalysis of Gas-Phase Reactions

Many gas-phase reactions are catalyzed on a solid surface. For a first-order, unimolecular reaction, the reaction mechanism can be written as

$$\mathrm{A}(g) + \mathrm{S}(s) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{AS}(s)$$

$$\mathrm{AS}(s) \xrightarrow{k_2} \mathrm{P}(g) + \mathrm{S}(g)$$

where the first step is reversible adsorption of the gas molecule, A, onto active sites on the catalyst surface, S, to form a transition state, AS, and the second step is the conversion of adsorbed A molecules to species P. Applying the steady-state approximation to species AS, we can write

$$\frac{d[\mathrm{AS}]}{dt} = k_1[\mathrm{A}][\mathrm{S}] - k_{-1}[\mathrm{AS}]_{ss} - k_2[\mathrm{AS}]_{ss} = 0$$

Because the concentration of total active sites on the catalyst surface is fixed at $[\mathrm{S}]_0$, the concentration of adsorbed species on the catalyst surface, $[\mathrm{AS}]$ can be written as

$$[\mathrm{AS}] = \theta\,[\mathrm{S}]_0$$

and $[\mathrm{S}]$ can be written as

$$[\mathrm{S}] = (1-\theta)\,[\mathrm{S}]_0$$

where θ is the fractional surface coverage of species A on the catalyst surface. We can now write Equation 29.8.23 as

$$k_1\,[\mathrm{A}]\,(1-\theta)\,[\mathrm{S}]_0 - (k_{-1}+k_2)\,\theta\,[\mathrm{S}]_0 = 0$$

Rearranging the above equation in terms of θ yields

$$\theta = \frac{k_1\,[\mathrm{A}]}{k_1\,[\mathrm{A}] + k_{-1} + k_2}$$

The rate of production of P can be written as

$$\frac{d\,[\mathrm{P}]}{dt} = k_2\,[\mathrm{AS}]_{ss} = k_2\theta\,[\mathrm{S}]_0 = \frac{k_1 k_2}{k_1\,[\mathrm{A}] + k_{-1} + k_2}\,[\mathrm{A}]\,[\mathrm{S}]_0$$

From the above equation, we can observe the importance of having high surface areas for catalytic reactions.

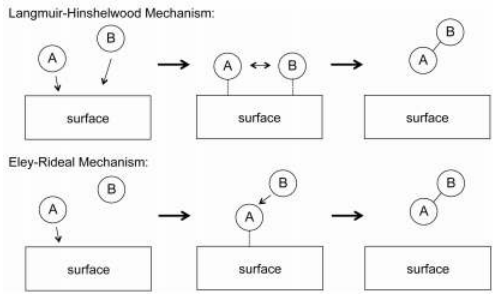


Figure 29.8.2 : Illustrations of the Langmuir-Hinshelwood and Eley-Rideal mechanisms for heterogeneous catalysis of bimolecular gas-phase reactions.

For bimolecular gas-phase reactions, two generally-used mechanisms to explain reactions kinetics are the Langmuir-Hinshelwood and Eley-Rideal mechanisms, shown in Figure 29.8.2 . In the Langmuir-Hinshelwood mechanism, A and B both adsorb onto the catalyst surface, at which they react to form a product. The reaction mechanism is

$$\mathrm{A}\,(g) + \mathrm{S}\,(s) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{AS}\,(s)$$

$$\mathrm{B}\,(g) + \mathrm{S}\,(s) \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{BS}\,(s)$$

$$\mathrm{AS}\,(s) + \mathrm{BS}\,(s) \xrightarrow{k_3} \mathrm{P}$$

The rate law for the Langmuir-Hinshelwood mechanism can be derived in a similar manner to that for unimolecular catalytic reactions by assuming that the total number of active sites on the catalyst surface is fixed. In the Eley-Rideal mechanism, only one species adsorbs onto the catalyst surface. An example of such a reaction is the partial oxidation of ethylene into ethylene oxide, as shown in Figure 29.8.3 . In this reaction, diatomic oxygen adsorbs onto the catalytic surface where it reacts with ethylene molecules in the gas phase.

The reactions for the Eley-Rideal mechanism can be written as

$$\mathrm{A}\,(g) + \mathrm{S}\,(s) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{AS}\,(s)$$

$$\mathrm{AS}\,(s) + \mathrm{B}\,(g) \xrightarrow{k_2} \mathrm{P}\,(g) + \mathrm{S}\,(s)$$

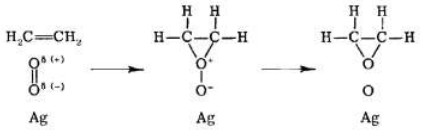


Figure 29.8.3 : Illustrations of the reaction mechanism for the partial oxidation of ethylene to ethylene oxide. [Reproduced from Kilty, PA and WMH Sacthler. Catal. Rev., 10, 1]

Assuming that $k_{-1} \gg k_1$, we can apply a steady-state approximation to species **AS**:

$$\frac{d[\mathrm{AS}]}{dt} = 0 = k_1[\mathrm{A}][\mathrm{S}] - k_{-1}[\mathrm{AS}]_{ss} - k_2[\mathrm{AS}]_{ss}[\mathrm{B}]$$

As in the case of unimolecular catalyzed reactions, we can express the concentrations of **AS** and **S** in terms of a fraction of the total number of active sites, $\mathbf{S_0}$ and rewrite the above equation as

$$0 = k_1[\mathrm{A}](1-\theta)[\mathrm{S}]_0 - k_{-1}[\mathrm{S}]_0 - k_2\theta[\mathrm{S}]_0[\mathrm{B}]$$

Solving for θ yields

$$\theta = \frac{k_1[\mathrm{A}]}{k_1[\mathrm{A}] + k_{-1} + k_2[\mathrm{B}]}$$

Furthermore, if $k_2 \ll k_1$ and k_{-1}, we can simplify θ to

$$\theta = \frac{k_1[\mathrm{A}]}{k_1[\mathrm{A}] + k_{-1}}$$

The rate of production of **P** can be expressed as

$$\frac{d[\mathrm{P}]}{dt} = k_2[\mathrm{AS}]_{ss}[\mathrm{B}] = k_2\theta[\mathrm{S}]_0[\mathrm{B}] = \frac{k_1k_2[\mathrm{A}]}{k_1[\mathrm{A}] + k_{-1}}[\mathrm{S}]_0[\mathrm{B}]$$

We can also write the above expression in terms of the equilibrium constant, K, which is equal to k_1/k_{-1}

$$\frac{d[\mathrm{P}]}{dt} = Kk_2[\mathrm{B}]\frac{K[\mathrm{A}]}{K[\mathrm{A}] + 1}$$

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12.9: The Michaelis-Menten Mechanism for Enzyme Catalysis

Enzymes are biological catalysts and functional proteins. Enzymes contain specificity in its protein structure in order to have its specialized function. It usually contains more than one subunit and they are critical to sustain life. Enzymes can increase the chemical reactions in living cells. However, enzymes are not consumed in the reaction and their main function is to assist in bringing the substrates together so they can undergo normal reaction faster.

The first enzyme was found in the process of fermentation in milk and alcohol during the nineteenth century. Later in the early 1830s, the term enzyme was used to replace the term ferment. Some scientists believe that ferments must contain living cells and some think ferments could be non-living cells. Finally, in the 1920s, Sumner purified the structure of enzyme and then properties of enzyme then was more clearly understood. Until today, enzymes are still the popular research field that many people are subject to study.

12.9.1: Michaelis-Menten Kinetics

In biological systems, enzymes act as catalysts and play a critical role in accelerating reactions, anywhere from 10^3 to 10^{17} times faster than the reaction would normally proceed. Enzymes are high-molecular weight proteins that act on a substrate, or reactant molecule, to form one or more products. In 1913, Leonor Michaelis and Maude Menten proposed the following reaction mechanism for enzymatic reactions:

$$\mathbf{E} + \mathbf{S} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathbf{ES} \xrightarrow{k_2} \mathbf{E} + \mathbf{P}$$

where $\mathbf{E}$ is the enzyme, $\mathbf{ES}$ is the enzyme-substrate complex, and $\mathbf{P}$ is the product. In the first step, the substrate binds to the active site of the enzyme. In the second step, the substrate is converted into the product and released from the substrate. For this mechanism, we can assume that the concentration of the enzyme-substrate complex, $\mathbf{ES}$, is small and employ a steady-state approximation:

$$\frac{d[\mathrm{ES}]}{dt} = k_1[\mathrm{E}][\mathrm{S}] - k_{-1}[\mathrm{ES}]_{ss} - k_2[\mathrm{ES}]_{ss} \approx 0 \tag{12.9.1}$$

Furthermore, because the enzyme is unchanged throughout the reaction, we express the total enzyme concentration as a sum of enzyme and enzyme-substrate complex:

$$[\mathrm{E}]_0 = [\mathrm{ES}] + [\mathrm{E}] \tag{12.9.2}$$

Plugging Equation 12.9.2 into Equation 12.9.1, we obtain

$$0 = k_1([\mathrm{E}]_0 - [\mathrm{ES}]_{ss})[\mathrm{S}] - k_{-1}[\mathrm{ES}]_{ss} + k_2[\mathrm{ES}]_{ss} \tag{12.9.3}$$

Solving for $[\mathrm{ES}]_{ss}$

$$[\mathrm{ES}]_{ss} = \frac{k_1[\mathrm{E}]_0[\mathrm{S}]}{k_1[\mathrm{S}] + k_{-1} + k_2} = \frac{[\mathrm{E}]_0[\mathrm{S}]}{[\mathrm{S}] + \frac{k_{-1} + k_2}{k_1}} \tag{12.9.4}$$

We can then write the reaction rate of the product as

$$\frac{d[\mathrm{P}]}{dt} = k_2[\mathrm{ES}]_{ss} = \frac{k_2[\mathrm{E}]_0[\mathrm{S}]}{[\mathrm{S}] + \frac{k_{-1} + k_2}{k_1}} = \frac{k_2[\mathrm{E}]_0[\mathrm{S}]}{[\mathrm{S}] + K_M} \tag{12.9.5}$$

where K_M is the Michaelis constant. Equation 12.9.5 is known as the Michaelis-Menten equation. The result for Michaelis-Menten kinetics equivalent to that for a unimolecular gas phase reaction catalyzed on a solid surface. In the limit where there is a large amount of substrate present ($[\mathrm{S}] \gg K_M$) Equation 12.9.5 reduces to

$$\frac{d[\mathrm{P}]}{dt} = r_{\max} = k_2[\mathrm{E}]_0 \tag{12.9.6}$$

which is a 0^{th} order reaction, since $[E]_0$ is a constant. The value $k_2 [E]_0$ represents the maximum rate, r_{max}, at which the enzymatic reaction can proceed. The rate constant, k_2, is also known as the *turnover number*, which is the number of substrate molecules converted to product in a given time when all the active sites on the enzyme are occupied. Figure 29.9.4 displays the dependence of the reaction rate on the substrate concentration, $[S]$. This plot is known as the Michaelis-Menten plot. Examining the figure, we can see that the reaction rate reaches a maximum value of $k_2 [E]_0$ at large values of $[S]$.

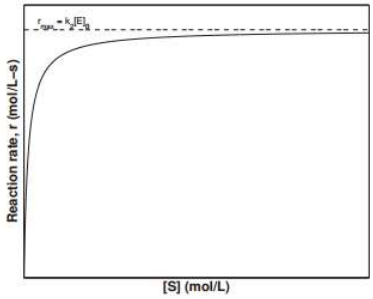


Figure 29.9.4 : Rate dependence on substrate concentration for an enzymatic reaction.

Another commonly-used plot in examining enzyme kinetics is the **Lineweaver-Burk plot**, in with the inverse of the reaction rate, $1/r$, is plotted against the inverse of the substrate concentration $1/[S]$. Rearranging Equation 12.9.5,

$$\frac{1}{r} = \frac{K_M + [S]}{k_2 [E]_0 [S]} = \frac{K_M}{k_2 [E]_0} \frac{1}{[S]} + \frac{1}{k_2 [E]_0} \tag{12.9.7}$$

The Lineweaver-Burk plot results in a straight line with the slope equal to $K_M / k_2 [E]_0$ and y-intercept equal to $1/k_2 [E]_0$.

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12.E: Chemical Kinetics II- Reaction Mechanisms (Exercises)

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CHAPTER OVERVIEW

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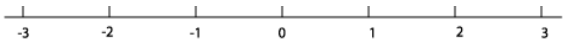
13.1: Complex Numbers
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13.1: Complex Numbers

13.1.1: Real Numbers

Let us think of the ordinary numbers as set out on a line which goes to infinity in both positive and negative directions. We could start by taking a stretch of the line near the origin (that is, the point representing the number zero) and putting in the integers as follows:



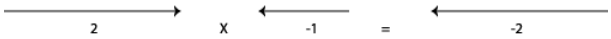
Next, we could add in rational numbers, such as ½, 23/11, etc., then the irrationals like $\sqrt{2}$, then numbers like π, and so on, so any number you can think of has its place on this line. Now let's take a slightly different point of view, and think of the numbers as represented by a *vector* from the origin to that number, so 1 is



and, for example, –2 is represented by:



Note that if a number is multiplied by –1, the corresponding vector is turned through 180 degrees. In pictures,



The "vector" 2 is turned through π, or 180 degrees, when you multiply it by –1.

Example A.1

What are the square roots of 4?

Solution

Well, 2, obviously, but also –2, because multiplying the backwards pointing vector –2 by –2 not only doubles its length, but also turns it through 180 degrees, so it is now pointing in the positive direction. We seem to have invented a hard way of stating that multiplying two negatives gives a positive, but thinking in terms of turning vectors through 180 degrees will pay off soon.

13.1.2: Solving Quadratic Equations

In solving the standard quadratic equation

$$ax^2 + bx + c = 0 \tag{13.1.1}$$

we find the solution to be:

$$x = \frac{-b \pm \sqrt{b^2 - ac}}{2a} \tag{13.1.2}$$

The problem with this is that sometimes the expression inside the square root is negative. What does that signify? For some problems in physics, it means there is no solution. For example, if I throw a ball directly upwards at 10 meters per sec, and ask when will it reach a height of 20 meters, taking g = 10 m per sec^2, the solution of the quadratic equation for the time t has a negative number inside the square root, and that means that the ball doesn't get to 20 meters, so the question didn't really make sense.

We shall find, however, that there are other problems, in wide areas of physics, where negative numbers inside square roots have an important physical significance. For that reason, we need to come up with a scheme for interpreting them.

The simplest quadratic equation that gives trouble is:

$$x^2 + 1 = 0 \tag{13.1.3}$$

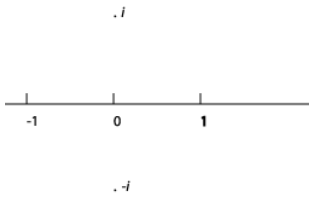
the solutions being

$$x = \pm\sqrt{-1} \tag{13.1.4}$$

What does that mean? We've just seen that the square of a positive number is positive, and the square of a negative number is also positive, since multiplying one negative number, which points backwards, by another, which turns any vector through 180 degrees, gives a positive vector. Another way of saying the same thing is to regard the minus sign itself, -, as an operator which turns the number it is applied to through 180 degrees. Now $(-2) \times (-2)$ has two such rotations in it, giving the full 360 degrees back to the positive axis.

To make sense of the square root of a negative number, we need to find something which when multiplied by itself gives a negative number. Let's concentrate for the moment on the square root of –1, from the quadratic equation above. Think of –1 as the operator – acting on the vector 1, so the – turns the vector through 180 degrees. We need to find the square root of this operator, the operator which applied *twice* gives the rotation through 180 degrees. Put like that, it is pretty obvious that the operator we want rotates the vector 1 through 90 degrees.

But if we take a positive number, such as 1, and rotate its vector through 90 degrees only, it isn't a number at all, at least in our original sense, since we put all known numbers on one line, and we've now rotated 1 away from that line. The new number created in this way is called a pure imaginary number, and is denoted by i.



Once we've found the square root of –1, we can use it to write the square root of any other negative number—for example, $2i$ is the square root of -4. Putting together a real number from the original line with an imaginary number (a multiple of i) gives a *complex number*. Evidently, complex numbers fill the entire two-dimensional plane. Taking ordinary Cartesian coordinates, any point P in the plane can be written as (x, y) where the point is reached from the origin by going x units in the direction of the positive real axis, then y units in the direction defined by i, in other words, the y axis.

Thus the point P with coordinates (x, y) can be identified with the complex number z, where

$$z = x + iy. \tag{13.1.5}$$

The plane is often called the *complex plane*, and representing complex numbers in this way is sometimes referred to as an Argand Diagram.

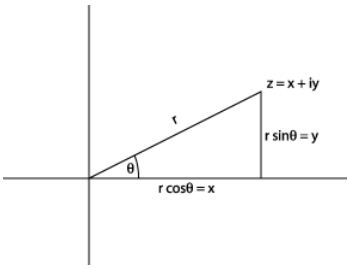
Visualizing the complex numbers as two-dimensional vectors, it is clear how to *add* two of them together. If $z_1 = x_1 + iy_1$, and $z_2 = x_2 + iy_2$, then $z_1 + z_2 = (x_1 + x_2) + i(y_1 + y_2)$. The real parts and imaginary parts are added separately, just like vector components.

Multiplying two complex numbers together does not have quite such a simple interpretation. It is, however, quite straightforward—ordinary algebraic rules apply, with i^2 replaced where it appears by -1. So for example, to multiply $z_1 = x_1 + iy_1$ by $z_2 = x_2 + iy_2$,

$$z_1 z_2 = (x_1 + iy_1)(x_2 + iy_2) = (x_1 x_2 - y_1 y_2) + i(x_1 y_2 + x_2 y_1). \tag{13.1.6}$$

13.1.3: Polar Coordinates

Some properties of complex numbers are most easily understood if they are represented by using the polar coordinates r, θ instead of (x, y) to locate z in the complex plane.



Note that $z = x + iy$ can be written $r(\cos\theta + i\sin\theta)$ from the diagram above. In fact, this representation leads to a clearer picture of multiplication of two complex numbers:

$$z_1 z_2 = r_2(\cos(\theta_1 + i\sin\theta_1) r_2(\cos(\theta_2 + i\sin\theta_2) \tag{13.1.7}$$

$$= r_1 r_2 \left[(\cos\theta_1\cos\theta_2 - \sin\theta_1\sin\theta_2) + i(\sin\theta_1\cos\theta_2 + \cos\theta_1\sin\theta_2)\right] \tag{13.1.8}$$

$$= r_1 r_2 \left[\cos(\theta_1 + \theta_2) + i\sin(\theta_1 + \theta_2)\right] \tag{13.1.9}$$

So, if

$$z = r(cos\theta + i\sin\theta) = z_1 z_2 \tag{13.1.10}$$

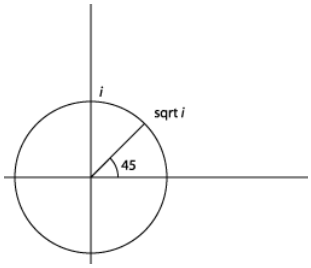
then

$$r = r_1 r_2 \tag{13.1.11}$$

and

$$\theta = \theta_1\theta_2 \tag{13.1.12}$$

That is to say, to multiply together two complex numbers, we *multiply* the *r*'s – called the *moduli* – and *add* the phases, the θ's. The modulus r is often denoted by \(|z|\), and called **mod** z, the phase θ is sometimes referred to as **arg** z. For example, $|i| = 1$, **arg** $i = \pi/2$.

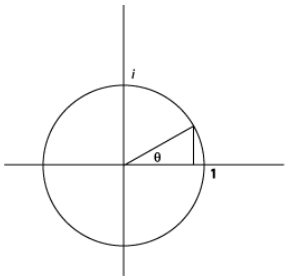


We can now see that, although we had to introduce these complex numbers to have a $\sqrt{-1}$, we do not need to bring in new types of numbers to get $\sqrt{-1}$, or $\sqrt{i}$. Clearly, $|\sqrt{i}| = 1$, $arg\sqrt{i} = 45°$. It is on the circle of unit radius centered at the origin, at 45°, and squaring it just doubles the angle.

13.1.4: The Unit Circle

In fact this circle—called the *unit circle*—plays an important part in the theory of complex numbers and every point on the circle has the form

$$z = \cos\theta + i\sin\theta = Cis(\theta) \tag{13.1.13}$$



Since all points on the unit circle have $|z| = 1$, by definition, multiplying any two of them together just amounts to adding the angles, so our new function $Cis(\theta)$ satisfies

$$Cis(\theta_1)Cis(\theta_2) = Cis(\theta_1 + \theta_2). \tag{13.1.14}$$

But that is just how multiplication works for exponents! That is,

$$a^{\theta_1}a^{\theta_2} = a^{\theta_1+\theta_2} \tag{13.1.15}$$

for a any constant, which strongly suggests that maybe our function $Cis(\theta$ is nothing but some constant a raised to the power θ, that is,

$$Cis(\theta) = a^{\theta} \tag{13.1.16}$$

It turns out to be convenient to write $a^{\theta} = e^{(\ln a)\theta} = e^{A\theta}$, where $A = \ln a$. This line of reasoning leads us to write

$$\cos\theta + i\sin\theta = e^{A\theta} \tag{13.1.17}$$

Now, for the above "addition formula" to work for multiplication, A must be a constant, *independent* of θ. Therefore, we can find the value of A by choosing θ for which things are simple. We take θ to be very small—in this limit:

$$\cos\theta = 1$$

$$\sin\theta = \theta$$

$$e^{A\theta} = 1 + A\theta$$

with we drop terms of order θ^2 and higher.

Substituting these values into Equation 13.1.17 gives θ

So we find:

$$(\cos\theta + i\sin\theta)e^{i\theta} \tag{13.1.18}$$

To test this result, we expand $e^{i\theta}$:

$$e^{i\theta} = 1 + i\theta + \frac{(i\theta)^2}{2!} + \frac{(i\theta)^3}{3!} + \frac{(i\theta)^4}{4!} + \frac{(i\theta)^5}{5!}... \tag{13.1.19}$$

$$= 1 + i\theta - \frac{\theta^2}{2!} - \frac{i\theta^3}{3!} + \frac{\theta^4}{4!} + \frac{i\theta^5}{5!}... \tag{13.1.20}$$

$$= \left(1 - \frac{\theta^2}{2!} + \frac{\theta^4}{4!}\right) + i\left(\theta - \frac{i\theta^3}{3!} + \frac{i\theta^5}{5!}\right) \tag{13.1.21}$$

$$= \cos\theta + i\sin\theta \tag{13.1.22}$$

We write $= \cos\theta + i\sin\theta$ in Equation 13.1.22 because the series in the brackets are precisely the Taylor series for $\cos\theta$ and $\sin\theta$ confirming our equation for $e^{i\theta}$. Changing the sign of θ it is easy to see that

$$e^{-i\theta} = \cos\theta - i\sin\theta \tag{13.1.23}$$

so the two trigonometric functions can be expressed in terms of exponentials of complex numbers:

$$\cos(\theta) = \frac{1}{2}\left(e^{i\theta} + e^{-i\theta}\right)$$

$$\sin(\theta) = \frac{1}{2i}\left(e^{i\theta} - e^{-i\theta}\right)$$

Euler Formula

The Euler formula states that any complex number can be written:

$$e^{i\theta} = \cos\theta + i\sin\theta$$

Contributors and Attributions

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13.2: Probability and Statistics

A random variable X can have more than one value x as an outcome. Which value the variable has in a particular case is a matter of *chance* and cannot be predicted other than that we associate a probability to the outcome. **Probability** p is a number between 0 and 1 that indicates the likelihood that the variable X has a particular outcome x. The set of outcomes and their probabilities form a ***probability distribution***. There are two kinds of distributions:

1. discrete ones
2. continuous ones

Total probability should always add up to unity.

13.2.1: Discrete Distributions

A good example of a discrete distribution is a *true coin*. The random variable X can have two values:

1. heads (0)
2. tails (1)

Both have equal probability and as the sum must equal unity, the probability must be ½ for each. 'The probability that X=heads' is written formally as:

$$Pr(X = heads) = Pr(X = 0) = 0.5$$

The random function is written as a combination of three statements.

- Pr(X=0) = ½
- Pr(X=1) = ½
- elsewhere Pr = 0

13.2.2: Continuous Distributions

Now consider a spherical die. One could say it has an infinite number of facets that it can land on. Thus the number of outcomes $n = \infty$, this make each probability

$$p = 1/\infty = 0.$$

This creates a bit of a mathematical problem, because how can we get a total probability of unity by adding up zeros? Also, if we divide the sphere in a northern and a southern hemisphere clearly the probability that it lands on a point in say, the north should be ½. Still, p = 0 for all points. We introduce a new concept: **probability density** over which we *integrate* rather than *sum*. We assign an equal density to each point of the sphere and make sure that if we integrate over a hemisphere we get ½. (This involves two angles θ and φ and an integration over them and I won't go into that).

A bit simpler example of a continuous distribution than the spherical die is the 1D ***uniform*** distribution. It is the one that the Excel function =RAND() produces to good approximation. Its probability density is defined as

- f(x) = 1 for 0<1>
- f(x) = 0 elsewhere

The figure shows a (bivariate) uniform distribution.

The probability that the outcome is smaller than 0.5 is written as Pr(X<0.5) and is found by integrating from 0 to 0.5 over f(x).

$$\Pr(X<0.5) = \int \mathbf{f(x)}.dx \text{ from 0 to } 0.5 = \int \mathbf{1}.dx \text{ from 0 to } 0.5 = [x]^{0.5}\text{-}[x]_0 = 0.5$$

Notice that in each individual outcome b the probability is indeed zero because an integral from b to b is always zero, even if the probability density f(b) is not zero. Clearly the probability and the probability density are not the same. Unfortunately the distinction between probability and probability density is often not properly made in the physical sciences. Moments can also be computed for continuous distributions by integrating over the probability density 

Another well-known continuous distribution is the ***normal*** (or ***Gaussian***) distribution, defined as:

\[f(x) = 1/[\sqrt{(2\pi)}\sigma] * \exp(-½[(x-\mu)/\sigma]^2) \nonumber \]

(Notice the normalization factor $1/[\sqrt{(2\pi)}\sigma]$)

We can also compute moments of continuous distribution. Instead of using a summation we now have to evaluate an integral:

$$\langle X \rangle = \int [f(x)^* x] dx$$

$$\langle X^2 \rangle = \int [f(x)^* x^2] dx$$

For the normal distribution $\langle X \rangle = \mu$

? Exercise

Compute $^2>$ and $^3>$ for the uniform distribution. answer>

13.2.3: Indistinguishable Outcomes

When flipping two coins we could get four outcomes: two heads (0), heads plus tails (1), tails plus heads (1), two tails (2)

Each outcome is equally likely, this implies a probability of ¼ for each:

X_{tot} = X1 + X2 = 0 + 0 = 0 p=¼
X_{tot} = X1 + X2 = 0 + 1 = 1 p=¼
X_{tot} = X1 + X2 = 1 + 0 = 1 p=¼
X_{tot} = X1 + X2 = 1 + 1 = 2 p=¼

The probability of a particular outcome is often abbreviated simply to p. The two middle outcomes collapse into one with p=¼+¼= ½ if the coins are **indistinguishable**. We will see that this concept has very important consequences in statistical thermodynamics.

If we cannot distinguish the two outcomes leading to X_{tot}=1 we get the following random function:

- Pr(X_{tot}=0) = ¼
- Pr(X_{tot}=1) = ½
- Pr(X_{tot}=2) = ¼
- elsewhere Pr = 0

Notice that it is quite possible to have a distribution where the probabilities differ from outcome to outcome. Often the p values are given as f(x), a function of x. An example:

X3 defined as:

- f(x) = (x+1)/6 for x=0,1,2;
- f(x) =0 elsewhere;

The factor 1/6 makes sure the probabilities add up to unity. Such a factor is known as a **normalization factor**. Again this concept is of prime importance in statistical thermodynamics.

Another example of a discrete distribution is a die. If it has 6 sides (the most common die) there are six outcomes, each with p= 1/6. There are also dice with n=4, 12 or 20 sides. Each outcome will then have p= 1/n.

13.2.4: Moments of Distributions

In important aspect of probability distributions are the **moments** of the distribution. They are values computed by summing over the whole distribution.

The **zero** order moment is simply the sum of all p and that is unity:

$^0> = \Sigma X^0 * p = \Sigma 1 * p = 1$

The **first** moment multiplies each outcome with its probability and sums over all outcomes:

$= \Sigma X * p$

This moment is known as the ***average*** or ***mean***. (It is what we have done to your grades for years...)

For one coin is ½, for two coins is 1. (Exercise: verify this)

The **second** moment is computed by summing the product of the square of X and p:

$^2> = \Sigma X^2 * p$

For one coin we have $^2> = ½$,
For two coins $^2> = [0*¼ + 1*½ + 4*¼] = 1.5$

What is $^2>$ for X3? answer

The notation is used a lot in quantum mechanics, often in the form <ψ*ψ> or <ψ*|h|ψ>. The <.. part is known as the ***bra***, the ..> part as the ***ket***. (Together ***bra***(c)***ket***)

Intermezzo: The strange employer

You have a summer job but your employer likes games of chance. At the end of every day he rolls a die and pays you the square of the outcome in dollars per hour. So on a lucky day you'd make $36.- per hour, but on a bad day $1.-. Is this a bad deal? What would you make on the average over a longer period?

To answer this we must compute the second moment $^2>$ of the distribution:

$^2> = 1/6 * [1+4+9+16+25+36] = 91/6 = \$15.17$ per hour.

(I have taken p=1/6 out of brackets because the value is the same for all six outcomes)

As you see in the intermezzo, the value of the second moment is in this case what you ***expect*** to be making on the long term. Moments are examples of what is know as **expectation values**. Another term you may run into that of a **functional**. A functional is a *number* computed by some operation (such as summation or integration) over a whole function. Moments are clearly an example of that too.

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13.3: Vectors

32.03: Vectors

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13.9: Series and Limits

13.9.1: 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:

$$\frac{1}{1-x} = 1 + x + x^2 + x^3 + x^4 + ... \tag{13.9.1}$$

We can write this statement in this more elegant way:

$$\frac{1}{1-x} = \sum_{n=0}^{\infty} x^n \tag{13.9.2}$$

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 13.9.1). 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 13.9.1 and 13.9.2 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:

$$e^x = 1 + x + \frac{1}{2}x^2 + \frac{1}{6}x^3 + \frac{1}{24}x^4 + ... \tag{13.9.3}$$

Or, more elegantly:

$$e^x = \sum_{n=0}^{\infty} \frac{1}{n!}x^n \tag{13.9.4}$$

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.

13.9.2: 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:

$$f(x) = \sum_{n=0}^{\infty} a_n x^n = a_0 + a_1 x + a_2 x^2 + ... + a_n x^n \tag{13.9.5}$$

Be sure you understand why the two expressions in Equation 13.9.5 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 13.9.3), $a_0 = 1, a_1 = 1, a_2 = 1/2, a_3 = 1/6, etc.$ In the example of Equation 13.9.1, 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:

$$a_n = \frac{1}{n!}\left(\frac{d^n f(x)}{dx^n}\right)_0 \tag{13.9.6}$$

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 13.9.1

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 13.9.2

Express the Maclaurin series of $\sin(x)$ as a sum.

Solution

In the previous example we found that:

$$\sin(x) = x - \frac{1}{3!}x^3 + \frac{1}{5!}x^5 - \frac{1}{7!}x^7 ... \tag{13.9.7}$$

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 13.9.7 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

13.9.3: Graphical Representation

From Equation 13.9.5 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.

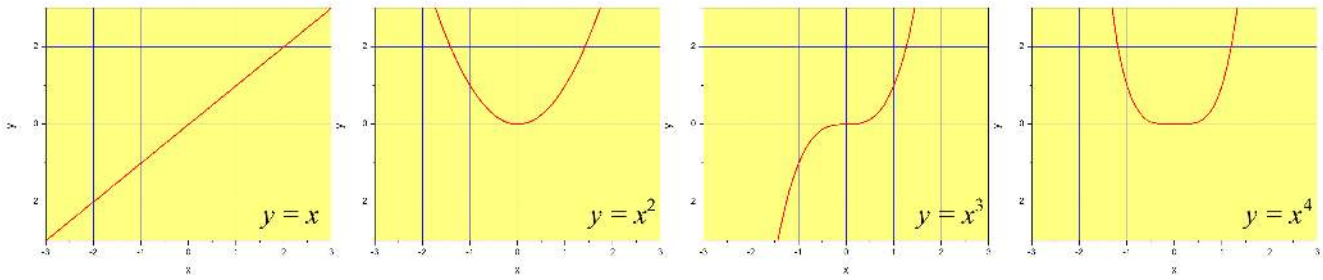


Figure 13.9.1: Some of the functions of the basis set for a Maclaurin expansion (CC BY-NC-SA; Marcia Levitus)

Figure 13.9.1 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 13.9.1. 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 13.9.7). This is illustrated in Figure 13.9.2, 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.

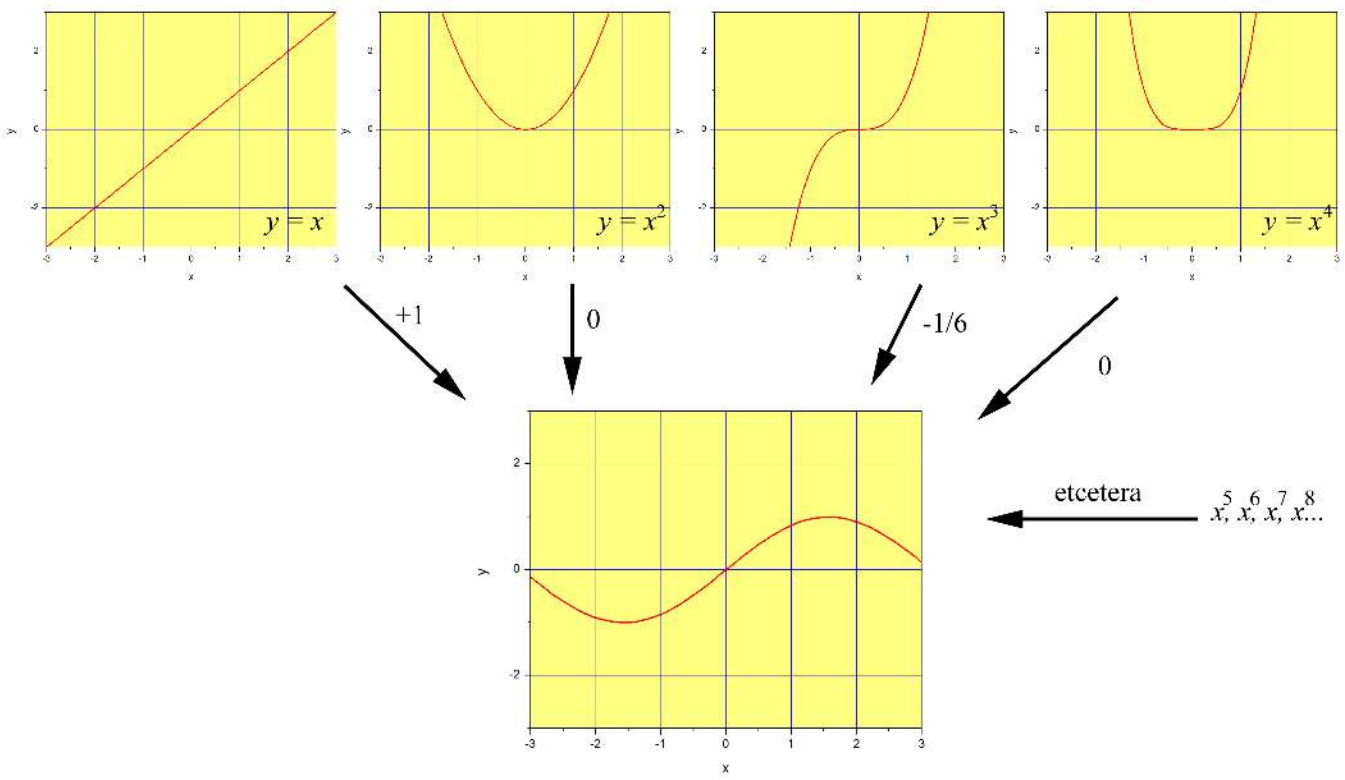


Figure 13.9.2: Construction of $\sin x$ using the powers of x as the basis set. (CC BY-NC-SA; Marcia Levitus)

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 13.9.3 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.

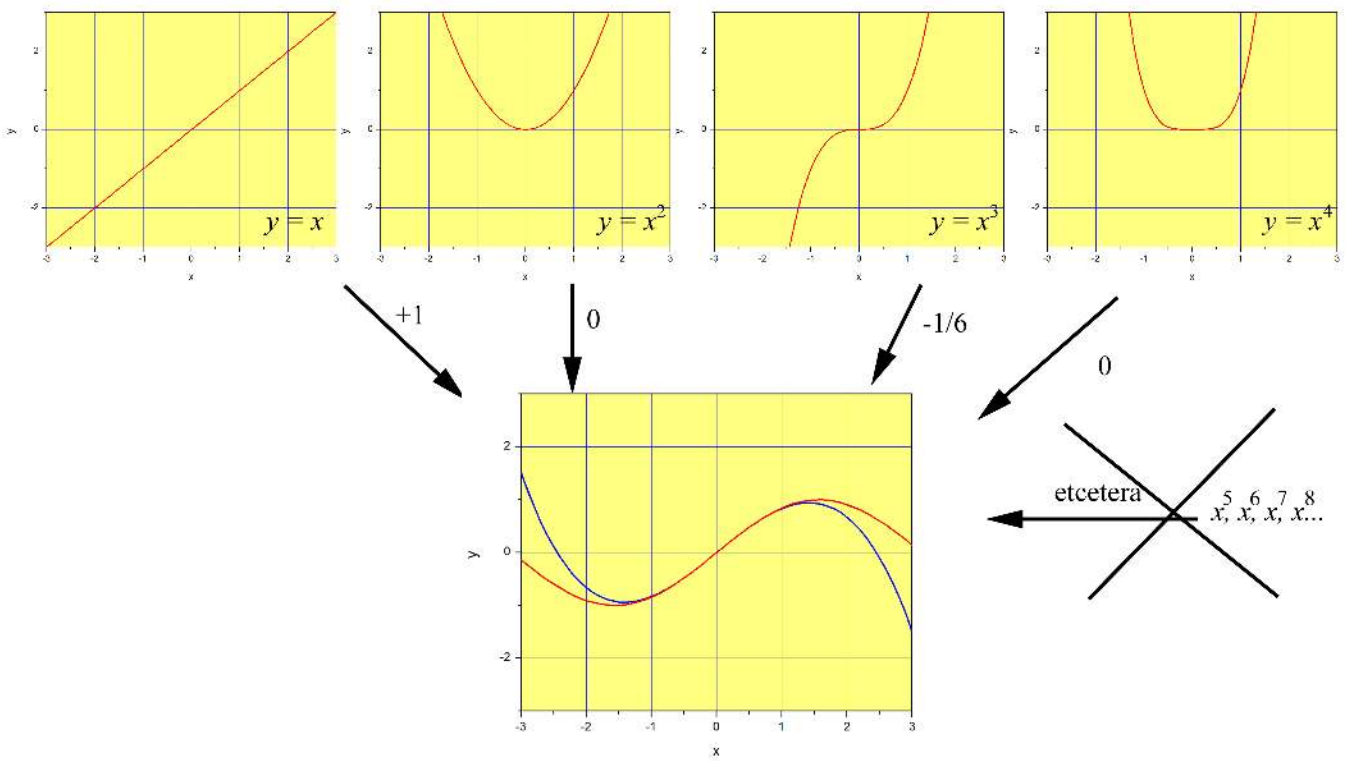


Figure 13.9.3: Approximation of $\sin x$ up to the third power of x. The curve in blue is the function $x - 1/6x^3$, and the curve in red is $\sin x$ (CC BY-NC-SA; Marcia Levitus)

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 13.9.4.

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 13.9.4? 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.

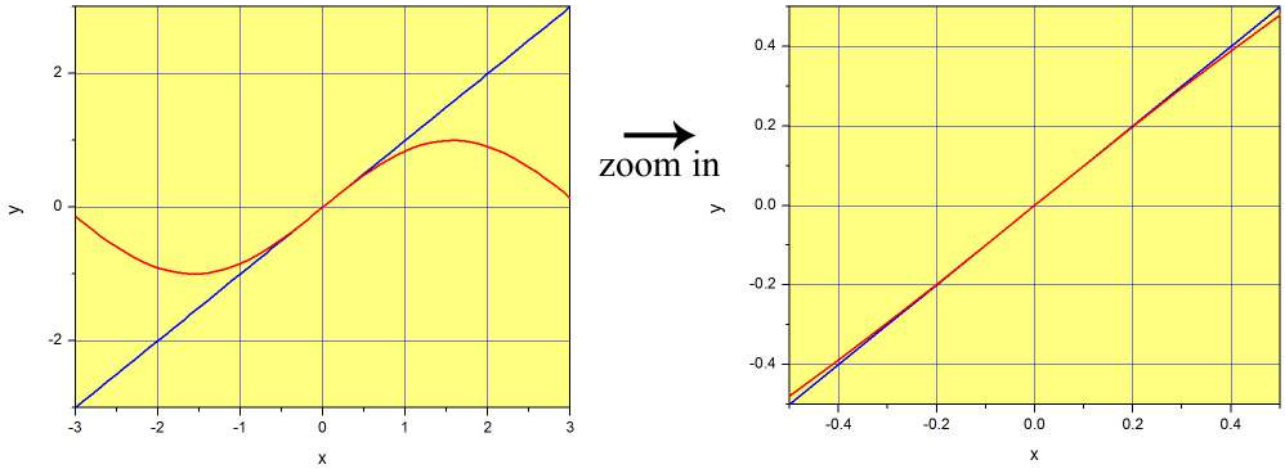


Figure 13.9.4: Approximation of $\sin x$ up to the first power of x. The curve in blue is the function x, and the curve in red is $\sin x$ (CC BY-NC-SA; Marcia Levitus)

13.9.4: 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:

Label 'eq1' multiply defined

We call this a linear approximation because Equation 13.9.1 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 13.9.1, 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:

$$\frac{d^2\theta(t)}{dt^2} + \frac{g}{l}\sin\theta(t) = 0$$

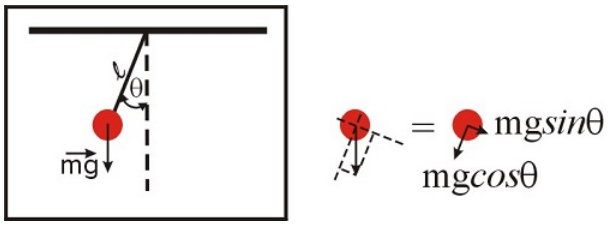


Figure 13.9.1: A rigid pendulum with massless and inextensible cord of length l. The motion is assumed to occur in two dimensions, and the friction is assumed to be negligible. The mass of the object is m, and g is the acceleration due to gravity. (CC BY-NC-SA; Marcia Levitus)

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.

$$V(R) = D_e\left(1 - e^{-k(R-R_e)}\right)^2 \tag{13.9.8}$$

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 13.9.2).

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).

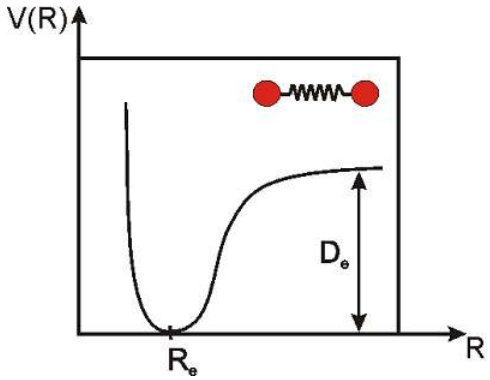


Figure 13.9.2: The Morse potential (CC BY-NC-SA; Marcia Levitus)

Example 13.9.1

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 13.9.8 as

$$V(R) = D_e\left(1 - e^{-kx}\right)^2 \tag{13.9.9}$$

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 13.9.9 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 13.9.9. Let's see how this works:

We want to expand e^{-kx} as $a_0 + a_1x + a_2x^2 ... a_nx^n$, 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

- $f'(x) = -ke^{-kx}$
- $f''(x) = k^2e^{-kx}$
- $f'''(x) = -k^3e^{-kx}$

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 13.9.9 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).

13.9.5: 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:

$$f(x) = a_0 + a_1(x - h) + a_2(x - h)^2 + ... + a_n(x - h)^n = \sum_{n=0}^{\infty} a_n(x - h)^n \tag{13.9.10}$$

The coefficients are calculated as

$$a_n = \frac{1}{n!}\left(\frac{d^n f}{dx^n}\right)_h \tag{13.9.11}$$

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

$$e\left[1 + (x-1) + \frac{1}{2}(x-1)^2 + \frac{1}{6}(x-1)^3 + ...\right] = \sum_{n=0}^{\infty} \frac{e}{n!}(x-1)^n \tag{13.9.12}$$

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 **13.9.1**, 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 13.9.12).

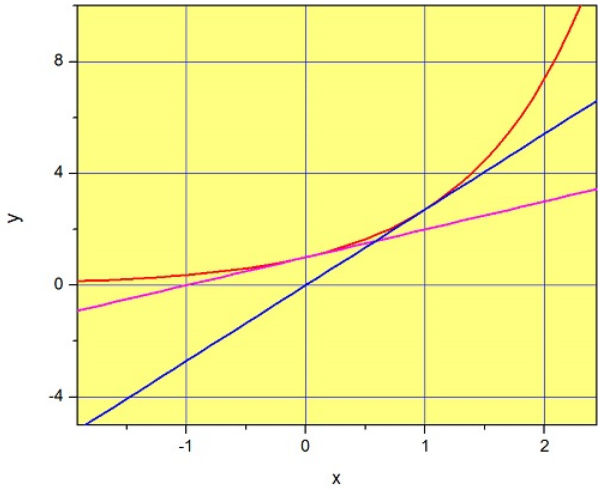


Figure **13.9.1**: Two linear approximations of the exponential function. The function e^x is plotted in red together with the function $y = 1 + x$ (magenta) and $y = ex$ (blue). (CC BY-NC-SA; Marcia Levitus)

Example 13.9.1:

Expand $f(x) = \ln x$ about $x = 1$

Solution

$$f(x) = a_0 + a_1(x-h) + a_2(x-h)^2 + ... + a_n(x-h)^n, a_n = \frac{1}{n!}\left(\frac{d^n f}{dx^n}\right)_h$$

$$a_0 = f(1) = \ln(1) = 0$$

The derivatives of $\ln x$ are:

$$f'(x) = 1/x, f''(x) = -1/x^2, f'''(x) = 2/x^3, f^{(4)}(x) = -6/x^4, f^{(5)}(x) = 24/x^5 ...$$

and therefore,

$$f'(1) = 1, f''(1) = -1, f'''(1) = 2, f^{(4)}(1) = -6, f^{(5)}(1) = 24....$$

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:

$$f(x) = 0 + 1(x-1) - 1/2(x-1)^2 + 1/3(x-1)^3 ... = \sum_{n=1}^{\infty} \frac{(-1)^{n+1}}{n}(x-1)^n$$

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/

13.9.6: 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 **13.9.1** illustrates this last point.

Example 13.9.1

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:

$$\sum_{k=0}^{\infty} \frac{\lambda^k e^{-\lambda}}{k!} = e^{-\lambda}\left[1 + \frac{\lambda^1}{1!} + \frac{\lambda^2}{2!} + \frac{\lambda^3}{3!} ...\right]$$

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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13.10: Fourier Analysis

The Fourier transform converts a function vs. continuous (or descrete) time and maps it into a function vs. continuous (or descrete) frequencies. Hence, the transform converts *time-domain* data into *frequency-domain* data (and vice versa). This decomposion of a function into sinusoids of different frequencies is a powerful approach to many experimental and theoretical problems. **Fourier transform spectroscopy** is an approach whereby spectra are collected based on measurements using time-domain or space-domain measurements of the electromagnetic radiation or other type of radiation. It can be applied to a variety of types of spectroscopy including optical spectroscopy, infrared spectroscopy (FT IR, FT-NIRS), Fourier transform nuclear magnetic resonance (NMR), mass spectrometry and electron spin resonance spectroscopy.

13.10.1: Introduction

Fourier analysis is a subject area which grew out of the study of Fourier series. The subject began with trying to understand when it was possible to represent general functions by sums of simpler trigonometric functions. The attempt to understand functions (or other objects) by breaking them into basic pieces that are easier to understand is one of the central themes in Fourier analysis. Fourier analysis is named after Joseph Fourier who showed that representing a function by a trigonometric series greatly simplified the study of heat propagation. Today the subject of Fourier analysis encompasses a vast spectrum of mathematics with parts that, at first glance, may appear quite different. In the sciences and engineering the process of decomposing a function into simpler pieces is often called an **analysis**. In Fourier analysis, the term Fourier transform often refers to the process that decomposes a given function into the basic pieces. This process results in another function that describes how much of each basic piece are in the original function. However, the transform is often given a more specific name depending upon the domain and other properties of the function being transformed, as elaborated below. Moreover, the original concept of Fourier analysis has been extended over time to apply to more and more abstract and general situations, and the general field is often known as harmonic analysis.

13.10.2: Fourier Series

When the function f is a function of time and represents a physical signal, the transform has a standard interpretation as the frequency spectrum of the signal. The magnitude of the resulting complex-valued function F at frequency ω represents the amplitude of a frequency component whose initial phase is given by the phase of F. However, it is important to realize that Fourier transforms are not limited to functions of time, and temporal frequencies. They can equally be applied to analyze *spatial* frequencies, and indeed for nearly any function domain.

13.10.3: Properties

http://www.math.ubc.ca/~feldman/demos/demo3.html

13.10.4: Continuous Fourier Trasnform (CFT)

Most often, the unqualified term **Fourier transform** refers to the transform of functions of a continuous real argument, such as time (t). In this case the Fourier transform describes a function $f(t)$ in terms of basic complex exponentials of various frequencies. In terms of ordinary frequency v, the Fourier transform is given by the complex number**:**

$$F(\nu) = \int_{-\infty}^{\infty} f(t) \cdot e^{-2\pi \cdot i \cdot \nu \cdot t} dt.$$

Evaluating this quantity for all values of v produces the *frequency-domain* function.

13.10.5: Discrete Fourier Transform (DFT)

Experimentally, we collect data that is not continuous, but samples a measurements at specific point. Hence we have to deal with the discrete version of the Fourier Transform.

13.10.5.1: Fast Fourier Transfer (FFT)

The discrete version of the Fourier transform (see below) can be evaluated quickly on computers using fast Fourier transform (FFT) algorithms. This algortihm sympically requires a 2^n number of measurements to operate. Hence you will notice data sets

often with such dimensions. (Conte & de Boor 1980)

13.10.6: References

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13.10.1: Fourier Analysis in Matlab

Fourier analysis encompasses a vast spectrum of mathematics with parts that, at first glance, may appear quite different. In the sciences and engineering the process of decomposing a function into simpler pieces is often called an analysis. The corresponding operation of rebuilding the function from these pieces is known as synthesis. In this context the term Fourier synthesis describes the act of rebuilding and the term Fourier analysis describes the process of breaking the function into a sum of simpler pieces. In mathematics, the term Fourier analysis often refers to the study of both operations.

13.10.1.1: Introduction

In Fourier analysis, the term Fourier transform often refers to the process that decomposes a given function into the basic pieces. This process results in another function that describes how much of each basic piece are in the original function. It is common practice to also use the term Fourier transform to refer to this function. However, the transform is often given a more specific name depending upon the domain and other properties of the function being transformed, as elaborated below. Moreover, the original concept of Fourier analysis has been extended over time to apply to more and more abstract and general situations and the general field is often known as harmonic analysis.

13.10.1.2: (Continuous) Fourier transform

Most often, the unqualified term Fourier transform refers to the transform of functions of a continuous real argument, such as time (t). In this case the Fourier transform describes a function f(t) in terms of basic complex exponentials of various frequencies. In terms of ordinary frequency ν, the Fourier transform is given by the complex number.

Evaluating this quantity for all values of ν produces the frequency-domain function.

13.10.1.3: Matlab and the FFT

Matlab's FFT function is an effective tool for computing the discrete Fourier transform of a signal.The following code examples will help you to understand the details of using the FFT function.

13.10.1.3.1: Example **1**

The typical syntax for computing the FFT of a signal is FFT(x,N) where x is the signal, x[n], you wish to transform, and N is the number of points in the FFT. N must be at least

as large as the number of samples in x[n]. To demonstrate the effect of changing the value of N,

synthesize a cosine with 30 samples at 10 samples per period.

- n = [0:29];
- x = cos(2*pi*n/10);

Define 3 different values for N. Then take the transform of x[n] for each of the 3 values that were

defined. The abs function find the magnitude of the transform, as we are not concerned with distinguishing between real and imaginary components.

- N1 = 64;
- N2 = 128;
- N3 = 256;
- X1 = abs(fft(x,N1));
- X2 = abs(fft(x,N2));
- X3 = abs(fft(x,N3));

The frequency scale begins at 0 and extends to N - 1 for an N-point FFT. We then normalize the scale so that it extends from 0 to 1 - 1/N

- F1 = [0 : N1 - 1]/N1;
- F2 = [0 : N2 - 1]/N2;

- F3 = [0 : N3 - 1]/N3;

Plot each of the transforms one above the other

- subplot(3,1,1)
- plot(F1,X1,'-x'),title('N = 64'),axis([0 1 0 20])
- subplot(3,1,2)
- plot(F2,X2,'-x'),title('N = 128'),axis([0 1 0 20])
- subplot(3,1,3)
- plot(F3,X3,'-x'),title('N = 256'),axis([0 1 0 20])

Upon examining the plot one can see that each of the transforms adheres to the same shape, differing only in the number of samples used to approximate that shape. What happens if N is the same as the number of samples in x[n]? To find out, set N1 = 30. What does the resulting plot look like? Why does it look like this?

13.10.1.3.2: Example 2

In the last example the length of x[n] was limited to 3 periods in length. Now, let's choose a large value for N (for a transform with many points), and vary the number of repetitions of the fundamental period.

- n = [0:29];
- x1 = cos(2*pi*n/10); % 3 periods
- x2 = [x1 x1]; % 6 periods
- x3 = [x1 x1 x1]; % 9 periods

- N = 2048;
- X1 = abs(fft(x1,N));
- X2 = abs(fft(x2,N));
- X3 = abs(fft(x3,N));
- F = [0:N-1]/N;

- subplot(3,1,1)
- plot(F,X1),title('3 periods'),axis([0 1 0 50])
- subplot(3,1,2)
- plot(F,X2),title('6 periods'),axis([0 1 0 50])
- subplot(3,1,3)
- plot(F,X3),title('9 periods'),axis([0 1 0 50])

The previous code will produce three plots. The first plot, the transform of 3 periods of a cosine, looks like the magnitude of 2 sincs with the center of the first sinc at 0.1fs and the second at 0.9fs.

The second plot also has a sinc-like appearance, but its frequency is higher and it has a larger magnitude at 0:1fs and 0:9fs. Similarly, the third plot has a larger sinc frequency and magnitude.

As x[n] is extended to a large number of periods, the sincs will begin to look more and more like impulses.

But I thought a sinusoid transformed to an impulse, why do we have sincs in the frequency domain? When the FFT is computed with an N larger than the number of samples in x[n], it fills in the samples after x[n] with zeros. Example 2 had an x[n] that was 30 samples long, but the FFT had an N = 2048. When Matlab computes the FFT, it automatically fills the spaces from n = 30 to n = 2047 with zeros. This is like taking a sinusoid and multiplying it with a rectangular box of length 30. A multiplication of a box and a sinusoid in the time domain should result in the convolution of a sinc with impulses in the frequency domain. Furthermore, increasing the width of the box in the time domain should increase the frequency of the sinc in the frequency domain. The previous Matlab experiment supports this conclusion.

13.10.1.4: Identifying Signals in noise with FFT

A common use of Fourier transforms is to find the frequency components of a signal buried in a noisy time domain signal. Consider data sampled at 1000 Hz. Form a signal containing a 50 Hz sinusoid of amplitude 0.7 and 120 Hz sinusoid of amplitude 1

and corrupt it with some zero-mean random noise:

- Fs = 1000; % Sampling frequency
- T = 1/Fs; % Sample time
- L = 1000; % Length of signal
- t = (0:L-1)*T; % Time vector
- x = 0.7*sin(2*pi*50*t) + sin(2*pi*120*t);
  % Sum of a 50 Hz sinusoid and a 120 Hz sinusoid
- y = x + 2*randn(size(t)); % Sinusoids plus noise
- plot(Fs*t(1:50),y(1:50))
- title('Signal Corrupted with Zero-Mean Random Noise')
- xlabel('time (milliseconds)')

It is difficult to identify the frequency components by looking at the original signal. Converting to the frequency domain, the discrete Fourier transform of the noisy signal y is found by taking the fast Fourier transform (FFT):

- NFFT = 2^nextpow2(L); % Next power of 2 from length of y
- Y = fft(y,NFFT)/L;
- f = Fs/2*linspace(0,1,NFFT/2+1); % Plot single-sided amplitude spectrum.
- plot(f,2*abs(Y(1:NFFT/2+1)))
- title('Single-Sided Amplitude Spectrum of y(t)')
- xlabel('Frequency (Hz)')
- ylabel('|Y(f)|')

The main reason the amplitudes are not exactly at 0.7 and 1 is because of the noise. Several executions of this code (including recomputation of y) will produce different approximations to 0.7 and 1. The other reason is that you have a finite length signal. Increasing L from 1000 to 10000 in the example above will produce much better approximations on average.

13.10.1.5: Outside Links

- http://www.chem.uoa.gr/applets/Apple...FourAnal2.html

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13.10.2: Fourier Synthesis of Periodic Waveforms

Java Developed by Dr. Constantinos E. Efstathiou, Laboratory of Analytical Chemistry, National and Kapodistrian University of Athens

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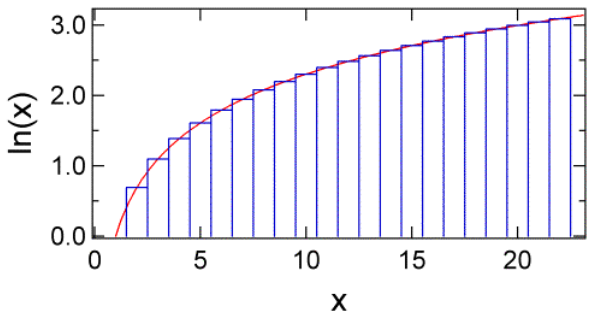
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13.11: The Binomial Distribution and Stirling's Appromixation

Stirling's approximation is named after the Scottish mathematician James Stirling (1692-1770). In confronting statistical problems we often encounter factorials of very large numbers. The factorial $N!$ is a product $N(N-1)(N-2)...(2)(1)$. Therefore, $\ln N!$ is a sum

$$\ln N! = \ln 1 + \ln 2 + \ln 3 + ... + \ln N = \sum_{k=1}^{N} \ln k. \tag{13.11.1}$$

where we have used the property of logarithms that $\log(abc) = \log(a) + \log(b) + \log(c)$. The sum is shown in figure below.



Using **Euler-MacLaurin** formula one has

$$\sum_{k=1}^{N} \ln k = \int_{1}^{N} \ln x\, dx + \sum_{k=1}^{p} \frac{B_{2k}}{2k(2k-1)} \left(\frac{1}{n^{2k-1}} - 1 \right) + R, \tag{13.11.2}$$

where $B_1 = -1/2$, $B_2 = 1/6$, $B_3 = 0$, $B_4 = -1/30$, $B_5 = 0$, $B_6 = 1/42$, $B_7 = 0$, $B_8 = -1/30$, ... are the **Bernoulli numbers**, and \(R\) is an error term which is normally small for suitable values of \(p\).

Then, for large N,

$$\ln N! \sim \int_{1}^{N} \ln x\, dx \approx N \ln N - N. \tag{13.11.3}$$

after some further manipulation one arrives at (apparently Stirling's contribution was the prefactor of $\sqrt{2\pi}$)

$$N! = \sqrt{2\pi N}\, N^N e^{-N} e^{\lambda_N} \tag{13.11.4}$$

where

$$\frac{1}{12N+1} < \lambda_N < \frac{1}{12N}. \tag{13.11.5}$$

The sum of the area under the blue rectangles shown below up to N is $\ln N!$. As you can see the rectangles begin to closely approximate the red curve as m gets larger. The area under the curve is given the integral of $\ln x$.

$$\ln N! = \sum_{m=1}^{N} \ln m \approx \int_{1}^{N} \ln x\, dx \tag{13.11.6}$$

To solve the integral use integration by parts

$$\int u\, dv = uv - \int v\, dy \tag{13.11.7}$$

Here we let $u = \ln x$ and $dv = dx$. Then $v = x$ and $du = \frac{dx}{x}$.

$$\int_{0}^{N} \ln x\, dx = x \ln x \Big|_{0}^{N} - \int_{0}^{N} x \frac{dx}{x} \tag{13.11.8}$$

Notice that $x/x = 1$ in the last integral and $x \ln x$ is 0 when evaluated at zero, so we have

$$\int_0^N \ln x\, dx = N \ln N - \int_0^N dx \tag{13.11.9}$$

Which gives us Stirling's approximation: $\ln N! = N \ln N – N$. As is clear from the figure above Stirling's approximation gets better as the number N gets larger (Table **13.11.1**).

Table **13.11.1**: Evaluation of Approximation with absolute values

N	N!	ln N!	N ln N – N	Error
10	3.63×10^{6}	15.1	13.02	13.8%
50	3.04×10^{64}	148.4	145.6	1.88%
100	9.33×10^{157}	363.7	360.5	0.88%
150	5.71×10^{262}	605.0	601.6	0.56%

Calculators often overheat at 200!, which is all right since clearly result are converging. In thermodynamics, we are often dealing very large N (i.e., of the order of Avagadro's number) and for these values Stirling's approximation is excellent.

13.11.1: References

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