PHYSICAL CHEMISTRY FOR THE BIOSCIENCES

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Physical Chemistry for the Biosciences

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Licensing

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CHAPTER OVERVIEW

1: Introduction to Physical Chemistry

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1.1: Nature of Physical Chemistry

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1.2: Units

There is international agreement that the units used for physical quantities in science and technology should be those of the International System of Units, or SI (standing for the French **Système International d'Unités**). The Physical Chemistry Division of the International Union of Pure and Applied Chemistry, or IUPAC, produces a manual of recommended symbols and terminology for physical quantities and units based on the SI. The manual has become known as the Green Book (from the color of its cover) and is referred to here as the IUPAC Green Book. This e-book will, with a few exceptions, use symbols recommended in the third edition (2007) of the IUPAC Green Book (E. Richard Cohen et al, *Quantities, Units and Symbols in Physical Chemistry*, 3rd edition. RSC Publishing, Cambridge, 2007). These symbols are listed for convenient reference in Appendices C and D.

Any of the symbols for units listed in Tables 1.1–1.3, except kg and $^{\circ}\mathrm{C}$, may be preceded by one of the prefix symbols of Table 1.4 to construct a decimal fraction or multiple of the unit. (The symbol g may be preceded by a prefix symbol to construct a fraction or multiple of the gram.) The combination of prefix symbol and unit symbol is taken as a new symbol that can be raised to a power without using parentheses, as in the following examples:

- The physical quantity formally called **amount of substance** is a counting quantity for particles, such as atoms or molecules, or for other chemical entities. The counting unit is invariably the **mole**, defined as the amount of substance containing as many particles as the number of atoms in exactly 12 grams of pure carbon-12 nuclide, $^{12}\mathrm{C}$. See Appendix A for the wording of the official IUPAC definition. This definition is such that one mole of $\mathrm{H_2O}$ molecules, for example, has a mass of 18.0153 grams (where 18.0153 is the relative molecular mass of $\mathrm{H_2O}$) and contains 6.02214×10^{23} molecules (where $6.02214 \times 10^{23}\ \mathrm{mol}^{-1}$ is the *Avogadro constant* to six significant digits). The same statement can be made for any other substance if 18.0153 is replaced by the appropriate atomic mass or molecular mass value.

  The symbol for amount of substance is n. It is admittedly awkward to refer to $n(\mathrm{H_2O})$ as "the amount of substance of water." This e-book simply shortens "amount of substance" to **amount**. An alternative name suggested for n is "chemical amount." Thus, "the amount of water in the system" refers not to the mass or volume of water, but to the *number* of $\mathrm{H_2O}$ molecules in the system expressed in a counting unit such as the mole.

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1.3: Atomic Mass, Molecular Mass, and the Chemical Mole

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CHAPTER OVERVIEW

2: Properties of Gases

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.

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2.1: Some Definitions

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2.2: An Operational Definition of Temperature

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2.3: Ideal Gases

In an ideal gas, there are no interactions between the particles, hence, the particles do not exert forces on each other. However, particles do experience a force when they collide with the walls of the container. Let us assume that each collision with a wall is elastic. Let us assume that the gas is in a cubic box of length *[Math Processing Error]* and that two of the walls are located at *[Math Processing Error]* and at *[Math Processing Error]*. Thus, a particle moving along the *[Math Processing Error]* 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 *[Math Processing Error]*. Since every action has an equal and opposite reaction, the wall exerts a force *[Math Processing Error]* on the particle. According to Newton's second law, the force *[Math Processing Error]* on the particle in this direction gives rise to an acceleration via

[Math Processing Error]

Here, *[Math Processing Error]* 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 *[Math Processing Error]* is the velocity in the *[Math Processing Error]* direction before the collision, then *[Math Processing Error]* is the velocity after, and *[Math Processing Error]*, so that

[Math Processing Error]

In order to find *[Math Processing Error]*, we recall that the particles move at constant speed. Thus, a collision between a particle and, say, the wall at *[Math Processing Error]* will not change the particle's speed. Before it strikes this wall again, it will proceed to the wall at *[Math Processing Error]* first, bounce off that wall, and then return to the wall at *[Math Processing Error]*. The total distance in the *[Math Processing Error]* direction traversed is *[Math Processing Error]*, and since the speed in the *[Math Processing Error]* direction is always *[Math Processing Error]*, the interval *[Math Processing Error]*. Consequently, the force is

[Math Processing Error]

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

[Math Processing Error]

The mechanical definition of pressure is

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where *[Math Processing Error]* is the average force exerted by all *[Math Processing Error]* particles on a wall of the box of area *[Math Processing Error]*. Here *[Math Processing Error]*. If we use the wall at *[Math Processing Error]* we have been considering, then

[Math Processing Error]

because we have *[Math Processing Error]* particles hitting the wall. Hence,

[Math Processing Error]

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

[Math Processing Error]

Hence, since *[Math Processing Error]*,

[Math Processing Error]

which is the ideal gas law.

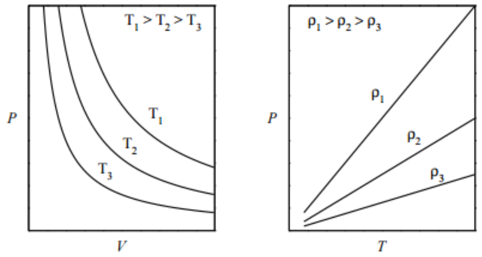

Figure 2.3.1: (Left) Pressure vs. volume for different temperatures (isotherms of the ideal-gas equation of state. (Right) Pressure vs. temperature for different densities *[Math Processing Error]*.

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

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

[Math Processing Error]

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

[Math Processing Error]

is called the *compressibility* of the gas. In an ideal gas, if we "compress" the gas by increasing *[Math Processing Error]* , the density *[Math Processing Error]* must increase as well so as to keep *[Math Processing Error]*. For a real gas, *[Math Processing Error]*, therefore, gives us a measure of how much the gas deviates from ideal-gas behavior.

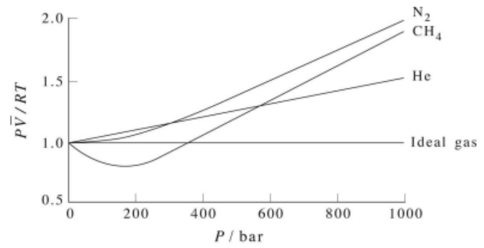

Figure 2.3.2: Plot of the compressibility *[Math Processing Error]* vs. *[Math Processing Error]* for several gases, together with the ideal gas, where *[Math Processing Error]*.

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

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2.4: Real Gases

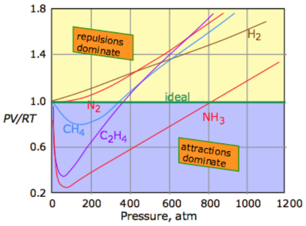
According to Boyle's law, the product *PV* is a constant at any given temperature, so a plot of *PV* as a function of the pressure of an ideal gas yields a horizontal straight line. This implies that any increase in the pressure of the gas is exactly counteracted by a decrease in the volume as the molecules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

$$\lim_{P\to 0} PV = nRT \tag{2.4.1}$$

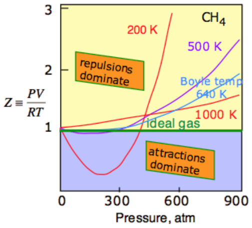
So what happens when a real gas is subjected to a very high pressure? The outcome varies with both the molar mass of the gas and its temperature, but in general we can see the the effects of both repulsive and attractive intermolecular forces:

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

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



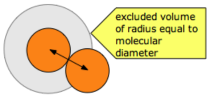
Intermolecular attractions, which generally increase with molecular weight, cause the *PV* product to decrease as higher pressures bring the molecules closer together and thus within the range of these attractive forces; the effect is to cause the volume to decrease more rapidly than it otherwise would.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



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

The van der Waals Equation of State

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



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

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

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

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

$$\underbrace{\overset{\substack{\text{actual pressure}\\ \downarrow}}{P}+a\left(\frac{n}{V}\right)^2}_{\text{ideal gas pressure}} \times \underbrace{\overset{\substack{\text{actual volume}\\ \downarrow}}{(V}-nb)}_{\text{ideal gas volume}} = nRT$$

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

Table 2.4.1 : van der Waals constants for some gases

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

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

Contributors and Attributions

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2.5: Condensation of Gases and the Critical State

The most striking feature of real gases is that they cease to remain gases as the temperature is lowered and the pressure is increased.

The Van der Waals Equation of State

In the last lecture, we saw that for the pair potential

$$u(r) = \begin{cases} \infty & r \leq \sigma \\ -\dfrac{C_6}{r^6} & r > \sigma \end{cases} \tag{2.5.1}$$

we could write the second virial coefficient as

$$B_2(T) = \frac{2}{3}\pi N_0 \sigma^3 \left[1 - \frac{C_6}{3k_B T \sigma^6}\right] \tag{2.5.2}$$

Let us introduce to simplifying variables

$$b = \frac{2}{3}\pi N_0 \sigma^3 \tag{2.5.3}$$

$$a = \frac{2\pi N_0^2 C_6}{9\sigma^3} \tag{2.5.4}$$

in terms of which

$$B_2(T) = b - \frac{a}{RT} \tag{2.5.5}$$

With these definitions, the virial equation of state becomes

$$P = \frac{nRT}{V} + \frac{n^2}{V^2} RT \left(b - \frac{a}{RT}\right) \tag{2.5.6}$$

$$= \frac{nRT}{V}\left(1 + \frac{nb}{V}\right) - \frac{an^2}{V^2} \tag{2.5.7}$$

If we assume nb/V is small, then we can also write

$$1 + \frac{nb}{V} \approx \frac{1}{1 - \dfrac{nb}{V}} \tag{2.5.8}$$

so that

$$P = \frac{nRT}{V - nb} - \frac{an^2}{V^2} \tag{2.5.9}$$

which is known as the *van der Waals* equation of state.

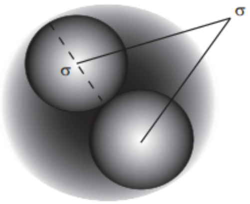


Figure 2.5.1: Two hard spheres of diameter σ at closest contact. The distance between their centers is also σ. A sphere of radius σ just containing the two particles is shown in cross-section.

The first term in this equation is easy to motivate. In fact, it looks very much like the equation of state for an ideal gas having volume $V - nb$ rather than V. This part of the van der Waals equation is due entirely to the hard-wall potential $u_o(r)$. Essentially, this potential energy term describes a system of “billiard balls” of diameter σ. The figure below shows two of these billiard ball type particles at the point of contact (also called the distance of closest approach). At this point, they undergo a collision and separate, so that cannot be closer than the distance shown in the figure. At this point, the distance between their centers is also σ, as the figure indicates. Because of this distance of closest approach, the total volume available to the particles is not V but some volume less than V. This reduction in volume can be calculated as follows: Figure $2.5.1$ 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 as the figure shows. Hence, 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 $2\pi\sigma^3/3$. The excluded volume for a mole of such particles is just $2\pi\sigma^3 N_0/3$, which is the parameter b:

$$b = \frac{2}{3}\pi\sigma^3 N_0 \tag{2.5.10}$$

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

Isotherms of the van der Waals equation are shown in the figure below (left panel). In the figure the volume axis is the molar volume denoted $\bar{V} = V/n$. At sufficiently high temperature, the isotherms approach those of an ideal gas. However, we also see something strange in some of the isotherms. Specifically, we see a region in which P and V increase together, and we know that this cannot actually happen in a real gas. 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.

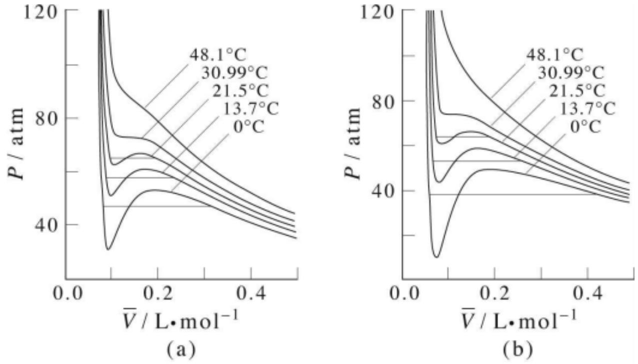


Figure $2.5.2$: Isotherms of the van der Waals equation of state using parameters a and b computed for carbon dioxide.

In fact, 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. Unfortunately, the van der Waals equation does not correctly predict this behavior, and hence, it must be added in *ad hoc*. This is done by drawing a horizontal line through the isotherm (Figure $2.5.2$) and in the figure below. The vertical position of the line is

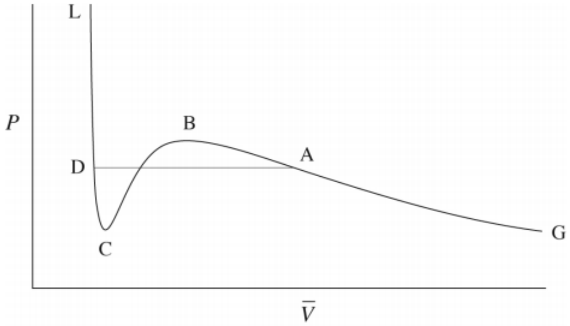


Figure $2.5.3$: Illustration of the tie line in the van der Waals equation.

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. 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. This horizontal line is called the *tie line*.

As it happens, there is exactly one isotherm along which the van der Waals equation correctly predicts the gas-to-liquid phase transition. Along this isotherm, 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 isotherm, in fact, corresponds to the highest possible temperature at which such a transition can occur. As we approach this isotherm from higher temperatures, this isotherm is a kind of dividing line between the system's remaining a gas at all value of P and V and the system's actually undergoing a gas-to-liquid transition. Hence, this isotherm is called the *critical isotherm* (Figure 2.5.4): The temperature of this isotherm is called the critical temperature, denoted T_c. The point at which the curve flattens out, signifying the phase transition, is called the *critical point*. 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. This is illustrated below:

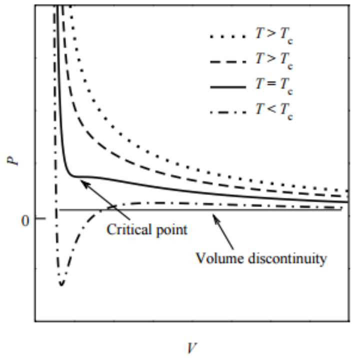


Figure 2.5.4: Isotherms of the van der Waals equation of state for four different temperatures with explicit illustration of the critical isotherm.

The shape of the critical isotherm at the critical point allows us to determine the exact temperature, pressure, and volume at which the phase transition from gas to liquid will occur. At this point, the isotherm is both horizontal and flat. This means that both the first and second derivatives of P with respect to V must vanish:

$$\frac{\partial P}{\partial V} = 0, \quad \frac{\partial^2 P}{\partial V^2} = 0 \tag{2.5.11}$$

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

$$-\frac{nRT}{(V-nb)^2} + \frac{2an^2}{V^3} = 0 \tag{2.5.12}$$

$$\frac{2nRT}{(V-nb)^3} - \frac{6an^2}{V^4} = 0 \tag{2.5.13}$$

Hence, we have two equations in two unknowns V and T for the critical temperature and critical volume. Once these are determined, the van der Waals equation, itself, allows us to determine the critical pressure.

To solve the equations, first divide one by the other. This gives us a simple condition for the volume:

$$\frac{V-nb}{2} = \frac{V}{3} \tag{2.5.14}$$

$$3V - 3nb = 2V \tag{2.5.15}$$

$$V = 3nb \equiv V_c \tag{2.5.16}$$

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

$$\frac{nRT_c}{(V_c-nb)^2}=\frac{2an^2}{V_c^3} \tag{2.5.17}$$

$$\frac{nRT_c}{(3nb-nb)^2}=\frac{2an^2}{(3nb)^3} \tag{2.5.18}$$

$$\frac{nRT_c}{4n^2b^2}=\frac{2an^2}{27n^3b^3} \tag{2.5.19}$$

$$RT_c=\frac{8a}{27b} \tag{2.5.20}$$

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

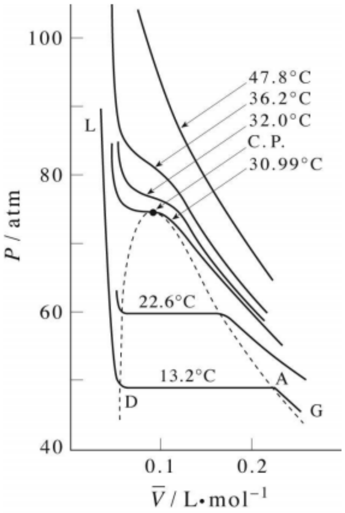


Figure 2.5.5: Illustration of the curve (dashed line) joining the beginning and ends of the tie lines. This curve reaches a maximum at the critical point.

as

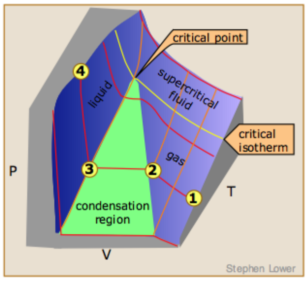
$$P=\frac{nRT_c}{V_c-nb}-\frac{an^2}{V_c^2} \tag{2.5.21}$$

$$=\frac{8an/27b}{3nb-nb}-\frac{an^2}{(3nb)^2} \tag{2.5.22}$$

$$=\frac{a}{27b^2} \tag{2.5.23}$$

PVT Surface of a real gas

The plot illustrates this behavior; as the volume is decreased, the lower-temperature isotherms suddenly change into straight lines. Under these conditions, the pressure remains constant as the volume is reduced. This can only mean that the gas is “disappearing" as we squeeze the system down to a smaller volume. In its place, we obtain a new state of matter, the liquid. In the green-shaded region, *two* phases, liquid, and gas, are simultaneously present. Finally, at very small volume all the gas has disappeared and only the liquid phase remains. At this point the isotherms bend strongly upward, reflecting our common experience that a liquid is practically incompressible.

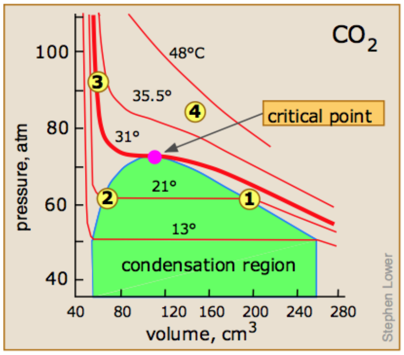


To better understand this plot, look at the isotherm labeled ①. As the gas is compressed from ① to ②, the pressure rises in much the same way as Boyle's law predicts. Compression beyond ②, however, does not cause any rise in the pressure. What happens instead is that some of the gas condenses to a liquid. At ③, the substance is entirely in its liquid state. The very steep rise to ④ corresponds to our ordinary experience that liquids have very low compressibilities. The range of volumes possible for the liquid diminishes as the critical temperature is approached.

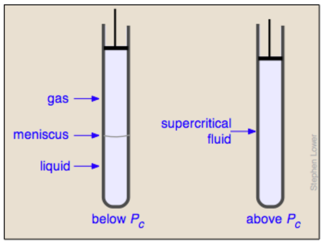
The critical point

Liquid and gas can coexist only within the regions indicated by the green-shaded area in the diagram above. As the temperature and pressure rise, this region becomes more narrow, finally reaching zero width at the *critical point*. The values of *P*, *T*, and *V* at this juncture are known as the *critical constants* P_c , T_c , and V_c . The isotherm that passes through the critical point is called the *critical isotherm*. Beyond this isotherm, the gas and liquids become indistinguishable; there is only a single fluid phase, sometimes referred to as a *supercritical liquid*.

Critical Behaviour of carbon dioxide



At temperatures below 31°C (the *critical temperature*), CO_2 acts somewhat like an ideal gas even at a rather high pressure (④). Below 31°, an attempt to compress the gas to a smaller volume eventually causes condensation to begin. Thus at 21°C, at a pressure of about 62 atm (①), the volume can be reduced from 200 cm^3 to about 55 cm^3 without any further rise in the pressure. Instead of the gas being compressed, it is replaced with the far more compact liquid as the gas is essentially being "squeezed" into its liquid phase. After all of the gas has disappeared (②), the pressure rises very rapidly because now all that remains is an almost incompressible liquid. Above this isotherm (③), CO_2 exists only as a *supercritical fluid*.



What happens if you have some liquid carbon dioxide in a transparent cylinder at just under its P_c of 62 atm, and you then compress it slightly? Nothing very dramatic until you notice that the meniscus has disappeared. By successively reducing and increasing the pressure, you can "turn the meniscus on and off".

One intriguing consequence of the very limited bounds of the liquid state is that you could start with a gas at large volume and low temperature, raise the temperature, reduce the volume, and then reduce the temperature so as to arrive at the liquid region at the lower left, without ever passing through the two-phase region, and thus *without undergoing condensation!*

Supercritical fluids

The *supercritical* state of matter, as the fluid above the critical point is often called, possesses the flow properties of a gas and the solvent properties of a liquid. The density of a supercritical fluid can be changed over a wide range by adjusting the pressure; this, in turn, changes its solubility, which can thus be optimized for a particular application. The picture at the right shows a commercial laboratory device used for carrying out chemical reactions under supercritical conditions.

Supercritical carbon dioxide is widely used to dissolve the caffeine out of coffee beans and as a dry-cleaning solvent. **Supercritical water** has recently attracted interest as a medium for chemically decomposing dangerous environmental pollutants such as PCBs. Supercritical fluids are being increasingly employed as as substitutes for organic solvents (so-called "green chemistry") in a range of industrial and laboratory processes. Applications that involve supercritical fluids include extractions, nano particle and nano structured film formation, supercritical drying, carbon capture and storage, as well as enhanced oil recovery studies.

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2.6: Kinetic Theory of Gases

The kinetic theory describes a gas as a large number of submicroscopic particles (atoms or molecules), all of which are in constant, random motion. The rapidly moving particles constantly collide with each other and with the walls of the container. Kinetic theory explains macroscopic properties of gases, such as pressure, temperature, viscosity, thermal conductivity, and volume, by considering their molecular composition and motion. The theory posits that gas pressure is due to the impacts, on the walls of a container, of molecules or atoms moving at different velocities.

The Model

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.

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.

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.

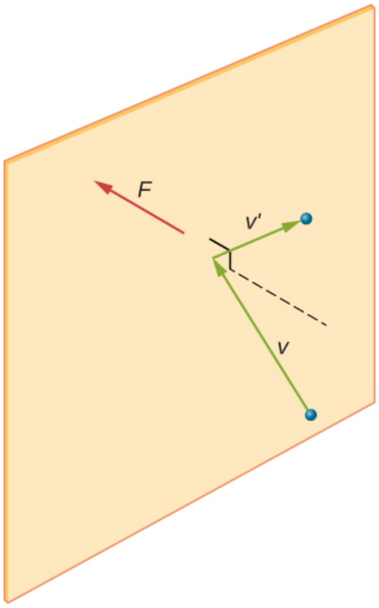


Figure 2.6.1: When a molecule collides with a rigid wall, the component of its momentum perpendicular to the wall is reversed. A force is thus exerted on the wall, creating pressure. Image used with permisison from OpenSTAX

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 Δ*V* is equivalent to a*n acceleration a*; according to Newton's second law, a *force f* = *ma* is thus exerted on the surface of area *A* exerting a pressure *P* = *f/A*.

Kinetic Interpretation of 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:

$$KE = \frac{mv^2}{2} \tag{2.6.1}$$

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. 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.

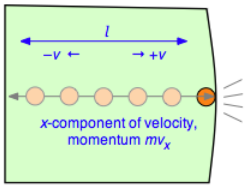
- **Kinetic explanation of Boyle's law**: Boyle's law is easily explained by the kinetic molecular theory. The pressure of a gas depends on the number of times per second that the molecules strike the surface of the container. If we compress the gas to a smaller volume, the same number of molecules are 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 one of the fundamental tenets of KMT theory 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.

Derivation of the Ideal Gas Law

One of the triumphs of the kinetic molecular theory was the derivation of the ideal gas law from simple mechanics in the late nineteenth century. This is a beautiful example of how the principles of elementary mechanics can be applied to a simple model to develop a useful description of the behavior of macroscopic matter. We begin by recalling that the pressure of a gas arises from the force exerted when molecules collide with the walls of the container. This force can be found from Newton's law

$$f = ma = m\frac{dv}{dt} \tag{2.6.2}$$

in which v is the velocity component of the molecule in the direction perpendicular to the wall and m is its mass.



To evaluate the derivative, which is the velocity change per unit time, consider a single molecule of a gas contained in a cubic box of length l. For simplicity, assume that the molecule is moving along the *x*-axis which is perpendicular to a pair of walls, so that it is continually bouncing back and forth between the same pair of walls. When the molecule of mass *m* strikes the wall at velocity +*v* (and thus with a momentum *mv*) it will rebound elastically and end up moving in the opposite direction with –*v*. The total change in velocity per collision is thus 2*v* and the change in momentum is $2mv$.

After the collision the molecule must travel a distance *l* to the opposite wall, and then back across this same distance before colliding again with the wall in question. This determines the time between successive collisions with a given wall; the number of collisions per second will be $v/2l$. The *force* F exerted on the wall is the rate of change of the momentum, given by the product of the momentum change per collision and the collision frequency:

$$F = \frac{d(mv_x)}{dt} = (2mv_x) \times \left(\frac{v_x}{2l}\right) = \frac{mv_x^2}{l} \tag{2.6.3}$$

Pressure is force per unit area, so the pressure P exerted by the molecule on the wall of cross-section l^2 becomes

$$P = \frac{mv^2}{l^3} = \frac{mv^2}{V} \tag{2.6.4}$$

in which V is the volume of the box.

As noted near the beginning of this unit, any given molecule will make about the same number of moves in the positive and negative directions, so taking a simple average would yield zero. To avoid this embarrassment, we square the velocities before averaging them

$$\bar{v^2} = \frac{v_1^2 + v_2^2 + v_3^2 + v_4^2 \ldots v_N^2}{N} = \frac{\sum_i v_i^2}{N} \tag{2.6.5}$$

and **then** take the square root of the average. This result is known as the *root mean square* (rms) velocity.

$$v_{rms} = \sqrt{\bar{v^2}} \tag{2.6.6}$$

We have calculated the pressure due to a single molecule moving at a constant velocity in a direction perpendicular to a wall. If we now introduce more molecules, we must interpret v^2 as an average value which we will denote by $\bar{v^2}$. Also, since the molecules are moving randomly in all directions, only one-third of their total velocity will be directed along any one Cartesian axis, so the total pressure exerted by N molecules becomes

$$P = \frac{N}{3}\frac{m\bar{v}^2}{V} \tag{2.6.7}$$

Recalling that $m\bar{v^2}/2$ is the average translational kinetic energy ϵ, we can rewrite the above expression as

$$PV = \frac{1}{3}Nm\bar{v^2} = \frac{2}{3}N\epsilon \tag{2.6.8}$$

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:

$$\epsilon = \frac{3}{2}kT \tag{2.6.9}$$

in which the proportionality constant *k* is known as the *Boltzmann constant*. Substituting Equation 2.6.9 into Equation 2.6.8 yields

$$PV = \left(\frac{2}{3}N\right)\left(\frac{3}{2}kT\right) = NkT \tag{2.6.10}$$

The Boltzmann constant *k* is just the gas constant per molecule. For *n* moles of particles, the Equation 2.6.10 becomes

$$PV = nRT \tag{2.6.11}$$

which is the Ideal Gas law.

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2.7: The Maxwell Distribution Laws

In the context of the Kinetic Molecular Theory of Gases, a gas contains a large number of particles in rapid motions. Each particle has a different speed, and each collision between particles changes the speeds of the particles. An understanding of the properties of the gas requires an understanding of the distribution of particle speeds.

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. The resulting quantity is known as the *root mean square (RMS)* velocity

$$v_{rms} = \sqrt{\frac{\sum \nu^2}{n}} \tag{2.7.1}$$

where n is the number of molecules in the system. The formula relating the RMS velocity to the temperature and molar mass is surprisingly simple (derived below), considering the great complexity of the events it represents:

$$v_{rms} = \sqrt{\frac{3RT}{M}} \tag{2.7.2}$$

where

- M is the molar mass in kg mol^{-1}, and
- R is gas constant.

Equation 2.7.2 can also be expressed as

$$v_{rms} = \sqrt{\frac{3k_bT}{m}} \tag{2.7.3}$$

where

- m is the molecular mass in kg
- k_b is *Boltzmann constant* and is just the “gas constant per molecule"

$$k_b = \frac{R}{N_a} = \frac{R}{6.02 \times 10^{23}} \tag{2.7.4}$$

Equation 2.7.3 is just the per atom version of Equation 2.7.2 which is expressed in terms of per mol. Either equation will work.

Example 2.7.1

What is the v_{rms} of a nitrogen molecule at 300 K?

Solution

The molar mass of N_2 is 28.01 g/mol. Substituting in the above equation and expressing *R* in energy units, we obtain

$$v^2 = \frac{(3)(8.31\ J\ mol^{-1}\ K^{-1})(300\ K)}{28.01 \times 10^{-3}\ Kg\ mol^{-1}} = 2.67 \times 10^5\ \frac{J}{Kg}$$

Recalling the definition of the joule (1 J = 1 kg m^2 s^{-2}) and taking the square root,

$$\bar{v} = \sqrt{\left(2.67 \times 10^5\ \frac{\cancel{J}}{\cancel{Kg}}\right)\left(\frac{1\ \cancel{kg}\ m^2\ s^{-2}}{1\ \cancel{J}}\right)} = 517\ m/s$$

or

$$517\ \frac{\cancel{m}}{s}\left(\frac{1\ km}{10^3\ \cancel{m}}\right)\left(\frac{3600\ \cancel{s}}{1\ hr}\right) = 1860\ km/hr$$

Comment: this is fast! The velocity of a rifle bullet is typically 300-500 m s^{-1}; convert to common units to see the comparison for yourself. A simpler formula for estimating average molecular velocities than 2.7.2 is

$$v_{rms} = 157\sqrt{\frac{T}{M}}$$

in which v is in units of meters/sec, T is the **absolute temperature** and M the molar mass in grams.

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 1850 by the great Scottish physicist, **James Clerk Maxwell** (left, 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 2.7.1: Maxwell (left) and Boltzman (right) are responsible for the velocity distrubtion of gas molecules

The Maxwell-Boltzmann distribution is used to determine how many molecules are moving between velocities v and $v+dv$. Assuming that the one-dimensional distributions are independent of one another, that the velocity in the *y* and *z* directions does not affect the *x* velocity, for example, the Maxwell-Boltzmann distribution is given by

$$\frac{dN}{N} = \left(\frac{m}{2\pi k_b T}\right)^{1/2} exp\left[\frac{-mv^2}{2k_b T}\right] dv \tag{2.7.5}$$

where

- dN/N is the fraction of molecules moving at velocity v to $v+dv$,
- m is the mass of the molecule,
- k_b is the Boltzmann constant, and
- T is the absolute temperature.[1]

Additionally, the function can be written in terms of the scalar quantity speed v instead of the vector quantity velocity. This form of the function defines the distribution of the gas molecules moving at different speeds, between v_1 and v_2, thus

$$f(v) = 4\pi v^2 \left(\frac{m}{2\pi k_b T}\right)^{3/2} exp\left[\frac{-mv^2}{2k_b T}\right] \tag{2.7.6}$$

Finally, the Maxwell-Boltzmann distribution can be used to determine the distribution of the kinetic energy of for a set of molecules. The distribution of the kinetic energy is identical to the distribution of the speeds for a certain gas at any temperature.[2] The Maxwell-Boltzmann distribution is a probability distribution and just like any such distribution, can be characterized in a variety of ways including.

- **Average Speed**: The average speed is the sum of the speeds of all of the particles divided by the number of particles.
- **Most Probable Speed**: The most probable speed is the speed associated with the highest point in the Maxwell distribution. Only a small fraction of particles might have this speed, but it is more likely than any other speed.
- **Width of the Distribution**: The width of the distribution characterizes the most likely range of speeds for the particles. One measure of the width is the Full Width at Half Maximum (FWHM). To determine this value, find the height of the distribution at the most probable speed (this is the maximum height of the distribution). Divide the maximum height by two to obtain the half height, and locate the two speeds in the distribution that have this half-height value. On speed will be greater than the most probably speed and the other speed will be smaller. The full width is the difference between the two speeds at the half-maximum value.

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 2.7.2 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.

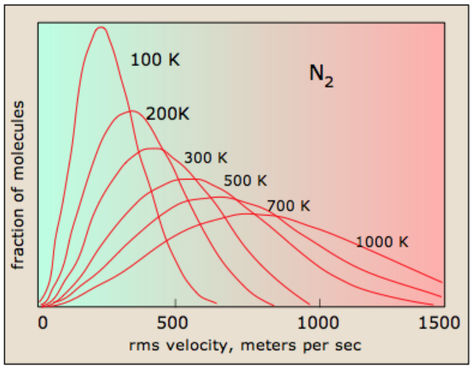

Figure 2.7.2: The Maxwell Distribution as a function of temperature for nitrogen molecules

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.

All molecules have the same kinetic energy ($mv^2/2$) at the same temperature, so the fraction of molecules with higher velocities will increase as m, and thus the molecular weight, decreases. Figure $2.7.3$ 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.

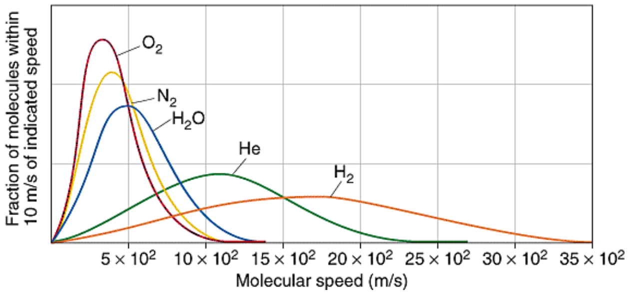

Figure $2.7.3$: The speed probability density functions of the speeds of a few gases at a temperature of 298.15 K). The y-axis is in s/m so that the area under any section of the curve (which represents the probability of the speed being in that range) is dimensionless.

The Maxwell-Boltzmann equation, which forms the basis of the kinetic theory of gases, defines the distribution of speeds for a gas at a certain temperature. From this distribution function, the most probable speed, the average speed, and the root-mean-square speed can be derived.

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:

$$v = \sqrt{v_x^2 + v_y^2 = v_z^2} \tag{2.7.7}$$

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 $2.7.4$}. This is established by finding the velocity when the derivative of Equation $2.7.6$ is zero

$$\frac{df(v)}{dv} = 0 \tag{2.7.8}$$

which is

$$v_{mp} = \sqrt{\frac{2RT}{M}} \tag{2.7.9}$$

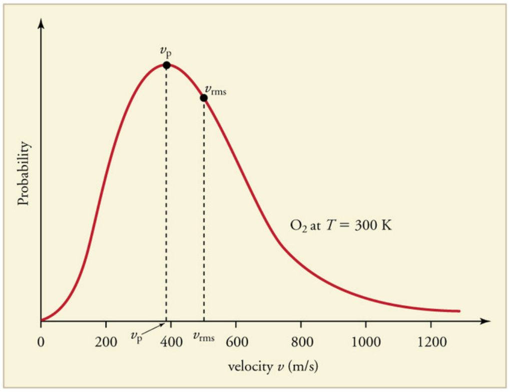

***Figure 2.7.4**: The Maxwell-Boltzmann distribution is shifted to higher speeds and is broadened at higher temperatures. from OpenStax. The speed at the top of the curve is called the most probable speed because the largest number of molecules have that speed.*

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

$$v_{avg} = \bar{v} = \int_0^\infty v f(v) dv = \sqrt{\frac{8RT}{\pi M}} \tag{2.7.10}$$

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

$$v_{rms} = \bar{v}^2 = \sqrt{\frac{3RT}{M}} \tag{2.7.11}$$

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:

$$v_{mp} < v_{avg} < v_{rms} \tag{2.7.12}$$

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 (Figure 1) 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?

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.

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2.8: Molecular Collisions and the Mean Free Path

Collision theory is a theory proposed independently by Max Trautz in 1916 and William Lewis in 1918, that qualitatively explains how chemical reactions occur and why reaction rates differ for different reactions. The collision theory states that when suitable particles of the reactant hit each other, only a certain percentage of the collisions cause any noticeable or significant chemical change; these successful changes are called successful collisions. The successful collisions have enough energy, also known as activation energy, at the moment of impact to break the preexisting bonds and form all new bonds. This results in the products of the reaction. Increasing the concentration of the reactant particles or raising the temperature, thus bringing about more collisions and therefore many more successful collisions, increases the rate of reaction.

Collision Energy

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

$$K_{AB} = \frac{\mathbf{p}_A^2}{2m_A} + \frac{\mathbf{p}_B^2}{2m_B} \tag{2.8.1}$$

Let us change to center-of-mass $(\mathbf{P})$ and relative $(\mathbf{p})$ momenta, which are given by

$$\mathbf{P} = \mathbf{p}_A + \mathbf{p}_B, \quad \mathbf{p} = \frac{m_B\mathbf{p}_a - m_A\mathbf{p}_B}{M} \tag{2.8.2}$$

where $M = m_A + m_B$ is the total mass of the two particles. Substituting this into the kinetic energy, we find

$$K_{AB} = \frac{\mathbf{p}_A^2}{2m_A} + \frac{\mathbf{p}_B^2}{2m_B} = \frac{\mathbf{P}^2}{2M} + \frac{\mathbf{p}^2}{2\mu} \tag{2.8.3}$$

where

$$\mu = \frac{m_A m_B}{M} \tag{2.8.4}$$

is called the *reduced mass* of the two particles. Note that the kinetic energy separates into a sum of a center-of-mass term and a relative term.

Now the relative position 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, being mass independent, is

$$\left\langle \frac{\mathbf{p}^2}{2\mu} \right\rangle = \frac{3}{2} k_B T \tag{2.8.5}$$

which is called the *collision energy.*

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 (see lecture 5). 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

$$\sigma_A = \pi d_A^2, \quad \sigma_B = \pi d_B^2 \tag{2.8.6}$$

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

$$d_{AB} = \frac{1}{2}(d_A + d_B) \tag{2.8.7}$$

and the resulting collision cross section becomes

$$\begin{align} \sigma_{AB} &= \pi d_{AB}^2 \tag{2.8.8} \\ &= \pi \left(\frac{d_A + d_B}{2} \right)^2 \tag{2.8.9} \\ &= \frac{\pi}{4}(d_A^2 + 2d_A d_B + d_B^2) \tag{2.8.10} \\ &= \frac{1}{4}(\sigma_A + 2\sqrt{\sigma_A \sigma_B} + \sigma_B) \tag{2.8.11} \\ &= \frac{1}{2}\left[\left(\frac{\sigma_A + \sigma_B}{2} \right) + \sqrt{\sigma_A \sigma_B} \right] \tag{2.8.12} \end{align}$$

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

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 $2.8.1$). If the system has a number density ρ, then the number of collisions that will occur is

$$N_{\text{coll}} = \rho \sigma l \tag{2.8.13}$$

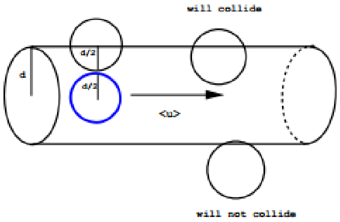

Figure $2.8.1$: Collision cylinder. Any particle that partially overlaps with this volume will experience a collision with a test particle tracing out this volume.

We define the average collision rate as $N_{\text{coll}}/\Delta t$, i.e.,

$$\gamma = \frac{N_{\text{coll}}}{\Delta t} = \frac{\rho \sigma l}{\Delta t} = \rho \sigma \langle |\mathbf{v}| \rangle \tag{2.8.14}$$

where $\langle |\mathbf{v}| \rangle$ is the average relative speed. If all of the particles are of the same type (say, type A), then performing the average over a Maxwell-Boltzmann speed distribution gives

$$\langle |\mathbf{v}| \rangle = \sqrt{\frac{8k_B T}{\pi \mu}} \tag{2.8.15}$$

where $\mu = m_A/2$ is the reduced mass. The average speed of a particle is

$$\langle |\mathbf{v}_A| \rangle = \sqrt{\frac{8k_B T}{\pi m_A}} \tag{2.8.16}$$

so that

$$\langle |\mathbf{v}| \rangle = \sqrt{2} \langle |\mathbf{v}_A| \rangle \tag{2.8.17}$$

Mean Free Path

The mean free path is defined as the distance a particle will travel, on average, before experiencing a collision event. This is defined as the product of the speed of a particle and the time between collisions. The former is $\langle |\mathbf{v}| \rangle / \sqrt{2}$, while the latter is $1/\gamma$.

Hence, we have

$$\lambda = \frac{\langle|\mathbf{v}|\rangle}{\sqrt{2}\rho\sigma\langle|\mathbf{v}|\rangle} = \frac{1}{\sqrt{2}\rho\sigma} \tag{2.8.18}$$

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 \(\PageIndex{2. Such a path is often referred to as a *random walk path*.

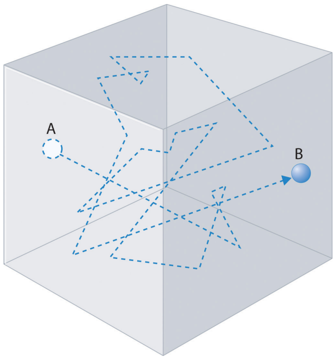

Figure 2.8.2: Random walk path. The Path of a Single Particle in a Gas Sample. The frequent changes in direction are the result of collisions with other gas molecules and with the walls of the container.

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.

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:

$$\mathcal{P}(\mathbf{r}) = P(x)\, P(y)\, P(z) = \frac{1}{(4\pi Dt)^{3/2}}\, e^{-(x^2+y^2+z^2)/4Dt} \tag{2.8.19}$$

where D is the *diffusion constant.* If we are only interested in diffusion over a distance r, we can introduce spherical coordinates, integrate over the angles, and we find that

$$P(r,t) = \frac{4\pi}{(4\pi Dt)^{3/2}}\, E^{-r^2/4Dt} \tag{2.8.20}$$

Rates of Diffusion or Effusion

Graham's law is an empirical relationship that states that the ratio of the rates of diffusion or effusion of two gases is the square root of the inverse ratio of their molar masses. The relationship is based on the postulate that all gases at the same temperature have the same average kinetic energy. We can write the expression for the average kinetic energy of two gases with different molar masses:

$$KE = \frac{1}{2}\frac{M_{\text{A}}}{N_A} v^2_{\text{rms,A}} = \frac{1}{2}\frac{M_{\text{B}}}{N_A} v^2_{\text{rms,B}} \tag{2.8.21}$$

Multiplying both sides by 2 and rearranging give

$$\frac{v^2_{\text{rms,B}}}{v^2_{\text{rms,A}}} = \frac{M_{\text{A}}}{M_{\text{B}}} \tag{2.8.22}$$

Taking the square root of both sides gives

$$\frac{v_{\mathrm{rms,B}}}{v_{\mathrm{rms,A}}} = \sqrt{\frac{M_{\mathrm{A}}}{M_{\mathrm{B}}}} \tag{2.8.23}$$

Thus the rate at which a molecule, or a mole of molecules, diffuses or effuses is directly related to the speed at which it moves. Equation 2.8.23 shows that Graham's law is a direct consequence of the fact that gaseous molecules at the same temperature have the same average kinetic energy.

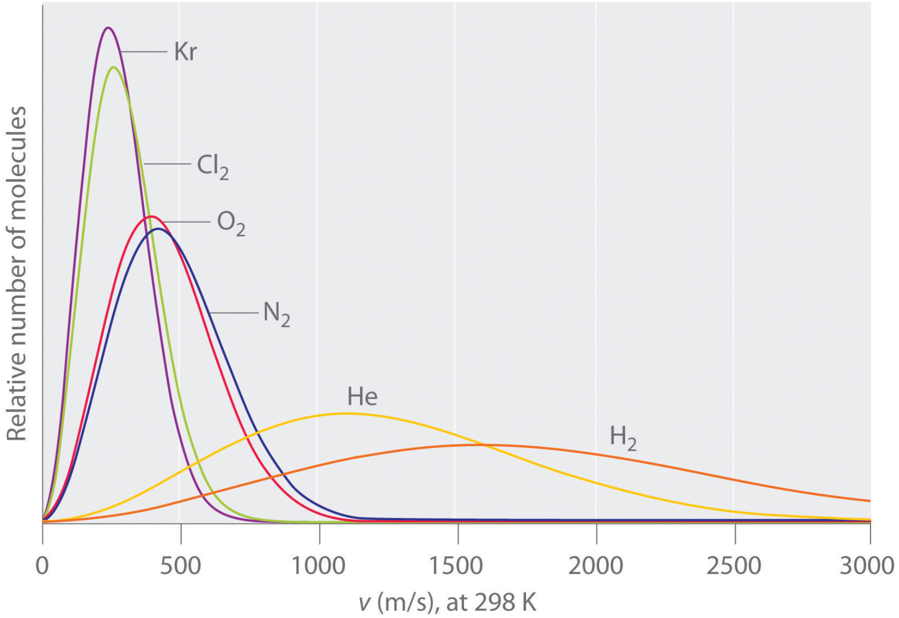

Figure 2.8.3 : The Wide Variation in Molecular Speeds Observed at 298 K for Gases with Different Molar Masses

The lightest gases have a wider distribution of speeds and the highest average speeds.

> Molecules with lower masses have a wider distribution of speeds and a higher average speed.

Gas molecules do not diffuse nearly as rapidly as their very high speeds might suggest. If molecules actually moved through a room at hundreds of miles per hour, we would detect odors faster than we hear sound. Instead, it can take several minutes for us to detect an aroma because molecules are traveling in a medium with other gas molecules. Because gas molecules collide as often as 10^{10} times per second, changing direction and speed with each collision, they do not diffuse across a room in a straight line.

> The **denser** the gas, the **shorter** the mean free path.

✓ Example 2.8.2

Calculate the rms speed of a sample of *cis*-2-butene (C_4H_8) at 20°C.

Given: compound and temperature

Asked for: rms speed

Strategy:

Calculate the molar mass of cis-2-butene. Be certain that all quantities are expressed in the appropriate units and then use Equation ??? to calculate the rms speed of the gas.

Solution:

To use Equation 2.8.23, we need to calculate the molar mass of *cis*-2-butene and make sure that each quantity is expressed in the appropriate units. Butene is C_4H_8, so its molar mass is 56.11 g/mol. Thus

$$u_{\mathrm{rms}}=\sqrt{\frac{3RT}{M}}=\sqrt{\frac{3\times 8.3145\ \frac{\mathrm{J}}{\mathrm{K}\cdot\mathrm{mol}}\times(20+273)\ \mathrm{K}}{56.11\times 10^{-3}\ \mathrm{kg}}}=361\ \mathrm{m/s} \tag{2.8.24}$$

or approximately 810 mi/h.

? Exercise 2.8.2

Calculate the rms speed of a sample of radon gas at 23°C.

Answer: 1.82 × 10^2 m/s (about 410 mi/h)

Contributors and Attributions

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- Wikipedia

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2.9: Graham's Laws of Diffusion and Effusion

Learning Objectives

- Understand the difference between effusion and diffusion
- To derive and apply Graham's Law of Effusion

Diffusion is the gradual mixing of gases due to the motion of their component particles even in the absence of mechanical agitation such as stirring. The result is a gas mixture with uniform composition. Diffusion is also a property of the particles in liquids and liquid solutions and, to a lesser extent, of solids and solid solutions. The related process, effusion, is the escape of gaseous molecules through a small (usually microscopic) hole, such as a hole in a balloon, into an evacuated space.

The phenomenon of effusion had been known for thousands of years, but it was not until the early 19th century that quantitative experiments related the rate of effusion to molecular properties. The rate of effusion of a gaseous substance is inversely proportional to the square root of its molar mass. This relationship *is referred to as Graham's law*, after the Scottish chemist Thomas Graham (1805–1869). The ratio of the effusion rates of two gases is the square root of the inverse ratio of their molar masses*:*

$$\frac{\text{rate of effusion A}}{\text{rate of effusion B}}=\sqrt{\frac{M_B}{M_A}} \tag{2.9.1}$$

Graham Law

The rate of effusion of a gaseous substance is inversely proportional to the square root of its molar mass.

Graham's law is an empirical relationship that states that the ratio of the rates of diffusion or effusion of two gases is the square root of the inverse ratio of their molar masses. The relationship is based on the postulate that all gases at the same temperature have the same average kinetic energy (recall that a result of the Kinetic Theory of Gases is that the temperature, in degrees Kelvin, is directly proportional to the average kinetic energy of the molecules.) . We can write the expression for the average kinetic energy of two gases with different molar masses:

$$KE=\frac{1}{2}\frac{M_{\mathrm{A}}}{N_A}v^2_{\mathrm{rms,A}}=\frac{1}{2}\frac{M_{\mathrm{B}}}{N_A}v^2_{\mathrm{rms,B}} \tag{2.9.2}$$

Multiplying both sides by 2 and rearranging give

$$\frac{v^2_{\mathrm{rms,B}}}{v^2_{\mathrm{rms,A}}}=\frac{M_{\mathrm{A}}}{M_{\mathrm{B}}} \tag{2.9.3}$$

Taking the square root of both sides gives

$$\frac{v_{\mathrm{rms,B}}}{v_{\mathrm{rms,A}}}=\sqrt{\frac{M_{\mathrm{A}}}{M_{\mathrm{B}}}} \tag{2.9.4}$$

Thus the rate at which a molecule, or a mole of molecules, diffuses or effuses is directly related to the speed at which it moves. Equation 2.9.4 shows that Graham's law is a direct consequence of the fact that gaseous molecules at the same temperature have the same average kinetic energy.

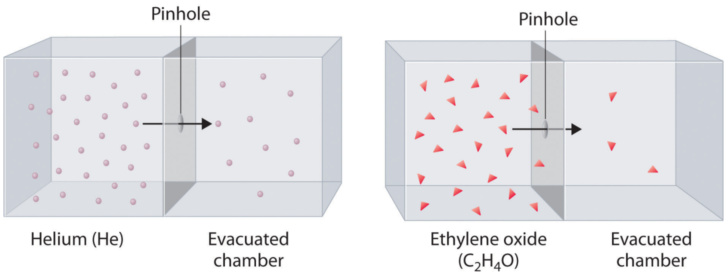

Figure 2.9.1: The Relative Rates of Effusion of Two Gases with Different Masses. The lighter He atoms (M = 4.00 g/mol) effuse through the small hole more rapidly than the heavier ethylene oxide (C_2H_4O) molecules (M = 44.0 g/mol), as predicted by Graham's law.

Heavy molecules effuse through a porous material more slowly than light molecules, as illustrated schematically in Figure 2.9.1 for ethylene oxide C_2H_4O and helium He. Helium (M = 4.00 g/mol) effuses much more rapidly than ethylene oxide (M = 44.0 g/mol). Because helium is less dense than air, helium-filled balloons "float" at the end of a tethering string. Unfortunately, rubber balloons filled with helium soon lose their buoyancy along with much of their volume. In contrast, rubber balloons filled with air tend to retain their shape and volume for a much longer time. Because helium has a molar mass of 4.00 g/mol, whereas air has an average molar mass of about 29 g/mol, pure helium effuses through the microscopic pores in the rubber balloon $\sqrt{\frac{29}{4.00}} = 2.7$ times faster than air. For this reason, high-quality helium-filled balloons are usually made of Mylar, a dense, strong, opaque material with a high molecular mass that forms films that have many fewer pores than rubber. Hence, mylar balloons can retain their helium for days.

✓ Example 2.9.1

During World War II, scientists working on the first atomic bomb were faced with the challenge of finding a way to obtain large amounts of ^{235}U. Naturally occurring uranium is only 0.720% ^{235}U, whereas most of the rest (99.275%) is ^{238}U, which is not fissionable (i.e., it will not break apart to release nuclear energy) and also actually poisons the fission process. Because both isotopes of uranium have the same reactivity, they cannot be separated chemically. Instead, a process of gaseous effusion was developed using the volatile compound UF_6 (boiling point = 56°C).

1. Calculate the ratio of the rates of effusion of $^{235}UF_6$ and $^{238}UF_6$ for a single step in which UF_6 is allowed to pass through a porous barrier. (The atomic mass of ^{235}U is 235.04, and the atomic mass of ^{238}U is 238.05.)
2. If *n* identical successive separation steps are used, the overall separation is given by the separation in a single step (in this case, the ratio of effusion rates) raised to the *n*th power. How many effusion steps are needed to obtain 99.0% pure $^{235}UF_6$?

Given: isotopic content of naturally occurring uranium and atomic masses of ^{235}U and ^{238}U

Asked for: ratio of rates of effusion and number of effusion steps needed to obtain 99.0% pure $^{235}UF_6$

Strategy:

A. Calculate the molar masses of $^{235}UF_6$ and $^{238}UF_6$, and then use Graham's law to determine the ratio of the effusion rates. Use this value to determine the isotopic content of $^{235}UF_6$ after a single effusion step.
B. Divide the final purity by the initial purity to obtain a value for the number of separation steps needed to achieve the desired purity. Use a logarithmic expression to compute the number of separation steps required.

Solution:

1. A The first step is to calculate the molar mass of UF_6 containing ^{235}U and ^{238}U. Luckily for the success of the separation method, fluorine consists of a single isotope of atomic mass 18.998. The molar mass of $^{235}UF_6$ is 234.04 + (6)(18.998) = 349.03 g/mol

   The molar mass of $^{238}UF_6$ is

   238.05 + (6)(18.998) = 352.04 g/mol

   The difference is only 3.01 g/mol (less than 1%). The ratio of the effusion rates can be calculated from Graham's law using Equation 2.9.1:

$$\frac{\text{rate } ^{235}\text{UF}_6}{\text{rate } ^{238}\text{UF}_6} = \sqrt{\frac{352.04 \text{ g/mol}}{349.03 \text{ g/mol}}} = 1.0043 \tag{2.9.5}$$

2.

Thus passing UF_6 containing a mixture of the two isotopes through a single porous barrier gives an enrichment of 1.0043, so after one step the isotopic content is (0.720%)(1.0043) = 0.723% $^{235}UF_6$.

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2.E: Properties of Gases (Exercises)

2.1: Some Definitions

2.2: An Operational Definition of Temperature

2.3: Ideal Gases

2.4: Real Gases

2.5: Condensation of Gases and the Critical State

Q2.2

There are some gases in existence, such as NS_2 and NCl_2, which do not follow Boyle's Law, regardless of the pressure conditions they're under. Explain why this is the case.

S2.2

Boyle's Law assumes that the only factors changing are pressure (P) and volume (V), therefore, in order to apply Boyle's Law, both number of molecules (n) and temperature (T) must remain constant. However, both NS_2 and NCl_2 do not have constant n because they undergo association reactions when in contact with like molecules.

$$2NH_2 \rightleftharpoons N_2S_2 \tag{2.E.1}$$

$$2NCl_2 \rightleftharpoons N_2Cl_2 \tag{2.E.2}$$

Therefore, Boyle's Law may not be applied for these gases.

Q2.3

An ideal gas originally at 0.85 atm and 66ºC was allowed to expand until its final volume, pressure, and temperature were 94 mL, 0.60 atm, and 45ºC, respectively. What was its initial volume?

S2.3

- $P_1 = 0.85\ atm$
- $T_1 = 339\ K$
- $V_2 = 94\ mL$
- $P_2 = 0.60\ atm$
- $T_2 = 318\ K$

$$V_1 = \frac{(P_2)(V_2)(T_1)}{(T_2)(P_1)} \tag{2.E.3}$$

$$= \frac{(0.60\ atm)(94\ mL)(339\ K)}{(318\ K)(0.85\ atm)} = 71\ mL \tag{2.E.4}$$

Q2.4

Some ballpoint pens have a small hole in the main body of the pen. What is the purpose of the hole?

S2.4

The hole is there to allow the pressure to equalize and allow the ink to flow out of the pen.

Q2.5

Starting with the ideal-gas equation, show how you ca calculate the molar mass of a gas from a knowledge of its density

S2.5

Q2.6

At STP (standard temperature and pressure), 0.280 /;L of a gas weighs 0.400/;g. Calculate the molar mass of the gas.

S2.6

First, we need to determine the moles of gas in the sample:

$$n = \frac{(P)(V)}{(R)(T)} \tag{2.E.5}$$

$$= \frac{(1.00\ atm)(0.280\ L)}{(0.08206\ L-atm/mol-K)(273\ K)} = 0.0125\ moL \tag{2.E.6}$$

$$= \frac{(0.400\ g)}{(0.0125\ mol)} = 32.0\ g/moL \tag{2.E.7}$$

Q2.7

Ozone molecules in the stratosphere absorb much of the harmful radiation from the sun. Typically, the temperature and partial pressure of ozone in the stratosphere are 250 K and 0.0010 atm, respectively. How many ozone molecules are present in 1.0 L of air under these conditions? Assume ideal-gas behavior.

Q2.9

Dissolving 3.00 g of an impure sample of $CaCO_3$ in an excess of HCl acid produced 0.656 L of CO_2 (measured at 20ºC and 792 mmHg). Calculate the percent by mass of $CaCO_3$ in the sample.

Q2.14

a. What volume of air at 1.0 atm and 22ºC is needed to fill a 0.98 L bicycle tire to a pressure of 5.0 atm at the same temperature? (Note that the 5.0 atm is the gauge pressure, which is the difference between the pressure in the tire and the atmospheric pressure. Initially, the gauge pressure in the tire was 0 atm.)
b. What is the total pressure in the tire when the gauge reads 5.0 atm?
c. The tire is pumped with a hand pump full of air at 1.0 atm; compressing the gas in the cylinder adds all of the air in the pump to the air in the tire. If the volume of the pump is 33% of the tire's volume, what is the gauge pressure in the tire after 2 full strokes of the pump?

Q2.15

A student breaks a thermometer and spills most of the mercury (Hg) onto the floor of a laboratory that measures 15.2 m long, 6.6 m wide, and 2.4 m high. The vapor pressure of mercury at 20ºC is 1.7 x 10^{-6} atm.

a. Calculate the mass of mercury vapor (in grams)in the room at 20ºC.
b. Does the concentration of mercury vapor exceed the air quality regulation of 0.050 mm Hg m^{-3} of air?
c. One way to treat small quantities of spilled mercury is to spray powdered sulfur over the metal. Suggest a physical and a chemical reason for this treatment.

S2.15

a) The volume of the room is 15.2 m x 6.6 m x 2.4 m = 240 m^3.

The pressure is 1.7 x 10^{-6} atm x 101325 Pa/atm = 0.17 Pa

Ideal gas equation:

$$PV = nRT \tag{2.E.8}$$

$$n = \frac{PV}{RT} \tag{2.E.9}$$

$$n = \frac{0.17\ Pa * (240)\ m^3}{\frac{8.314\ Pa-m^3}{K-mol} * (293K)} \tag{2.E.10}$$

$$= 0.017\ mole \tag{2.E.11}$$

Mass of mercury vapor : m_{Hg} = n_{Hg} * M_{Hg} =(0.017 mole)(200.6 g/mole)(1000 mg/gram)} = 3400 mg

b) The mass density of mercury vapor :

[Hg] = m_{Hg} / $V_{Hg(l)}$ =

$$\frac{3400\ mg}{240\ m^{-3}} \tag{2.E.12}$$

=14 mg/m^3

This value is indeed larger than the 0.050 mg Hg m^{-3} allowed.

c) Using powdered sulfur to absorb the spilled mercury works because the sulfur molecules will strongly bind to the mercury, and the mercury sulfide that forms is a solid. This makes removing spilled mercury (a liquid) easier.

Q2.16

An oxide has the density of 1.75 g L^{-1} at 1.12 atm and 100°C. Is this oxide O_2(g) or $O_{3(g)}$?

S2.16

$$M = \frac{\rho RT}{P} \tag{2.E.13}$$

$$= \frac{(1.75gL^{-1})(0.08206LatmK^{-1}mol^{-1})(100+273)K)}{1.12atm} = 47.8\frac{g}{mol} \tag{2.E.14}$$

The molar mass of O_3(g) is 48 g mol^{-1}, so the oxide must be O_3(g)

Q2.21

You are given a gas at 750 torr with a volume of 0.62 Liters at 25°C. A while later, you measure the temperature and notice a 5°C temperature increase in the system. Assuming there is no pressure change and that this is an ideal gas, what is the new volume?

S2.21

First: List out what you have

$$P_i = 750torr * \frac{(1atm)}{760torr} = 0.987atm$$

Vi=0.62 L

T_i=25ºC +273.15= 298.15

We do not know the amount of moles so we should find that.

PV=nRT

$$n = \frac{PV}{RT} = \frac{(0.987atm)(0.62L)}{8.3145\frac{J}{mol K}298.15K}$$

So n_i=2.47x10^{-4} moles

P_f=0.987 atm

V_f=?

T_f=298.15 K + 5 K= 303.15 K

V_f=(nRT)/P

$$= \frac{(2.47 \cdot 10^{-4}mol \cdot 8.3145\frac{J}{mol \cdot K}303.15K)}{(0.987atm)}$$

=0.631 L

Q2.23a

The composition of air in your alveoli is 75% $N_{2,}$ 14% O_2, 5% CO_2, and 6% H_2O, by volume. (a) Calculate the average molar mass of this air sample. (b) Calculate the partial pressures of N_2, O_2, CO_2, and H_2O in your alveoli. assuming that alveolar pressure is 760 torr (At constant pressure and temperature, the volume of a gas is directly proportional to the number of moles of gas).

Q2.23b

The composition of air in your alveoli is 75% $N_{2,}$ 14% O_2, 5% CO_2, and 6% H_2O, by volume. (a) Calculate the average molar mass of this air sample. (b) Calculate the partial pressures of N_2, O_2, CO_2, and H_2O in your alveoli. (At constant pressure and temperature, the volume of a gas is directly proportional to the number of moles of gas.)

Q2.24

In an expandable balloon we find a mixture of two gases only. The mass percent of the gases are: 65% 0_2 and 35 % $H_{Q2.}$ The mass of the gases combined is 4.6 grams. Calculate the total volume these two gases occupy at 298 K and 1.00 atm.

S2.24

You can find the Volume by using the Ideal Gas Law equation:

$$V=\frac{nRT}{P} \tag{2.E.15}$$

The mass of the two gases is given by:

$m_{H_2}=4.6\times 0.35=1.6g$

$m_{O_2}=4.6\times 0.65=3.0g$

The number of moles of the mixture= $n_{total}=n_{H_2}+n_{O_2}$

$$n_{total}=\frac{1.60g}{Q2.0g.\,mol^{-1}}+\frac{3.0g}{32g.\,mol^{-1}}=0.884mol$$

The volume the two gases occupy = $V=\dfrac{(0.884mol)(0.08206\frac{L.\,atm}{K.\,mol})(298K)}{1.0atm}=21.6L$

Q2.25

The temperature in a small room in summer time is 31oC. The room (dimension 4mx4mx3m) is filled with 0.88 kg of water vapor. What is the partial pressure of water vapor in the air?

Q2.27

A flask contains a mixture of two ideal gases, A and B. Show graphically how the total pressure of the system depends on the amount of A present. That is, plot the total pressure versus the mole fraction of A. Do the same for B on the same graph. The total number of moles of A and B is remained as constant.

S2.27

Q2.29

When you drink something from a straw, how does the liquid get from the glass up through the straw into your mouth?

S2.29

When you close your mouth around the straw, you close off the atmosphere from outside to inside. During suction, you increase the volume inside your mouth, thus lowering the internal pressure and the atmospheric pressure exerted onto the liquid over comes the internal pressure and so the liquid flows into your mouth.

Q2.31

Consider the reaction of ferrous sulfide with a dilute acid:

$$FeS_{(s)}+2HCl_{(aq)}\rightarrow H_2S_{(g)}+FeCl_{2(l)} \tag{2.E.16}$$

An amount of 5.10 grams of ferrous sulfide completely reacted in this reaction. The gas collected over the water at 27ºC has a volume 1.78 L. Find the pressure of the collected gas in atm. The vapor pressure of water at 27°C is 26.7 mmHg.

Hint: Look at Dalton's law of partial pressure

S2.31

Base on the amount of reactant, use stoichiometry to find the number of moles of H2S gas produced and get partial pressure of hydrogen sulfide gas. Then use Dalton's law of partial pressure to find the total pressure of collected gas.

$$5.10gFeS \times \frac{1moleFeS}{87.92gFeS} \times \frac{1moleH_2S}{1moleFeS} = 0.058moleH_2S \tag{2.E.17}$$

$$P_{H_2S} = \frac{nRT}{V} = \frac{0.058moleH_2S \times 0.08206\frac{L\cdot atm}{mole\cdot K} \times (27+273)K}{1.78L} = 0.802atm \tag{2.E.18}$$

$$P_{total} = P_{H_2S} + P_{H_2O} = 0.802atm + (26.7mmHg \times \frac{1atm}{760mmHg}) = 0.837atm \tag{2.E.19}$$

Q2.32a

Tanks containing mixtures of oxygen and nitrogen are routinely lowered to the Aquarius underwater research lab in Florida. What is the percent composition of oxygen gas in the tank if the total pressure in the tank once it has reached Aquarius is 6.5 atm, and the partial pressure is 0.55 atm?

S2.32a

For any ideal gas,

$$PV = nRT \tag{2.E.20}$$

At constant pressure and temperature, V is proportional to n. Thus:

$$P_{O^2} = x_{O^2} P_{total} \tag{2.E.21}$$

$$x_{O^2} = \frac{P_{O^2}}{P_{total}} = \frac{0.55atm}{6.5atm} = .085 \tag{2.E.22}$$

The percent composition is 8.5%

Q2.32b

A mixture of helium and oxygen gas is used to fill up an apparatus. If the total pressure within the apparatus is 10 atm and the partial pressure of helium is 2 atm within that apparatus, calculate the percent by volume of diatomic oxygen gas.

S2.32b

$$\chi_{He} = \frac{P_{He}}{P_{total}},\ where\ \chi = Mole\ Fraction \tag{2.E.23}$$

$$\chi_{He} = \frac{2atm}{10atm}$$

$$\chi_{He} = 0.2$$

$$\begin{aligned}\%\ by\ volume\ He &= \chi_{He} \cdot 100\\ &= 0.2\ \cdot 100 = 20\%\end{aligned}$$

$$100\%\ by\ volume\ total\ gas - 20\%\ by\ volume\ He = \underline{80\%\ by\ volume\ O_2} \tag{2.E.24}$$

Click here for more on mole fractions.

Q2.33

An unknown mass of NO_2 in a closed chamber decomposes completely to oxygen and nitrogen gases. The final pressure in the chamber is 0.687 atm. What are the partial pressures of each component of the gas mixture in the chamber?

S2.33

Every two moles of NO_2 produce one mole of N_2 and O_2. By the ideal gas equation, since we know that the gases are at the same temperature and occupy the same volume, the pressure of each gas is proportional to the number of moles of that gas present, and thus the pressure of each gas is proportional to the mole fractions of that gas. Because NO_2 represents 1/3 of the total moles of gas present, and O_2 represents 2/3 of the total gas present, NO_2 represents 1/3 of the total pressure, and O_2 represents 2/3 of the total pressure.

- P_{N2} = 1/3 * 0.687 atm = 0.229 atm
- P_{O2} = 2/3 * 0.687 atm = 0.458 atm

Q2.41

Choose the more ideal system

a. H_2O at 110 °C and 1 atm vs H_2O at 100°C and I atm
b. Cl_2 at 10 atm vs Cl_2 at 0.5 atm
c. N_2 at 60 °C vs N_2 at 100°C

2.6: Kinetic Theory of Gases

Q2.41

List the ideal conditions (the conditions that help allow a gas to behave ideally).

S2.41

Ideal conditions come from the kinetic theory of gases. This theory relies on three primary assumptions (as follows):

a. The gas is made up of a large amount of molecules. These molecules obey Newton's laws pertaining to motion and are always moving around in random motion.
b. In comparison to the volume of the gas, the volume of the molecules are so negligible that they can essentially be ignored.
c. No forces are capable of acting on the molecules except for extremely short durations of elastic collisions.

Ideal conditions are at:

- high temperatures, and
- low pressures

This is because at these conditions is when there are relatively large distance between molecules.

Q2.42

1.00 mole of an unknown gas occupies a 0.865 L container at 0.90 atm and 25ºC. If the value of van der Waals constant *a*= *0*.550, what is the value of *b* for the gas? What does the value of *b* indicate about the gas?

S2.42

$$\begin{gathered} P = 4.0atm \\ V = 0.70L \\ T = 77.2K \\ a = 2.50\frac{atm \cdot L^2}{mol^2} \end{gathered} \tag{2.E.25}$$

$$(P + \frac{an^2}{V^2})(V - nb) = nRT \rightarrow b = \frac{nRT}{P + \frac{an^2}{V^2}} - V(\frac{1}{-1}) \tag{2.E.26}$$

$$\begin{aligned} b &= \frac{(1mol)(.08206\frac{L \cdot atm}{mol \cdot K})(77.2K)}{4.0atm + \frac{(Q2.5)1mol^2}{.70L^2}} - .70L(\frac{1}{-1mol}) \\ &= 4 \times 10^-3\frac{L}{mol} \end{aligned} \tag{2.E.27}$$

The small value of b indicates that the gas molecules have a small molecular mass.

Q2.48

The compressibility for compound 1 is 0.84 and 0.56 for compound. Which compound will occupy a smaller volume?

S2.48

Z is a prediction of the behavior of gases. A smaller value means that there are stronger intermolecular forces amongst the molecules, meaning a smaller volume occupied. Therefore, compound 2 will occupy a smaller volume than compound 1.

Q2.50

True or false: The concept of temperature is a macroscopic. Explain your reasoning.

S2.50

True. The kinetic theory of gases hypothesizes that it deals with an extremely large amount of molecules. Therefore, temperature is a macroscopic concept since the average kinetic energy of the molecules within a given system is proportional to the temperature. A large amount of molecules must be included into this average in order for it to be properly utilized.

Q2.51

What assumptions are made when applying the kinetic molecular theory to gases? Are all of these assumptions necessary? Why or why not?

S2.51

There are five assumptions made when applying the kinetic molecular theory to gases are:

1. Gases consist of a large amount of atoms or molecules and these atoms/ molecules have spaces of separation between them that are much larger than their size.
2. Although the molecules have mass, we treat them as if they do not since their volume is negligibly small.
3. The molecules are always moving around randomly.
4. All collisions, both molecule-molecule collisions and molecule-wall collisions, are considered to be elastic rather than inelastic.
5. The molecules are not considered to be attracted nor repulsed to/ by one another.

Most of these assumptions are in fact necessary to consider when applying the kinetic molecular theory to gases, however, assumption number 4 is not always crucial. This is due to the fact that it does not matter whether or not the collisions between the molecules and the walls are elastic if the walls of the container are at the same temperature as the molecules inside of the the container (*i.e.* the gas) because although kinetic energy may be transferred from molecule to molecule, it will not be converted into any other forms of energy.

Q2.52

A 3.50 L cube-shaped container container 3.5x10^{23} molecules of N_2 at 30ºC. What is pressure exerted on one wall?

S2.52

$$\begin{gathered} N = 3.5 \times 10^{23} \\ V = 3.50L \\ T = 303K \\ k_B = 1.38 \times 10^{-23} \end{gathered} \tag{2.E.28}$$

$$P = \frac{2N}{3V}\overline{E}_t rans \rightarrow P = \frac{2N}{3V}(\frac{3}{2}k_BT) \tag{2.E.29}$$

$$= \frac{2(3.5 \times 10^{23})}{3(3.50L)}[\frac{3}{2}(1.38 \times 10^{-23})(303K)] \tag{2.E.30}$$

$$= 4.18 \times 10^2 atm \tag{2.E.31}$$

Q2.53

Imagine a container with walls 123 cm³. Argon (with a speed of 700 m/s) atoms at 300 K are colliding at right angles with the container's walls at a rate of $5.0 \times 10^{20} m/s$. What would the force and pressure exerted on the container's walls be?

2.7: The Maxwell Distribution Laws

Q2.54

Calculate the root-mean-square speed and the molar kinetic energy of N_2 at 25ºC

S2.54

The root-mean-square speed of N_2 is:

$$v_{rms} = \sqrt{\frac{3k_BT}{m}} \tag{2.E.32}$$

or in terms of molar mass M instead of molecular mass (m)

$$v_{rms} = \sqrt{\frac{3RT}{M}} \tag{2.E.33}$$

$$= \sqrt{\frac{(3)(8.3145\, J\ \cancel{K}\ \cancel{mol^{-1}})(298.15\ \ \cancel{K})}{28.02\ \ \cancel{g}\ \ \cancel{mol^{-1}} \frac{1\ kg}{1000\ \ \cancel{g}}}} = 5.15\ m/s \tag{2.E.34}$$

The molar kinetic energy of N_2 at 25ºC is:

$= \dfrac{3}{2} * \dfrac{8.3145J}{Kmol} * 298.15K * \dfrac{1kJ}{1000J}$

= 3.72 kJ/mol

Q2.55

Find the v_{rms} of N_{2(g)} at 25ºC. What temperature must $Cl_{2(g)}$ be to have the same v_{rms}?

S2.55

$$v_{rms} = \sqrt{\frac{3RT}{M}} \tag{2.E.35}$$

$$v_{rmsN_2} = \sqrt{\frac{3(8.314J \cdot K^{-1} \cdot mol^{-1})(25+273)K}{28.02x10^{-3}kg \cdot mol^{-1}}} = 515m\ s^{-1} \tag{2.E.36}$$

$$since\ v_{rmsN_2} = v_{rmsCl_2}, then\ v_{rmsCl_2} = 515m\ s^{-1} \tag{2.E.37}$$

$$v_{rmsCl_2} = \sqrt{\frac{3(8.314J \cdot K^{-1} \cdot mol^{-1})(T)}{70.9x10^{-3}g \cdot mol^{-1}}} = 515m\ s^{-1} \tag{2.E.38}$$

T = 754 K

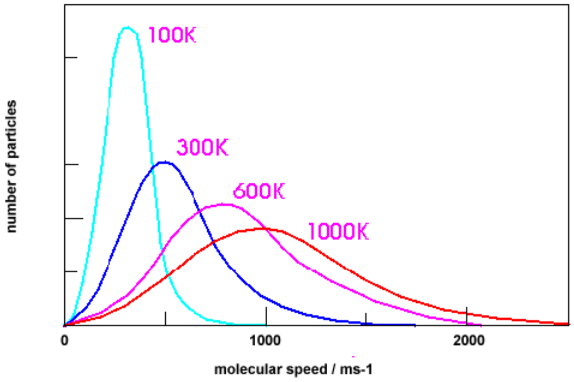
Therefore, Cl_2(g) must be 754 K to have the same v_{rms} as N_2(g) at 298 K

Q2.60

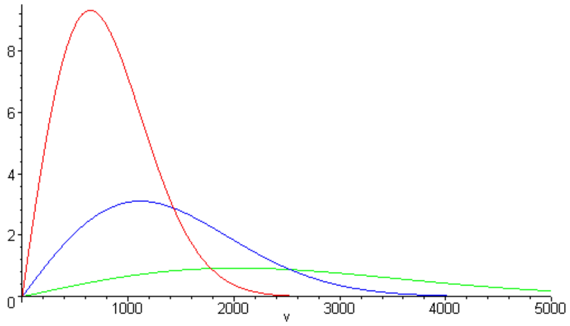
a. Plot the distribution of speeds for Cl_2 at 100 K, 300 K, 600 K, and 1000 K.
b. Plot the distribution of speeds for three gases: N_2, Cl_2, and CH_4 at the same temperature.

S2.60

a) The plot of the distribution of speeds for Cl_2 at 100 K, 300 K, 600 K, and 1000 K



b) The plot of the distribution of $N_{2,}Cl_2$ and CH_4 at the same temperature (300K)



Q2.60

Which gas would you expect to move faster at 255K, O_2 or I_2? And why?

S2.60

We'd expect O_2 to move faster. This is because it is lighter. Think of the formula for average speed because it is divided by kg/mol the smaller the mass, the faster it goes.

Q2.61

According to the Maxwell speed distribution, would $O_{2(g)}$ have a wider speed distribution at 200 K or 1000 K?

S2.61

At lower temperatures, the speed distribution will be narrower and there will will be a smaller most probable speed while the higher temperature will have a wider speed distribution and a higher most probable speed. Therefore, $O_{2(g)}$ will have a wider speed distribution at 1000 K.

Q2.62a

A CO_2 molecule at unknown temperature at sea level is released to travel upward. Assuming that the temperature is constant and that the molecule doesn't collide with another molecules and reaches a terminal height of 8.5 meters above sea level, what is the temperature? Do the same calculation for a H_2 atom. [Hint: To calculate the altitude, h, the molecule will travel, equate its kinetic energy with the potential energy, mgh, where m is the mass and g is the acceleration due to gravity (9.81 m s^{-2}).]

Q2.62b

A CO_2 molecule at unknown temperature at sea level is released to travel upward. Assuming that the temperature is constant and that the molecule doesn't collide with another molecules and reaches a terminal height of 5000 meters above sea level, what is the temperature? Do the same calculation for a H_2 atom. [Hint: To calculate the altitude, h, the molecule will travel, equate its kinetic energy with the potential energy, mgh, where m is the mass and g is the acceleration due to gravity (9.81 m s^{-2}).]

Q2.63

Calculate the root-mean-square speed in cm/s for the following particles (hint, what is the average speed?): 0.010, 0.043, 0.027, 0.012, 0.041, 0.023, 0.011, 0.004, 0.007, and 0.009 (all in m/s).

Q2.63

The root-mean-square speed of 6 particles is 2.47 ms^{-1}. The speed of 5 of the particles are 1.0, 2, 1.5, 3.0 and Q2.5. Calculate the unknown speed of the 6th particle. Find the average speed of the 6 particles.

S2.63

The root-mean-square of the ensemble of particles is

$$v_{rms} = \sqrt{\frac{\sum_{i=1}^{6} c_i^2}{m}} \tag{2.E.39}$$

$$2.47 = \sqrt{\frac{1.0^2 + Q2.0^2 + 1.5^2 + 3.0^2 + 2.5^2 + c_6}{6}} \tag{2.E.40}$$

We solve for c_6 and we get

$$c_6^2 = (Q2.47ms^{-1})^2(6) - (1.0^2 + 2.0^2 + 1.5^2 + 3.0^2 + 2.5^2)\ m^2s^{-2} \tag{2.E.41}$$

$$c_6^2 = 36.6m^2s^{-2} - 22.5m^2s^{-2} \tag{2.E.42}$$

$$c_6^2 = 14.1m^2s^{-2} \tag{2.E.43}$$

$$c_6 = 3.75ms^{-1} \tag{2.E.44}$$

The average speed of the 6 particles is

$$\bar{c} = \frac{\sum_{i=1}^{6} c_i}{N} \tag{2.E.45}$$

$$\bar{c} = \frac{(1.0 + Q2.0 + 1.5 + 3.0 + Q2.5 + 3.75)ms^{-1}}{6} \tag{2.E.46}$$

$$= 2.30ms^{-1} \tag{2.E.47}$$

Q2.64a

Compare the velocities of Oxygen and Hydrogen at room temperature (25°C) by computing their root mean square speed?

Q2.64b

The speeds of six gaseous molecules at a given temperature are 1.0m/s , 1.2m/s, 1.5m/s, 1.7m/s, 2.0m/s, and 2.3m/s.

a. Compare the root-mean-square (rms) speeds and the average speed of those molecules.
b. Is always the average speed of the molecules the smaller of the two? Explain.

S2.64b

a) The root-mean-square-speed of those gases:

\[v_{rms} = \sqrt{\dfrac{1}{N}*(v_1^{2}+v2^{2}+v_3^{2}+v_4^{2}+v_5^{2}+v_6^{2})}\]

$$= \sqrt{\frac{1}{N} * (1^2 + 1.2^2 + 1.5^2 + 1.7^2 + 2^2 + 2.3^2)} \tag{2.E.48}$$

$$= 1.68\ m/s \tag{2.E.49}$$

The average speed is :

\[v_{avg} = \dfrac{1+1.2+1.5+1.7+2+2.3}{6}\]

$$= 1.62\ m/s \tag{2.E.50}$$

b) The average speed is *always* smaller then the root-mean-square speed ~~because the average speed depends on the temperature, rather than the molecular sizes.~~

Q2.65

Calculate c_{mp} for a sample of $N_2(g)$ at 500K.

S2.65

$$c_{mp} = \sqrt{\frac{2RT}{M}} \tag{2.E.51}$$

$$c_{mp} = \sqrt{\frac{2\,(8.314J\,K^{-1}\,mol^{-1})(500K)}{.02802kg\,mol^{-1}}} = 545m\;s^{-1} \tag{2.E.52}$$

Q2.66

Using the initial equation $f(c) = 4\pi c^2 \frac{m}{\pi K_BT}^{3/2} e^{-\frac{mc^2}{2K_BT}}$ derive an expression for c_{mp}

S2.66

Step 1: $$f(c)=4\pi c^2 \dfrac{m}{\pi K_BT} ^{3/2} e^{-\dfrac{mc^2}{2K_BT}}\]

$$=c^2 \dfrac{m}{\pi K_BT} ^{3/2} e^{-\dfrac{mc^2}{2K_BT}}\]

Step 2: (Hint: Apply the chain rule to c^2 and $e^{-\frac{mc^2}{2K_BT}}$)

$$\frac{df(c)}{dc} = 4\pi \frac{m}{2\pi K_BT}^{3/2} [2ce^{-\frac{mc^2}{2K_BT}} + c^2 e^{-\frac{mc^2}{2K_BT}} - \frac{mc}{2K_BT}] \tag{2.E.53}$$

Step 3:

$$4\pi (\frac{m}{2\pi K_BT})^{3/2} ce^{-\frac{mc^2}{2K_BT}} (2 - \frac{mc^2}{K_BT}) \tag{2.E.54}$$

Step 4: (Hint: Set $\frac{df(c)}{dc} = 0$, $c = c_{mp}$)

$$\pi (\frac{m}{2\pi K_BT})^{3/2} c_{mp} e^{-\frac{mc_{mp}^2}{2K_BT}} (2 - \frac{mc_{mp}^2}{K_BT}) = 0 \tag{2.E.55}$$

Step 5:

$$2 - \frac{mc_{mp}^2}{K_BT} = 0 \tag{2.E.56}$$

Step 6:

$$c_{mp}^2 = \frac{2K_BT}{m} \tag{2.E.57}$$

Step 7: (Hint: Use Avogadro's number)

$$c_{mp}^2 = \frac{2K_BT}{m}\frac{N_A}{N_A} = \frac{2RT}{M} \tag{2.E.58}$$

Step 8:

$$c_{mp} = \sqrt{\frac{2RT}{M}} \tag{2.E.59}$$

Q2.68a

Calculate the value of c_{mp} for CH_3OH at 30°C. What is the ratio of the number of molecules of speed 400 m s^{-1} to the number of molecules of speed c_{mp}?

Q2.68b

Calculate the value of the most probable speed, average speed, and the root-mean-square speed for C_5H_{12} at 25°C.

S2.68b

$$c_{mp} = \sqrt{\frac{2RT}{M}} = \sqrt{\frac{2(8.314J/K*mol)(298.15K)}{72.15\times10^{-3}kg/mol}} = 26Q2.13m/s \tag{2.E.60}$$

$$\begin{aligned} \bar{c} &= \sqrt{\frac{8RT}{\pi*M}} = \sqrt{\frac{4}{\pi}}*\sqrt{\frac{2RT}{M}} = \sqrt{\frac{4}{\pi}}*c_{mp} \\ &= \sqrt{\frac{4}{3.14159}}*262.13\ m/s = 295.78m/s \\ c_{rmp} &= \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3}{2}}*\sqrt{\frac{2RT}{M}} = \sqrt{\frac{3}{2}}*c_{mp} \\ &= \sqrt{\frac{3}{2}}*262.13\ m/s = 321.04\ m/s \end{aligned}$$

Q2.68

Calculate the value of c_{mp} for CH_3OH at 30°C. What is the ratio of the number of molecules of speed 400 m s^{-1} to the number of molecules of speed c_{mp}?

2.8: Molecular Collisions and the Mean Free Path

Q2.69

You open a container that has 1 mole of Neon gas and 1 mole of hydrogen gas. Hydrogen gas moves at faster speeds than Neon.

a. Compare the mean free path between the two gases in a closed room.
b. Assume travels across the room and there are no collision between molecules. Which gas reaches the other end first?

S2.69

a. The Neon gas molecules are larger than the Hydrogen gas molecules. This decreases the distance the molecules have to travel before they run into each other. For this reason, the mean free path for Neon will be lower than the mean free path for Hydrogen.
b. Since there are no collisions between molecules the mean free path does not play a role in this case. Therefore, Hydrogen will reach the other end first because it travels faster than Neon.

Q2.70a

How many times is the average distance between collision for a gas molecule larger than its molecular diameter, given that Pressure

P_o= 780mm Hg, and temperature T=300K, molecular diameter is $2x10^{-10}$ meters.

Q2.70b

The mean free path of gas molecules is given as:

$$\gamma = \frac{1}{\sqrt{2}\pi d^2(N/V)} \tag{2.E.61}$$

a. rewrite the equation so that the mean free path is expressed in terms of gas pressure
b. Name some that factors affect this property directly and indirectly?
c. Consider a gas piston containing only hydrogen gas. While not changing the temperature, there observed to be an increase in the mean free path of the gas molecules. What action could have caused this to happen?

Hint: Look at concept of mean free path

S2.70b

Mean free path is the average distance molecules traveled between each successive collision. Think of what could have affect this distance

a)

$$PV = nRT \Rightarrow V = \frac{nRT}{P} \tag{2.E.62}$$

$$N/V = \frac{N}{n}\frac{P}{RT} \tag{2.E.63}$$

$$but(N/n) = N_A \tag{2.E.64}$$

$$\Rightarrow \frac{N}{V} = \frac{PN_A}{RT} \Rightarrow \gamma = \frac{RT}{\sqrt{2}\pi d^2 PN_A} \tag{2.E.65}$$

b) direct factors: density and molecule's dameter, indirect factors: temperature, pressure, volume

c) An increase in mean free path means that the collisions are happen less frequently, therefore the density of the gas decreased. An action that could have caused this to happen is an increase in volume. A larger volume while molecules while not changing the number of molecules and speed lead to molecules are further apart and have less collisions.

Q2.70c

Gas A has a density of 0.835 g/cm3 and Gas B has a density of 14.67 g/cm3. From just this information, which do you expect to have a larger mean free path? Explain why.

S2.70c

We would expect gas A to have a larger mean free path.

Q2.71

A cylinder contains 25 molecules of an unknown ideal gas. What is the mean free path of the gas molecules? The cylinder has a volume of 20.0 cm^3 and the gas has an atomic radius of 1.24 Å. (1 cm = 10^8 Å)

S2.71

For an ideal gas, the mean free path is calculated by:

$$\lambda = \frac{\bar{c}}{Z_1} = \frac{1}{\sqrt{2}\pi d^2 \frac{N}{V}} \tag{2.E.66}$$

Thus, the mean free path of the unknown gas is:

$$\lambda = \frac{1}{\sqrt{2}\pi(1.24 \times 10^8\ cm)^2\ \frac{25}{20.0cm^2}} = 1.17 \times 10^{-17} cm = 1.17 \times 10^{-19} m \tag{2.E.67}$$

Q2.71

A rattle containing 50 spherical beads is shaken around by a toddler. What is the mean free path of the beads if the volume of the rattle is 500 cm^3 and the diameter of each individual bead is 0.2 cm?

S2.71

Use the appropriate equation and plug in given values.

$$\lambda = \frac{1}{\sqrt{2}\pi d^2(N/V)} \tag{2.E.68}$$

$$\lambda = \frac{1}{\sqrt{2}\pi(\frac{0.2}{100}m)^2(50beads/\frac{500}{100}m^3)} \tag{2.E.69}$$

$$\underline{\lambda = 1.8 \cdot 10^{-4}\ \ m} \tag{2.E.70}$$

Click here for more details about mean free path.

Q2.72a

Calculate the mean free path and the binary number of collisions per liter per second between Ar molecules at 298 K and 1.00 atm. Use 3.62 Å as the collision diameter of the Ar molecules. Assume ideal gas behavior.

Q2.72b

Calculate the mean free path and the binary number of collisions per liter per second between Ar molecules at 298 K and 1.00 atm. Use 3.62 Å as the collision diameter of the Ar molecules. Assume ideal gas behavior.

Q2.72c

CO_2 has a collision diameter of 0.4 nanometers. At 25 oC and 1.2 atm pressure, what is the mean free path between binary collisions, and what is the rate of binary collisions per liter assuming the volume contains only pure carbon dioxide gas behaving ideally?

Q2.72d

For the molecules HCl at 350K and 1.21 atm, calculate the mean free path and the binary number of collisions per liter per second. The collision diameter of HCl molecules is 5.50 Å. Assume the HCl acts as an ideal gas.

S2.72d

Step 1:

Calculate $\dfrac{N}{V}$ to calculate the mean free path

$$PV=NRT=\dfrac{N}{N_A}RT$$

Step 2:

$$\dfrac{N}{V}=\dfrac{PN_A}{RT}=\dfrac{(1.21atm)(6.022\times 10^{23}mol^{-1})}{(0.08206L\,atm\,K^{-1}mol^{-1})(350K)}=Q2.537$$

Step 3:

Turn L into m^{-3}

$$Q2.537\times 10^{22}L^{-1}(\dfrac{1000L}{1m^{3}})=Q2.537\times 10^{22}m^{-3}$$

Step 4:

$$\lambda=\dfrac{1}{\sqrt{2}\pi d^{2}(\dfrac{N}{V})}=\dfrac{1}{\sqrt{2}\pi (5.50\times 10^{-10}m)^{2}(Q2.537\times 10^{22}m^{-3})}=Q2.93\times 10^{-5}m$$

Calculating the binary number of collisions

Step 1: (Hint: Use the equation for average molecular speed.)

$$\bar{C}=\sqrt{\dfrac{8RT}{\pi M}}=\sqrt{\dfrac{8(8.3145JK^{-1}mol^{-1}(300K)}{\pi (36.46\times 10^{-3}\dfrac{kg}{mol})}}$$

Step 2:

$$z_{11}=\sqrt{\dfrac{2}{2}}\pi d^2\bar{C}\dfrac{N}{V}^{2}$$

$$=1.80526\times 10^{29}m^{-3}s^{-1}$$

Step 3: (Hint: Turn into $L^{-1}s^{-1}$)

$$z_{11}=\sqrt{\dfrac{2}{2}}\pi (5.50\times 10^{-10}m)^{2}(417.39ms^{-1})(\dfrac{1m^{3}}{1000L})=1.80527\times^{26}L^{-1}s^{-1}$$

Q2.73

In a 4L container you have 5 grams of 0Q2. Assume the collision diameter of 0_2 is 3.55 Angstrongs . Calculate the mean free path of the gas.

S2.73

The mean free path is given by

$$\lambda = \frac{1}{\sqrt{2}\pi d^2(\frac{N}{V})} \tag{2.E.71}$$

V is given and we can find $\left(\frac{N}{V}\right)$ by calculating N.

$$N = N_A.n = (6.022\times10^{23}mol^{-1})(5gO_2)(\frac{1mol}{32gO_2}) \tag{2.E.72}$$

$$N = 9.40\times10^{22} \tag{2.E.73}$$

$$\left(\frac{N}{V}\right) = \frac{9.41\times10^{22}}{4L} = Q2.35\times10^{22}L^{-1}(1000Lm^{-3}) \tag{2.E.74}$$

$$\left(\frac{N}{V}\right) = Q2.35\times10^{25}m^3 \tag{2.E.75}$$

The mean free path is

$$\lambda = \frac{1}{\sqrt{2}\pi d^2(\frac{N}{V})} \tag{2.E.76}$$

$$\lambda = \frac{1}{\sqrt{2}\pi(3.55\times10^{-10}m)^2(Q2.35\times10^{25}m^{-3})} = 7.60\times10^{-8}m \tag{2.E.77}$$

Q2.74a

If a sealed container has of xenon molecules traveling at a speed of 24.6 m/s at 108 °C. How many moles of xenon gas do we have in the container?

S2.74a

$$\bar{E}_{trans} = \frac{1}{2}mv^2 = \frac{3}{2}k_BT$$

$$m = \frac{3k_BT}{v^2} = \frac{3(1.381\times10^{-23}J/K)(381.15K)}{(24.6m/s)^2} * \frac{1kg*m^2/s^2}{1J} = Q2.609\times10^{-23}kg$$

$$n = \frac{m}{molarmass} = Q2.609\times10^{-23}kg*\frac{1000g}{1kg} * \frac{mol}{131.3g} = 1.987\times10^{-22}mol$$

Q2.74b

At room temperature (25oC) there are two flasks A and B containing gaseous Oxygen and Hydrogen, respectively, at their equilibrium states. Assuming there is no exchange of heat or work between the systems inside the flasks and the surroundings. Compare the initial velocities between an Oxygen and a Hydrogen molecule in each flask.

Q2.76a

In a insulated container of volume 2.50 L filled with nitrogen gas, the Z_1 value is $6.75e^{19}$ collisions/second. The temperature measured is 55ºC. Assuming that the collision diameter of N_2 is 3.75 Å,

a. how many moles of nitrogen gas are present the container?
b. find the Z_{11} value of the gas.
c. How does the number of moles affect Z_1 and Z_{11} values of the gas?

Hint: look at collision frequency

S2.76a

a)

$$Z_1=\sqrt{2}\pi d^2\bar{c}(\frac{N}{V}) \tag{2.E.78}$$

$$\Rightarrow N=\frac{VZ_1}{\sqrt{2}\pi d^2\bar{c}} \tag{2.E.79}$$

$$\bar{c}=\sqrt{\frac{8RT}{\pi M}}=\sqrt{\frac{8(8.314\frac{J}{mol\cdot K})(55+273)K}{\pi\cdot 0.014kg})}=704.3m/s \tag{2.E.80}$$

$$N=\frac{(2.50L)(\frac{1m^3}{1000L})(6.75\times 10^{19}collision/s)}{\sqrt{2}\pi(3.75\times 10^{-10}m)^2(704.3m/s)}=1.017\times 10^{23}molecules \tag{2.E.81}$$

$$n=\frac{N}{N_A}=\frac{1.017\times 10^{23}molecules}{6.022\times 10^{23}\frac{molecules}{mole}}=0.169moleN_2 \tag{2.E.82}$$

b)

$$Z_{11}=\frac{1}{2}Z_1(\frac{N}{V}) \tag{2.E.83}$$

$$Z_{11}=\frac{1}{2}(6.75\times 10^{19})\frac{1.017\times 10^{23}molecules}{2.50L\times\frac{1m^3}{1000L}}=1.37\times 10^{45}\frac{collisions}{m^3\cdot s} \tag{2.E.84}$$

c) Since N = nN_A and Z_1 is proportional to N, therefore

$$Z_1\propto n \tag{2.E.85}$$

similarly, Z_{11} is proportional to N^2, therefore:

$$Z_{11}\propto n^2 \tag{2.E.86}$$

Q2.76b

For molecular oxygen at 56^oC, calculate the number of collisions a single molecule makes in 1 second and the total number of binary collisions at P=1.0 atm and P=0.25 atm. How does pressure relate to these two quantities? The collision diameter of oxygen is 3.02 A.

S2.76b

Step 1: (Hint: Calculate the density and average molecular speed)

At P=1.0atm

$$\dfrac{N}{V}=\dfrac{PN_A}{RT}=\dfrac{(1.0atm)(6.022\times 10^{23}mol^{-1})}{0.08206\,L\,atm\,K^{-1}mol^{-1})(273+56)}=Q2.23\times 10^{22}L^{-1}(\dfrac{1000L}{1m^{3}})=2.23\times 10^{22}m^{-3}\]

Step 2:

$$\bar{c}=\sqrt{\dfrac{8RT}{\pi M}}=\sqrt{\dfrac{8(8.3145JK^{-1}mol^{-1})(273+56K)}{\pi (31.998\times 10^{-3}kg\,mol^{-1})}}=466.578ms^{-1}\]

Step 3:

$$z_1=\sqrt{2}\pi d^2\bar{c}\dfrac{N}{V}=\sqrt{2}\pi(3.02\times 10^{-10}m)^{2}(466.578ms^{-1})(2.23\times 10^{22}m^{-3})=4.683\times 10^{28} collisions m^{-3}s^{-1}\]

Step 4:

$$z_{11}=\dfrac{\sqrt{2}}{2}\pi d\bar{c}(\dfrac{N}{V})^{2}=\dfrac{1}{2}(4.2\times 10^{6})(2.23\times 10^{22}m^{-3})=4.683\times 10^{28} collisionsm^{-3}s^{-1}\]

For an ideal gas, z_1 is proportional to P and z_{11} is proportional to P^2. Reducing P to a fourth of its original value (from 1.0 atm to 0.25 atm) will also reduce 2, to one fourth its value at P=1.0atm.

Therefore at P=0.25 atm,

$$z_1 = 4.2\times 10^5 \, collisions\, s^{-1}\$\$\$\$ z_{11} = 4.683\times 10^{26}\, collisions\, m^{-3}\, s{-}1 \tag{2.E.87}$$

Q2.77a

The relationship between the molar mass and root mean square speed of an ideal gas can be described as:

$$v_{rms} = \sqrt{\frac{3RT}{\mathfrak{M}}} \tag{2.E.88}$$

Use this equation to derive Grahm's Law of Effusion:

$$\frac{r_1}{r_2} = \sqrt{\frac{\mathfrak{M}_2}{\mathfrak{M}_1}} \tag{2.E.89}$$

S2.77a

For two gasses at standard temperature and pressure,

$$v_{1rms} = \sqrt{\frac{3RT}{\mathfrak{M}_1}} \qquad v_{2rms} = \sqrt{\frac{3RT}{\mathfrak{M}_2}} \tag{2.E.90}$$

For any of the two gases,

$$v_{1rms}^2 = \frac{3RT}{\mathfrak{M}_1} \qquad v_{2rms}^2 = \frac{3RT}{\mathfrak{M}_2} \tag{2.E.91}$$

$$R = \frac{v_{1rms}^2\mathfrak{M}_1}{3T} = \frac{v_{2rms}^2\mathfrak{M}_2}{3T} \tag{2.E.92}$$

$$v_{1rms}^2\mathfrak{M}_1 = v_{2rms}^2\mathfrak{M}_2 \tag{2.E.93}$$

$$\frac{v_{1rms}^2}{v_{2rms}^2} = \frac{\mathfrak{M}_2}{\mathfrak{M}_1} \tag{2.E.94}$$

$$\frac{v_{1rms}}{v_{2rms}} = \sqrt{\frac{\mathfrak{M}_2}{\mathfrak{M}_1}} \tag{2.E.95}$$

Which can be rewritten as:

$$\frac{r_1}{r_2} = \sqrt{\frac{\mathfrak{M}_2}{\mathfrak{M}_1}} \tag{2.E.96}$$

2.9: Graham's Laws of Diffusion and Effusion

Q2.77b

Derive Graham's Law of Effusion (1) from the equation for calculating Kinetic Energy (2).

$$(1) \quad \frac{v_1}{v_2} = \sqrt{\frac{m_2}{m_1}} \tag{2.E.97}$$

$$(2) \quad KE = \frac{1}{2}mv^2 \tag{2.E.98}$$

S2.77b

$$\frac{v_1}{v_2}=\sqrt{\frac{m_2}{m_1}}\;\; KE=\frac{1}{2}mv^2 \tag{2.E.99}$$

$$KE_1=KE_2,\; for\; two\; substances \tag{2.E.100}$$

$$\frac{1}{2}m_1v_1^2=\frac{1}{2}m_2v_2^2,\; multiply\; both\; sides\; by\; two \tag{2.E.101}$$

$$m_1v_1^2=m_2v_2^2 \tag{2.E.102}$$

$$\frac{v_1^2}{v_2^2}=\frac{m_2}{m_1},\; square\; root\; both\; sides\; of\; the\; equation \tag{2.E.103}$$

$$\frac{v_1}{v_2}=\sqrt{\frac{m_2}{m_1}} \tag{2.E.104}$$

Click here and here for more information about effusion and Graham's law.

Q2.78a

How long would it take for oxygen to diffuse in and carbon dioxide to diffuse out of a cell that is 0.1µm^2 thick given that the rate of diffusion of carbon dioxide is 0.0016 mm^2/s?

S2.78a

$$\frac{t_{CO_2}}{t_{O_2}}=\frac{r_{O_2}}{r_{CO_2}}=\sqrt{\frac{M_{CO_2}}{M_{O_2}}}$$

$$r_{O_2}=(0.0016mm^2/s)\sqrt{\frac{44.01g/mol}{3Q2.0g/mol}}=0.0019mm^2/s$$

$$t_{CO_2}=0.1\mu m^2*\frac{(1mm)^2}{(100\mu m)^2}*\frac{s}{0.0016mm^2}=6.25\times10^{-3}s$$

$$t_{O_2}=0.1\mu m^2*\frac{(1mm)^2}{(100\mu m)^2}*\frac{s}{0.0019mm^2}=5.26\times10^{-3}s$$

Q2.78b

A sample of red gas collected from the emissions of a paper mill effuses through an orifice of unknown size at standard temperature and pressure in 14.1 minutes. Pure diatomic nitrogen gas at standard temperature and pressure effuses through the hole in 11.0 minutes. What is the red gas? How do you know?

S2.78b

m_{N2} = 28.01 g/mol

$t_{N2}/t_{unk} = (m_{unk}/m_{N2})^{1/2}$

$m_{unk} = (t_{N2}/t_{unk})^2 * m_{N2}$ = (14.1 min/11.0 min)^2 * 28.01 g mol^{-1}
m_{unk} = 46.02 g mol^{-1}

The red gas is nitrogen dioxide, a common emission from pulp mills. We know because the diffusion rate corresponds with a molar mass of 46.01g, the molar mass of NO_2

Q2.80

An amount of CO_2 gas is effused through a small opening at the rate of 0.596 L/min. A homogenous mixture of O_2 and N_2 in the atmosphere is put under the same conditions for effusion and after 5 minutes, 5.03 L of the mixture was effused. Find the percent composition of the homogenous mixture (molar fraction).

Hint: Look at concept of effusion and its rate

S2.80

$$\frac{r_{CO_2}}{r_{mixture}} = \sqrt{\frac{M_{mixture}}{M_{CO_2}}} \tag{2.E.105}$$

$$M_{mixture} = (\frac{r_{CO^2}}{r_{mixture}})^2(M_{CO_2}) = (\frac{0.596\frac{L}{min}}{\frac{5.03L}{5min}})^2(44.01\frac{g}{mol}) = 15.447\frac{g}{mol} \tag{2.E.106}$$

$$M_{mixture} = M_{N_2}X_{N_2} + M_{O_2}X_{O_2} \tag{2.E.107}$$

$$M_{mixture} = M_{N_2}X_{N_2} + M_{O_2}(1 - X_{N_2}) \tag{2.E.108}$$

$$15.447\frac{g}{mol} = (14.01\frac{g}{mol})(X_{N_2}) + (16.00\frac{g}{mol})(1 - X_{N_2}) \tag{2.E.109}$$

$$15.447 = 14.01X_{N_2} + 16.00 - 16.00X_{N_2} = -1.99X_{N_2} + 16.00 \tag{2.E.110}$$

$$X_{N_2} = 0.278 \tag{2.E.111}$$

$$X_{O_2} = 1 - 0.278 = 0.722 \tag{2.E.112}$$

$$\% of N_2 = 27.8\% \tag{2.E.113}$$

$$\% of O_2 = 72.2\% \tag{2.E.114}$$

Q2.81a

You are trying to isolate gaseous Nitrogen-14 via effusion in a 50:50 mixture of Nitrogen-14 and Nitrogen-15 respectively. What will be the percentage of enrichment of the mixture after a single stage of separation?

S2.81a

Use Graham's Law of Diffusion and Effusion to solve this problem.

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}} \tag{2.E.115}$$

$$\frac{rate\ of\ {}^{14}\text{N}}{rate\ of\ {}^{15}\text{N}} = \sqrt{\frac{{}^{15}\text{N}}{{}^{14}\text{N}}} \tag{2.E.116}$$

$$\frac{rate\ of\ {}^{14}\text{N}}{rate\ of\ {}^{15}\text{N}} = \sqrt{\frac{15.0001\ g\,mol^{-1}}{14.00307\ g\,mol^{-1}}} \tag{2.E.117}$$

$$\frac{rate\ of\ {}^{14}\text{N}}{rate\ of\ {}^{15}\text{N}} = 1.035 \tag{2.E.118}$$

Since the ratio of rates of effusion is 1.035, in a single step of separation 3.5% more nitrogen-14 will effuse out of the mixture than nitrogen-15. Thus the percent of enrichment would be 3.5% since there is 3.5% more of N-14 now.

Click here and bhere for more information about effusion and Graham's law.

Q2.81b

A mixture of Neon and Helium gas is effused at standard temperature and pressure. Assuming the mixture is equimolar, what is the composition of the gas mixture after effusion?

S2.81b

For the effusion of a binary gas mixture, we can use Graham's Law:

$$\frac{r_1}{r_2} = \sqrt{\frac{\mathfrak{M}_2}{\mathfrak{M}_1}} \tag{2.E.119}$$

The ratio of the two gasses following effusion given r_1 corresponds with neon and r_2 corresponds with helium is:

$$\frac{r_1}{r_2} = \sqrt{\frac{4.003\frac{g}{mol}}{20.180\frac{g}{mol}}} = 0.4454 \tag{2.E.120}$$

Therefore, to calculate the mole fraction of each gas,

$$x_{Ne} = \frac{0.4454}{0.4454+1} = 0.3081 \tag{2.E.121}$$

$$x_{He} = 1 - x_{Ne} = 1 - 0.3081 = 0.6919 \tag{2.E.122}$$

Q2.82

An equimolar mixture of diatomic nitrogen gas and an unknown monatomic gas diffuse through an aperture of unknown size. It is determined that 1.18 times as many moles of the monatomic gas pass through the opening as moles of nitrogen gas. What is the gas?

Q2.82

m_{N2} = 28.01 g mol^{-1}

$n_{unk}/n_{N2} = (m_{N2}/m_{unk})^{1/2}$

$m_{unk} = m_{N2}/(n_{unk}/n_{N2})^{2} =$ 28.01 g $mol^{-1}/(1.18)^2$ = 20.11 g mol^{-1}

The gas is monatomic and has a mass of roughly 20.11 g/mol, so Neon is the most likely gas.

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CHAPTER OVERVIEW

3: The First Law of Thermodynamics

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3.1: Work and Heat

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

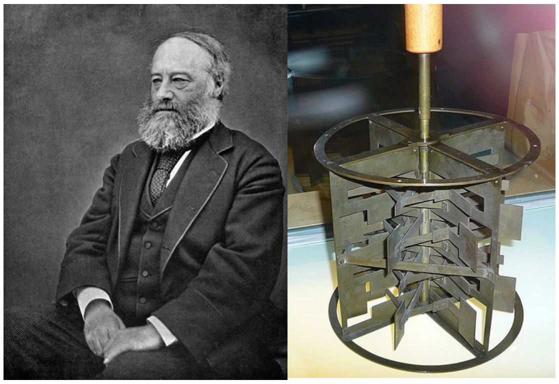

Figure *[Math Processing Error]*: (left) James Prescott Joule (1818 - 1889) (right) Joule's apparatus for measuring the work equivalent of heat. (CC BY-SA 3.0; Dr. Mirko Junge)

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 (*[Math Processing Error]*) can be calculated by

[Math Processing Error]

where the subscripts *[Math Processing Error]* and *[Math Processing Error]* indicate initial and final states of the system. *[Math Processing Error]* 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

[Math Processing Error]

or

[Math Processing Error]

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

Heat

Heat is the kind of energy that in the absence of other changes would have the effect of changing the temperature of the system. A process in which heat flows into a system is **endothermic** from the standpoint of the system (*[Math Processing Error]*, *[Math Processing Error]*). Likewise, a process in which heat flows out of the system (into the surroundings) is called **exothermic** (*[Math Processing Error]*, *[Math Processing Error]*). 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

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

[Math Processing Error]

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 *[Math Processing Error]*: 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

[Math Processing Error]

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 *[Math Processing Error]* by

[Math Processing Error]

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

[Math Processing Error]

So that each contribution to the total change in the function *[Math Processing Error]* 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.

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The partial derivatives of p can be expressed in terms of *[Math Processing Error]* and *[Math Processing Error]* as well.

[Math Processing Error]

and

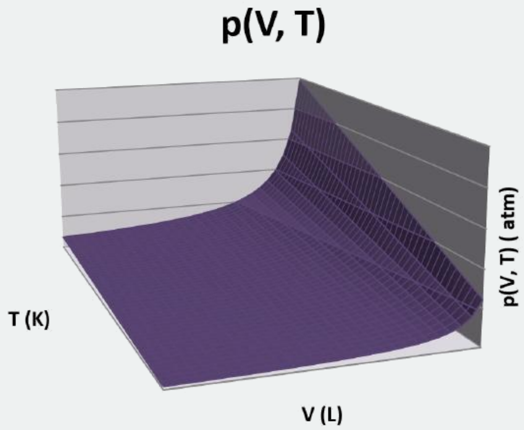
[Math Processing Error]

So that the change in pressure can be expressed

[Math Processing Error]

or by substituting Equations *[Math Processing Error]* and *[Math Processing Error]*

[Math Processing Error]



Macroscopic changes can be expressed by integrating the individual pieces of Equation *[Math Processing Error]* over appropriate intervals.

[Math Processing Error]

This can be thought of as two consecutive changes. The first is an **isothermal** (constant temperature) expansion from *[Math Processing Error]* to *[Math Processing Error]* at *[Math Processing Error]* and the second is an **isochoric** (constant volume) temperature change from *[Math Processing Error]* to *[Math Processing Error]* at *[Math Processing Error]*. 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.

[Math Processing Error]

or

[Math Processing Error]

Alternatively, one could calculate the change as an isochoric temperature change from *[Math Processing Error]* to *[Math Processing Error]* at *[Math Processing Error]* followed by an isothermal expansion from *[Math Processing Error]* to *[Math Processing Error]* at *[Math Processing Error]*:

[Math Processing Error]

or

[Math Processing Error]

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

Work

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

Table 3.1.1: Changes to the System

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

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

✓ Example *[Math Processing Error]*: 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

[Math Processing Error]

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

[Math Processing Error]

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

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3.2: The First Law of Thermodynamics

12.4: The First Law of Thermodynamics

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3.3: Heat Capacities

Let us turn our attention from the macroscopic to the microscopic level. According to the first law of thermodynamics, the heat energy absorbed as we raise the temperature of a substance cannot be destroyed. But where does it go? In the case of a monatomic gas, like neon, this question is easy to answer. All the energy absorbed is converted into the kinetic energy of the neon molecules (atoms). In other sections, we found that the kinetic energy of the molecules in a sample of gas is given by the expression

[Math Processing Error]

Thus if the temperature of a sample of neon gas is raised from T_1 to T_2, the kinetic energy of the molecules increases from $^{3}/_{2}\,nRT_1$ to $^{3}/_{2}\,nRT_2$, a total change of

[Math Processing Error]

Inserting the value of R in appropriate units, we obtain

[Math Processing Error]

This is the same quantity that is obtained by substituting the experimental value of C_V for neon (calculated in Example 2 from Heat Capacities) into Eq. (4) from Heat Capacities. In other words the quantity of heat found experimentally exactly matches the increase in kinetic energy of the molecules required by the kinetic theory of gases.

Table *[Math Processing Error]* lists the C_V values not only for neon but for some other gases as well. We immediately notice that only the noble gases and other mon-atomic gases such as Hg and Na have molar heat capacities equal to $^{3}/_{2}R$, or 12.47 J K^{-1} mol^{-1}. All other gases have higher molar heat capacities than this. Moreover, as the table shows, the more complex the molecule, the higher the molar heat capacity of the gas. There is a simple reason for this behavior.

Table *[Math Processing Error]*: Molar Heat Capacities at Constant Volume (CV) for Various Gases (Values at 298 K Unless Otherwise Stated).

Gas	C_v /J K^{-1} mol^{-1}	Gas	C_v /J K^{-1} mol^{-1}
Monoatomic Gases		**Triatomic Gases**	
Ne	12.47	CO_2	28.81
Ar	12.47	N_2O	30.50
Hg	12.47 (700K)	SO_2	31.56
Na	12.47 (1200K)		
Diatomic Gases		**Alkanes**	
N_2	20.81	CH_4	27.42
O_2	21.06	C_2H_6	44.32
Cl_2	25.62	C_3H_8	65.20
		C_4H_{10}	89.94

A molecule which has two or more atoms is not only capable of moving from one place to another (**translational motion**), it can also *rotate* about itself, and it can change its shape by *vibrating*. When we heat a mole of Cl_2 molecules, for example, we not only need to supply them with enough energy to make them move around faster (increase their translational kinetic energy), we must also supply an additional quantity of energy to make them rotate and vibrate more strongly than before. For a mole of more complex molecules like *n*-butane even more energy is required since the molecule is capable of changing its shape in all sorts of ways. In the butane molecule there are three C—C bonds around which segments of the molecule can rotate freely. All the bonds can bend or stretch, and the whole molecule can rotate as well. Such a molecule is constantly flexing and writhing at room temperature. As we raise the temperature, this kind of movement occurs more rapidly and extra energy must be absorbed in order to make this possible.

When we heat solids and liquids, the situation is somewhat different than for gases. The rapid increase of vapor pressure with temperature makes it virtually impossible to heat a solid or liquid in a closed container, and so heat capacities are always measured at constant pressure rather than at constant volume. Some C_p values for selected simple liquids and solids at the melting point are shown in Table *[Math Processing Error]*. In general the heat capacities of solids and liquids are higher than those of gases. This is because of the intermolecular forces operating in solids and liquids. When we heat solids and liquids, we need to supply them with potential energy as well as kinetic energy. Among the solids, the heat capacities of the metals are easiest to explain since the solid consists of individual atoms. Each atom can only vibrate in three dimensions. According to a theory first suggested by Einstein, this vibrational energy has the value $3RT$, while the heat capacity is given by $3R = 24.9\ \text{J K}^{-1}\ \text{mol}^{-1}$.

Table *[Math Processing Error]*: Molar Heat Capacities at Constant Pressure Cp for Various Solids and Liquids at the Melting Point.

Substance	C_p (solid)/J K^{-1} mol^{-1}	C_p (liquid)/J K^{-1} mol^{-1}
Monoatomic Substances		
Hg	27.28	27.98
Pb	29.40	30.33
Na	28.20	31.51
Diatomic Substances		
Br_2	53.8	75.7
I_2	54.5	80.7
HCl	50.5	62.2
HI	47.5	68.6
Polyatomic Substances		
H_2O	37.9	76.0
NH_3	49.0	77.0
Benzene	129.0	131.0
n-Heptane	146.0	203.1

As can be seen from the table, most monatomic solids have C_p values slightly larger than this. This is because solids expand slightly on heating. The atoms get farther apart and thus increase in potential as well as vibrational energy.

Solids which contain molecules rather than atoms have much higher heat capacities than $3R$. In addition to the vibration of the whole molecule about its site in the crystal lattice, the individual atoms can also vibrate with respect to each other. Occasionally molecules can rotate in the crystal, but usually rotation is only possible when the solid melts. As can be seen from the values for molecular liquids in Table *[Math Processing Error]*, this sudden ability to rotate causes a sharp increase in the heat capacity. For monatomic substances, where there is no motion corresponding to the rotation of atoms around each other, the heat capacity of the liquid is only very slightly higher than that of the solid.

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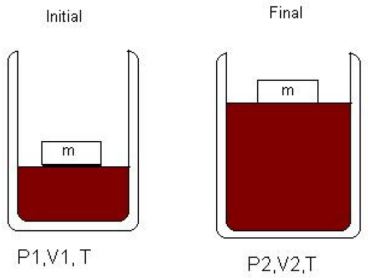
3.4: Gas Expansion

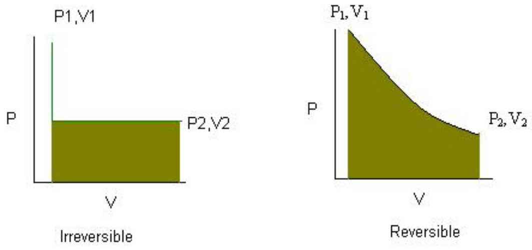
In Gas Expansion, we assume Ideal behavior for the two types of expansions:

Isothermal Expansion



This shows the expansion of gas at constant temperature against weight of an object's mass (m) on the piston. Temperature is held constant, therefore the change in energy is zero (U=0). So, the heat absorbed by the gas equals the work done by the ideal gas on its surroundings. Enthalpy change is also equal to zero because the change in energy zero and the pressure and volume is constant.

Isothermal Irreversible/Reversible process



The graphs clearly show work done (area under the curve) is greater in a reversible process.

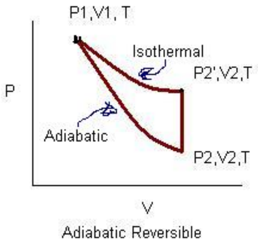
Adiabatic Expansions

Adiabatic means when no heat exchange occurs during expansion between system and surrounding and the temperature is no longer held constant.

Reversible Adiabatic Expansion

This equation shows the relationship between PV and is useful only when it applies to ideal gas and reversible adiabatic change. The equation is very similar to Boyle's law except it has exponent (gamma) due to change in temperature. The work done by an adiabatic reversible process is given by the following equation:

where T_2 is less than T_1. The internal energy of the system decreases as the gas expands. The work can be calculated in two ways because the Internal energy (U) does not depend on path. The graph shows that less work is done in an adiabatic reversible process than an Isothermal reversible process.



References

1. Chang, Raymond. Physical Chemistry for the Biosciences. Sausalito, CA: University Science, 2005.

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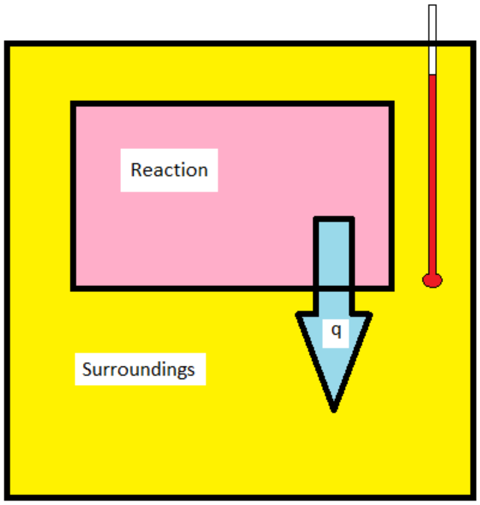
3.5: Calorimetry

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

Calorimetry

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



Bomb Calorimetry

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

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

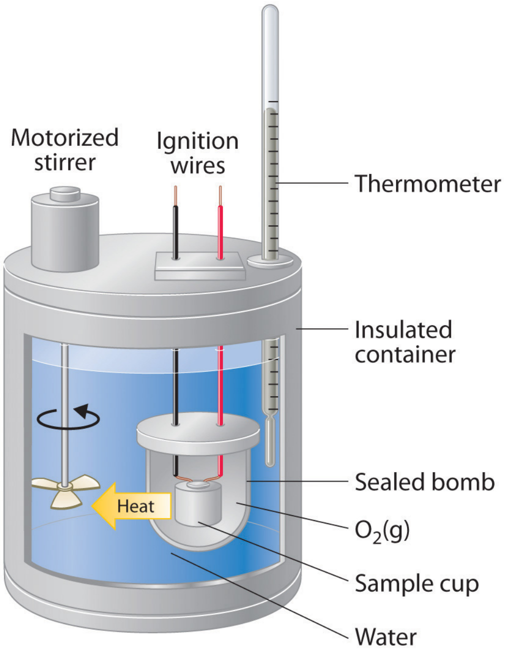


Figure 3.5.1: A Bomb Calorimeter. After the temperature of the water in the insulated container has reached a constant value, the combustion reaction is initiated by passing an electric current through a wire embedded in the sample. Because this calorimeter operates at constant volume, the heat released is not precisely the same as the enthalpy change for the reaction. (CC BY-SA-NC; Anonymous by request).

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

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

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

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

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

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

Finding ΔU_c

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

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

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

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

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

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

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

✓ Example 3.5.1: Combustion of Naphthalene

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

Solution

First, the water equivalent:

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

Then ΔU_c for the sample:

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

ΔH_c is then given by

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

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

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

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

So

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

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

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3.6: Thermochemistry

The standard enthalpy of formation is defined as the change in enthalpy when one mole of a substance in the standard state (1 atm of pressure and 298.15 K) is formed from its pure elements under the same conditions.

Introduction

The standard enthalpy of formation is a measure of the energy released or consumed when one mole of a substance is created under standard conditions from its pure elements. The symbol of the standard enthalpy of formation is ΔH_f.

- Δ = A change in enthalpy
- ^{o} = A degree signifies that it's a standard enthalpy change.
- f = The f indicates that the substance is formed from its elements

The equation for the standard enthalpy *change* of formation (originating from Enthalpy's being a State Function), shown below, is commonly used:

[Math Processing Error]

This equation essentially states that the standard enthalpy *change* of formation is equal to the **sum of the standard enthalpies of formation of the *products*** minus the **sum of the standard enthalpies of formation of the *reactants***.

Example *[Math Processing Error]*

Given a simple chemical equation with the variables A, B and C representing different compounds:

[Math Processing Error]

and the standard enthalpy of formation values:

- $\Delta H_f^o[A] = 433$ KJ/mol
- $\Delta H_f^o[B] = -256$ KJ/mol
- $\Delta H_f^o[C] = 523$ KJ/mol

the equation for the standard enthalpy change of formation is as follows:

$$\Delta H_{reaction}^{o} = \Delta H_f^o[C] - (\Delta H_f^o[A] + \Delta H_f^o[B])$$

$$\Delta H_{reaction}^{o} = (1\ \cancel{mol})(523\ kJ/\cancel{mol}) - ((1\ \cancel{mol})(433\ kJ/\cancel{mol}) + (1\ \cancel{mol})(-256\ kJ/\cancel{mol})\backslash)$$

Because there is one mole each of A, B and C, the standard enthalpy of formation of each reactant and product is multiplied by 1 mole, which eliminates the mol denominator:

$$\Delta H_{reaction}^{o} = \mathbf{346\ kJ}$$

The result is 346 kJ, which is the standard enthalpy change of formation for the creation of variable "C".

> The standard enthalpy of formation of a pure element is in its reference form its standard enthalpy formation is **zero**.

Carbon naturally exists as graphite and diamond. The enthalpy difference between graphite and diamond is too large for both to have a standard enthalpy of formation of zero. To determine which form is zero, the more stable form of carbon is chosen. This is also the form with the lowest enthalpy, so graphite has a standard enthalpy of formation equal to zero. Table 1 provides sample values of standard enthalpies of formation of various compounds.

Table 1: Sample Table of Standard Enthalpy of Formation Values. Table T1 is a more comprehensive table.

Compound	**ΔH_f^o**
$O_2(g)$	0 kJ/mol
C(graphite)	0 kJ/mol
CO(g)	-110.5 kJ/mol

Compound	ΔH_f^o
CO_2(g)	-393.5 kJ/mol
H_2(g)	0 kJ/mol
H_2O(g)	-241.8 kJ/mol
HF(g)	-271.1 kJ/mol
NO(g)	90.25 kJ/mol
NO_2(g)	33.18 kJ/mol
N_2O_4(g)	9.16 kJ/mol
SO_2(g)	-296.8 kJ/mol
SO_3(g)	-395.7 kJ/mol

All values have units of kJ/mol and physical conditions of 298.15 K and 1 atm, referred to as the "standard state." These are the conditions under which values of standard enthalpies of formation are typically given. Note that while the majority of the values of standard enthalpies of formation are exothermic, or negative, there are a few compounds such as NO(g) and N_2O_4(g) that actually require energy from its surroundings during its formation; these endothermic compounds are generally unstable.

✓ Example *[Math Processing Error]*

Between Br_2(l) and Br_2(g) at 298.15 K, which substance has a nonzero standard enthalpy of formation?

Solution

Br_2(l) is the more stable form, which means it has the lower enthalpy; thus, Br_2(l) has $\Delta H_f = 0$. Consequently, **Br_2(g) has a nonzero standard enthalpy of formation.**

Note: that the element phosphorus is a unique case. The reference form in phosphorus is not the most stable form, red phosphorus, but the less stable form, white phosphorus.

Recall that standard enthalpies of formation can be either positive or negative.

✓ Example *[Math Processing Error]*

The enthalpy of formation of carbon dioxide at 298.15K is ΔH_f = -393.5 kJ/mol CO_2(g). Write the chemical equation for the formation of CO_2.

Solution

This equation must be written for one mole of CO_2(g). In this case, the reference forms of the constituent elements are O_2(g) and graphite for carbon.

[Math Processing Error]

The general equation for the standard enthalpy change of formation is given below:

[Math Processing Error]

Plugging in the equation for the formation of CO_2 gives the following:

$$\Delta H_{reaction}^o = \Delta H_f^o[CO_2(g)] - (\Delta H_f^o[O_2(g)] + \Delta H_f^o[C(graphite)]$$

Because O_2(g) and C(graphite) are in their most elementally stable forms, they each have a standard enthalpy of formation equal to 0:

$$\Delta H_{reaction}^o = -393.5\text{ kJ} = \Delta H_f^o[CO_2(g)] - ((1\text{ mol})(0\text{ kJ/mol}) + (1\text{ mol})(0\text{ kJ/mol}))$$

$$\Delta H_f^o[CO_2(g)] = -393.5\text{ kJ}$$

Example [Math Processing Error]

Using the values in the above table of standard enthalpies of formation, calculate the $\Delta H_{reaction}{}^{o}$ for the formation of $NO_2(g)$.

Solution

[Math Processing Error] is formed from the combination of [Math Processing Error] and [Math Processing Error] in the following reaction:

[Math Processing Error]

To find the $\Delta H_{reaction}{}^{o}$, use the formula for the standard enthalpy change of formation:

[Math Processing Error]

The relevant standard enthalpy of formation values from Table 1 are:

- $O_2(g)$: 0 kJ/mol
- $NO(g)$: 90.25 kJ/mol
- $NO_2(g)$: 33.18 kJ/mol

Plugging these values into the formula above gives the following:

[Math Processing Error]

[Math Processing Error]

Kirchhoff's Law describes the enthalpy of a reaction's variation with temperature changes. In general, enthalpy of any substance increases with temperature, which means both the products and the reactants' enthalpies increase. The overall enthalpy of the reaction will change if the increase in the enthalpy of products and reactants is different.

Kirchoff's Law - Enthalpy is Temperature Dependent

At constant pressure, the heat capacity is equal to change in enthalpy divided by the change in temperature.

[Math Processing Error]

Therefore, if the heat capacities do not vary with temperature then the change in enthalpy is a function of the difference in temperature and heat capacities. The amount that the enthalpy changes by is proportional to the product of temperature change and change in heat capacities of products and reactants. A weighted sum is used to calculate the change in heat capacity to incorporate the ratio of the molecules involved since all molecules have different heat capacities at different states.

[Math Processing Error]

If the heat capacity is temperature independent over the temperature range, then Equation [Math Processing Error] can be approximated as

[Math Processing Error]

with

- [Math Processing Error] is the (assumed constant) heat capacity and
- [Math Processing Error] and [Math Processing Error] are the enthalpy at the respective temperatures.

Equation [Math Processing Error] can only be applied to small temperature changes, (<100 K) because over a larger temperature change, the heat capacity is not constant. There are many biochemical applications because it allows us to predict enthalpy changes at other temperatures by using standard enthalpy data.

Contributors and Attributions

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3.7: Bond Energies and 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** *[Math Processing Error]* is defined by

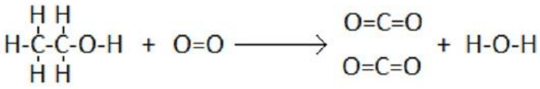
[Math Processing Error]

with *[Math Processing Error]*

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

[Math Processing Error]

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

[Math Processing Error]

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%.

Contributors and Attributions

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3.E: Exercises

Q3.6

Calculate the work done by the reaction

[Math Processing Error]

when 1 mole of hydrogen gas is collected at 273 K and 1.0 atm. (Neglect volume changes other than the change in gas volume, and assume that the has behaves ideally.)

Q3.11a

If the internal energy of 3 moles of Cl_2 is 3.96 KJ, what is the temperature of the system?

Q3.11b

The internal energy of 3 moles of neon gas (Ne) is 4.87 kJ. Assuming conditions are ideal, what is the temperature of the system?

S3.11b

Since we can assume that conditions are ideal, we know that the temperature is 25°C or 298 K. This assumption allows us to ignore the small change in volume of the gas.

Q3.12a

Some ice cubes are placed inside a sealed plastic bag on a hot day, what is the sign of *[Math Processing Error]*, *[Math Processing Error]*, *[Math Processing Error]*, *[Math Processing Error]*? What does this mean about the system?

Q3.12b

A sports bottle containing Gatorade is held in a man's hand while running on a treadmill. Suppose the Gatorade is the system in question. Answer the subsequent questions.

a. Will the temperature rise due to the movement caused by the man's running?
b. Was any heat actually added to the system? If so, what was the source?
c. Was work done onto the system?
d. In what ways has the internal energy of the system been affected, if affected at all?

S3.12b

a. The man's running motion causes the Gatorade to be shaken. The shaking motion adds energy to the system and increases the random motion of the molecules. Since the motion of the molecules rises, so does the temperature of the system.
b. Yes, heat exchange did occur between the system and its surroundings (the heat given off from the man's hand).
c. Yes, work was done onto the system via the shaking motion.
d. The internal energy has been increased.

Q3.12c

Consider an ice cube melting.

a. Is the change of enthalpy positive or negative for this process?
b. Is the change of entropy positive or negative for this process?

S3.12c

a. Enthalpy is positive because the ice must gain heat in order to melt.
b. Entropy is also positive because the water molecules are gaining kinetic energy and moving to a more disordered state.

Q3.13

2.5 moles of CO_2 expands against an external pressure of 1.5 atm. It was initially at 9.0 atm and 30^{o}C. The final volume is 35.0 L.

a. What is the final temperature?
b. Calculate q, w, and *[Math Processing Error]* for the process.

S3.13

a) *[Math Processing Error]*

b) *[Math Processing Error]*

[Math Processing Error]

[Math Processing Error]

- For calculating work, expression for Isothermal reversible process has been used instead of correct -Pext*dV as it is a irreversible expansion against external pressure. -Wrong method for calculating q. Instead Internal energy would be calculated using nCv*dT.

Q3.17

Determine the $\Delta_{\text{vap}}\overline{H}^{\circ}$ at 343.15 K for $\mathrm{H_2O}$. (Note: The heat of vaporization for water is known to be 40.79 kJ $\mathrm{mol^{-1}}$ at 273.15 K, the $\overline{C}_P$ of $\mathrm{H_2O}(l)$ was determined to be 85.6 J $\mathrm{K^{-1}}$ $\mathrm{mol^{-1}}$ and the $\overline{C}_P$ of $\mathrm{H_2O}(s)$ was determined to be 54.35 J $\mathrm{K^{-1}}$ $\mathrm{mol^{-1}}$). Use the reaction below and give your final answer in kJ $\mathrm{mol^{-1}}$.

$$\mathrm{H_2O}(s, 273.15\mathrm{K}, 0.1\mathrm{atm}) \rightarrow \mathrm{H_2O}(l, 273.15\mathrm{K}, 0.1\mathrm{atm})$$

S3.17

$$\Delta_{\text{vap}}\overline{H}_{343.15\mathrm{K}} = \Delta\overline{H}_1 + \Delta\overline{H}_2 + \Delta\overline{H}_3$$

$$\Delta\overline{H}_1 = \overline{C}_P(l)\Delta T = 85.6 \times (273.15 - 343.15) = 3.852\mathrm{kJmol^{-1}}$$

$$\Delta\overline{H}_2 = \Delta_{\text{vap}}\overline{H}^{\circ}_{273.15\mathrm{K}} = +40.79\mathrm{kJmol^{-1}}$$

$$\Delta\overline{H}_3 = \overline{C}_P(g)\Delta T = 54.35 \times (343.15 - 273.15) = -2.446\mathrm{kJmol^{-1}}$$

$$\Delta H = 3.825 + 40.79 + (-2.446) = 42.17\mathrm{kJmol^{-1}}$$

$$\Delta_V\overline{H}_{343.15\mathrm{K}} - \Delta_V\overline{H}_{273.15\mathrm{K}} = \Delta\overline{C}_P(T_{343.15} - T_{273.15})$$

$$\Delta_V\overline{H}_{343.15\mathrm{K}} = \Delta_V\overline{H}_{273.15\mathrm{K}} + \Delta\overline{C}_P(T_{343.15} - T_{273.15})$$

$$= 40.79 + (54.35 - 85.6) \times (343.15 - 273.15) = 40.79\mathrm{kJmol^{-1}}$$

Q3.18

,Is *[Math Processing Error]* true for a cyclic process?

S3.18

Yes, *[Math Processing Error]* is a true statement. It is true because *[Math Processing Error]* for any cyclic process is equal to zero.

Q3.22

A 10.0 g sheet of gold with a temperature of 18.0°C is laid flat on a sheet of iron that weights 20.0 g and has a temperature of 55.6°C. Given that the specific heats of Au and Fe are 0.129 J $\mathrm{g^{-1}}$ $\mathrm{°C^{-1}}$ and 0.444 J $\mathrm{g^{-1}}$ $\mathrm{°C^{-1}}$, respectively, what is the final temperature of the combined metals? (Hint: The heat gained by the gold must be equal to the heat lost by the iron.)

Q3.23

You are cooking 100 grams of chicken soup at 300K. You know that it will take 500 J to raise the temperature of your soup to the desired 350K. Assuming constant pressure, calculate the molar heat capacity of this chicken soup.

Q3.24

Why does the molar heat of vaporization for water decrease as temperature increases?

Q3.24

The value of ΔH for heating 1 mole of hexane is 28.9kJ/mole at 342 K and 25.6 kJ/mole at 298 K. Explain why those values are different.

Q3.25

What is ΔH if of 3.00 moles of $\mathrm{O_2}$(g) are cooled from 175°C to 35.0°C and *[Math Processing Error]*

S3.25

[Math Processing Error]

[Math Processing Error]

[Math Processing Error]

[Math Processing Error]

[Math Processing Error]

[Math Processing Error]

Q3.25

For a constant-pressure process, the heat capacity per mole is given by the expression:

C_p per mole = (16.0 + 4.35 x 10^{-3} T + 1.15 T^2) J K^{-1} mol^{-1}

Find the molar heat capacity of oxygen gas from 38°C to 115^{o}C

S3.25

[Math Processing Error]

Q3.26

What is the heat capacity ratio (*[Math Processing Error]*) if of an ideal gas if its *[Math Processing Error]*?

S3.26

since *[Math Processing Error]*

[Math Processing Error]

Q3.29

Explain (in terms of thermo chemistry) why Emperor Penguins huddle together in the Antarctic.

Q3.30a

Through laboratory experiment, a group of students found out that molar mass of a solid element can be calculated in term of the specific heat capacity :

Molar mass x the specific heat of metals= 25 (Eq.1)

They were also obtaining the values of the three metals, Aluminum (0.900 J/g ^{o}C), Zinc (0.381 J/g ^{o}C), and Arsenic (0.329 J/g ^{o}C).

Determine which metal violate the above equation (Eq.1)

S3.30a

Aluminum (Al) can not be applied in this equation because the specific heat capacity of Al is approximately equal 1.0 J g^{-1} ($^{o}C^{-1}$)

Q3.30b

What is the molar heat capacity of lead given its specific heat is 0.128J/(g°C) at 25°C?

S3.30b

The first thing we do is find the molar mass of lead which is 207.2 g/mol.

We multiply our molar mass by the specific heat to get the molar heat capacity.

$$207.2\frac{g}{mol} * 0.128\frac{J}{g^{\circ}C} = 26.52\frac{J}{mol^{\circ}C}$$

Q3.31

What is the total work done on 2.00 moles of an ideal monatomic gas at 3.00 atm and 4.00 L when it adiabatically expands to 7.00 L?

S3.31

The equation for work is

[Math Processing Error]

For a monatomic gas,

[Math Processing Error]

[Math Processing Error]

Solve for T_1:

[Math Processing Error]

[Math Processing Error]

[Math Processing Error]

Solve for T_2:

[Math Processing Error]

[Math Processing Error]

[Math Processing Error]

[Math Processing Error]

Solve for work:

[Math Processing Error]

[Math Processing Error]

[Math Processing Error]

Q3.31

You notice your system changes volume from 10 L to 30 L with a constant pressure at 770 torr. Then, there is a decrease in pressure to 740 torr with the volume staying constant at 30 L. Calculate the total amount of work done.

S3.31

We split up the solution into two parts.

Work done during the volume change and the work done during the pressure change.

First part:

$w = P_{ex}\Delta V$

$770 torr \cdot \frac{1 atm}{760 torr} = 1.01 atm$

$w = (-1.01 atm)(20 L)(101.3\frac{J}{1 L \cdot atm}) = -2046.3 J$

Second part:

Convert pressure to atm:

$740 torr \cdot \frac{1 atm}{760 torr} = 0.974 atm$

$w = -P_2 V_2 ln\frac{P_1}{P_2}$

$w = -(0.974 atm)(30 L) ln\frac{0.974}{1.0} \cdot \frac{101.3 J}{1 L \cdot atm}$

=107.4 J

Then add up the two works

w_{tot}= -2046.3+107.4=-1938.9 J

Q3.33

Calculate the values of q, w, ΔU, and ΔH for the reversible adiabatic expansion of 1 mole of a diatomic ideal gas from 10.00 m^3 to 35.0 m^3 with an initial temperature of 298 K.

Q3.33

Calculate the values of q, w, ΔU, and ΔH for the reversible adiabatic expansion of 1 mole of a diatomic ideal gas from 10.00 m^3 to 40.0 m^3 with an initial temperature of 298K.

Q3.34

A quantity of 0.27 mole of argon is confined in a container at 3.0 atm and 298 K and then allowed to expand adiabatically under two different conditions: (a) reversibly to 0.80 atm and (b) against a constant pressure of 0.80 atm. Calculate the final temperature in each case.

Q3.34

In an adiabatic process 0.5 moles of He_2 in a container are allowed to expand against a constant pressure of 1.00 atm and 298 K. The final temperature after the gas has expanded is 205 K. Calculate the initial pressure inside the container.

S3.34

In an adiabatic process

[Math Processing Error]

we get

[Math Processing Error]

we rearrange and get

[Math Processing Error]

we solve for

[Math Processing Error] and get *[Math Processing Error]*

[Math Processing Error]

[Math Processing Error]

Q3.34

A quantity of 0.27 mole of argon is confined in a container at 3.0 atm and 298 K and then allowed to expand adiabatically under two different conditions:

1. reversibly to 0.80 atm and
2. against a constant pressure of 0.80 atm.

Calculate the final temperature in each case.

Q3.35a

Two moles of ideal diatomic gas *[Math Processing Error]* expand from 2.00 atm to 1.30 atm while being cooled from 550 K to 250 K. Compute the Change of Enthalpy (ΔH) and Change of Internal Energy (ΔU) for 2 different processes: a. reversible and b. irreversible. Explain and calculate the difference a and b?

Q3.35b

0.5 mole of Helium at 298 K are allowed to expand reversibly from 5 atm to 1 atm. Find q, w and ΔU if

a. the process is adiabatic and
b. if the process is isothermal.

Q3.36a

808 kJ/mol of heat is released by burning x (gram) amount of Iron in a constant volume bomb calorimeter. The calorimeter containing 100 g water inside has a heat capacity of 2100 JoC^{-1}. Evaluate the amount of Iron needed to increase the water by 5.20C?

Q3.36b

In your constant-volume bomb calorimeter you have a 0.3677 g sample of Potassium. The water surrounding the sample increase from 18.08 ºC to 20.667 ºC. The calorimeter has a heat capacity of 1515 J/(gºC). What is the change in internal energy?

S3.36b

Since the bomb calorimeter has a constant volume *[Math Processing Error]*, there is no (PV) work so the first law of thermodynamics

[Math Processing Error]

can be simplified to

[Math Processing Error]

Then the relationship between heat and temperature change

[Math Processing Error]

can be changed

[Math Processing Error]

which for this case is

[Math Processing Error]

[Math Processing Error]

Q3.37

The enthalpy of combustion for benzoic acid (*[Math Processing Error]*) is commonly used as the standard *[Math Processing Error]*, for calibrating bomb calorimeters at a constant-volume process.

a. When 1.567 g of benzoic acid burned in a calorimeter the temperature increased by *[Math Processing Error]*. Calculate the heat capacity of the calorimeter.
b. For a different experiment 0.6792g of ethanol was burned in the calorimeter which rose from 16.42*[Math Processing Error]*C to 26.58*[Math Processing Error]*C. Calculate the enthalpy of combustion for ethanol, the value of *[Math Processing Error]* for the combustion, and the molar enthalpy of formation.

S3.37

(a)

[Math Processing Error]

[Math Processing Error]

[Math Processing Error]

(b) (Hint: Calorimeter absorbs heat transfered from the combustion of maltose)

[Math Processing Error]

Step 1: Calculate *[Math Processing Error]*

[Math Processing Error]

[Math Processing Error]

Step 2: Calculation of enthalpy of combustion

[Math Processing Error]

[Math Processing Error]

Therefore,

[Math Processing Error]

Step 3: Calculate the molar enthalpy of formation.

[Math Processing Error]

[Math Processing Error]

[Math Processing Error]

Q3.38a

A quantity of 2.50 x 10^2 mL of 0.468 M HBr is mixed with 2.50 x 10^2 mL of 0.425 M KOH in a constant-pressure calorimeter that has a heat capacity of 437 J °C^{-1}. The initial temperature if the HBr and KOH solutions is the same at 21.35°C. For the process

[Math Processing Error]

the heat of neutralization is -56.2 kJ mol^{-1}. What is the final temperature of the mixed solution?

Q3.38b

In a constant-pressure calorimeter with a heat capacity of 395*[Math Processing Error]*, you mix *[Math Processing Error]* of HBr at 0.788M and *[Math Processing Error]* *[Math Processing Error]* at .394M. For this process to occur the heat of neutralization is *[Math Processing Error]*. The initial temperature of both solutions is *[Math Processing Error]*.

[Math Processing Error]

Find the final temperature of the mixed solution.

S3.38b

Step 1: (Hint: Determine the number of moles of the reactants)

[Math Processing Error]

[Math Processing Error]

Step 2: (Hint: Calculate the the thermal energy released by the reaction)

[Math Processing Error]

Step 3: (Hint: Assume the the density of the solutions are the same as water and specific heat is same as water too.)

[Math Processing Error]

[Math Processing Error]

[Math Processing Error]

Step 4:

[Math Processing Error]

[Math Processing Error]

[Math Processing Error]

Step 5:

[Math Processing Error]

[Math Processing Error]

Q3.38

A quantity of *[Math Processing Error]* of *[Math Processing Error]* is mixed with *[Math Processing Error]* of *[Math Processing Error]* in a constant-pressure calorimeter that has a heat capacity of 437 J °C^{-1}. The initial temperatures of the *[Math Processing*

Error] and *[Math Processing Error]* solutions are the same at 21.35 °C. The heat of neutralization for the below reaction is \(-56.2\; kJ/mol\)

[Math Processing Error]

What is the final temperature of the mixed solution?

Q3.39

1.52 g of toluene *[Math Processing Error]* is combusted in a constant volume bomb calorimeter at 25°C. Calculate the *[Math Processing Error]* and *[Math Processing Error]* for this reaction given that 39.183 kJ of heat was released.

S3.39

First we need to construct the balanced reaction that occurs

[Math Processing Error]

[Math Processing Error]

[Math Processing Error]

Q3.39

The of ΔU a of the combustion of naphthalene ($C_{10}H_8$) are -480 kj mol^{-1}. The heat evolved from the combustion in a constant-volume calorimeter is 7.5 KJ. Calculate the mass of naphthalene in grams in the calorimeter.

Q3.40

For the reaction

[Math Processing Error]

a. Balance the reaction
b. Calculate the *[Math Processing Error]* of reaction using the *[Math Processing Error]* data

Q3.40B

Consider the following reaction:

[Math Processing Error]

What is the value of *[Math Processing Error]* if

a. the equation is multiplied throughout by 4;
b. the direction of the reaction is reversed;
c. *[Math Processing Error]* was a liquid instead of gas?

S3.40B

a. *[Math Processing Error]*;
b. *[Math Processing Error]*;
c. Ethane exist as a liquid at temperatures of below 184.6 K. If we used ethane liquid instead of ethane gas, then according to *[Math Processing Error]* the number of moles would change and the temperature of the reaction would also change.

Q3.41a

On what basis is the 0 value for standard enthalpy of formation assigned to a substance at a specific temperature? Base on that, identify which substances have $\Delta_f H°$ = 0 and which do not at 1 atm and 25°C (give explanation for those that do not).

H_2(g), O_3(g), Al(s), Br_2(g), NaCl(s), Cl_2(g)

Hint: Look at standard enthalpy of formation

S3.41a

0 value for standard enthalpy of formation is assigned to elemental substances that are in their natural/standard physical state at that specific condition of temperature and pressure.

a. $H_2(g)$, Al(s), $Cl_2(g)$ are substances with $\Delta_fH° = 0$ kJ/mol
b. $O_3(g)$ is an elemental substance but does not occur naturally at 25°C, $O_2(g)$ is.
c. $Br_2(g)$ is also not the standard state of bromine. At STP, the physical state of bromine is liquid
d. NaCl does not have a 0 value because it is not an elemental substance

Q3.41b

Which of the following substances has a standard enthalpy of formation, at 298 K, of 0 K?

$O_2(g)$, $Br_2(g)$, Hg(s), $CH_4(g)$

Q3.41c

Why is the standard enthalpy of formation of O_2 zero at a temperature of 298 K?

S3.41c

The standard enthalpy of formation of O_2 is zero at 298 K since O_2 is the most stable allotropic form of oxygen at that particular temperature.

Q3.42a

a) The ionization of a weak acetic acid is written as:

[Math Processing Error]

Suppose the change of reaction enthalpy for this reaction is +1.0 kJ/mol and the $\Delta_fH°$ of CH_3COO^- is -486.01 kJ/mol. What would be the molar enthalpy of formation of aqueous acetic acid?

b) The acetic acid is reacted with a strong base NaOH. Calculate the enthalpy of neutralization for this reaction of weak acid strong base.

$\Delta_fH°[OH^-(aq)] = -229.6$ kJ/mol and $\Delta_fH°[H_2O(l)] = -285.8$ kJ/mol

Hint: Look at enthalpy of neutralization

S3.42a

a) [Math Processing Error]

[Math Processing Error]

[Math Processing Error]

[Math Processing Error]

b) Note that acetic acid is a weak acid, therefore only dissociates partially or does not dissociate at all. Therefore the complete ionic reaction of reaction is:

[Math Processing Error]

Since Na^+ cancels out, the net equation is

[Math Processing Error]

[Math Processing Error]

[Math Processing Error]

[Math Processing Error]

Q3.42b

Calculate the enthalpy of formation for Br^- ions in the following reactions:

a. *[Math Processing Error]*
b. *[Math Processing Error]*

S3.42b

[Math Processing Error]

[Math Processing Error]

[Math Processing Error]

[Math Processing Error]

Q3.42c

When determining standard enthalpies of formation of ions in aqueous solutions, set the value of *[Math Processing Error]* ion to 0 for *[Math Processing Error]*

a. For the following reaction *[Math Processing Error]*, *[Math Processing Error]*. Calculate the value of *[Math Processing Error]* for the Br ions.
b. The standard enthalpy of neutralization between HBr and NaOH solutions is *[Math Processing Error]*. At *[Math Processing Error]*, calculate the standard enthalpy of formation of the hydroxide ion.

S3.42c

(a)

$$\Delta rH^{o}=-98.4kj\,mol^{-1}=\Delta _f\bar{H}^{o}[H^+_{(aq)}]+\Delta _f\bar{H}^{o}[Br^-_{(aq)}]-\Delta _f\bar{H}^{o}[HBr_{(g)}]$$

$$\Delta _f\bar{H}^{o}[Br^-_{(aq)}]=-98.4kj\,mol^{-1}-\Delta _f\bar{H}^{o}[H^+_{(aq)}]+\Delta _f\bar{H}^{o}[HBr_{(g)}]$$

$$=-98.4kj\,mol^{-1}-0kj\,mol^{-1}+(-36.29kj\,mol^{-1})$$

$$=-134.69kj\,mol^{-1}$$

(b) The neutralization for 1 mole of *[Math Processing Error]* is *[Math Processing Error]*

$$\Delta rH^{o}=\Delta_f\bar{H}^{o}[H_2O_{(l)}]-\Delta_f\bar{H}^{o}[H^+_{(aq)}]-\Delta_f\bar{H}^{o}[OH^-_{(aq)}]$$

$$\Delta_f\bar{H}^{o}[OH^-_{(aq)}]=\Delta_f\bar{H}^{o}[H_2O_{(l)}]-\Delta_f\bar{H}^{o}[H^+_{(aq)}]+53.4kj\,mol^{-1}$$

$$=(-285.8kj\,mol^{-1})-0kj\,mol^{-1}+53.4kj\,mol^{-1}$$

$$=-232.4kj\,mol^{-1}$$

Q3.42d

For the following chemical reaction, calculate the $\Delta_r H^{o}$.

[Math Processing Error]

S3.42d

Use the following equation:

[Math Processing Error]

Solve

[Math Processing Error]

Click here for more information about standard enthalpies of reaction.

Q3.42e

The reaction for the dissociation of hydrobromic acid in water is as follows:

[Math Processing Error]

[Math Processing Error]

a.) Given the enthalpy of formation for HBr, what is the enthalpy of formation for the Bromine ion? Assume that the enthalpy of formation for the Hydrogen ion is 0.

b.) What is the enthalpy of reaction for the neutralization of HBr with KOH? Assume that the potassium and bromine ions remain in solution following the neutralization.

[Math Processing Error]

S3.42e

a.) For any reaction,

[Math Processing Error]

For this reaction,

[Math Processing Error]

[Math Processing Error]

[Math Processing Error]

b.) For any neutraliztion reaction in solution,

[Math Processing Error]

[Math Processing Error]

[Math Processing Error]

Q3.43a

How much heat is given off when one explodes 24.65 grams of nitroglycerin? The equation for the combustion of nitroglycerin is given below:

[Math Processing Error]

S3.43a

The molar mass of nitroglycerin is 227.0865 g/mol.

To solve this question simply multiple the enthalpy of reaction by the amount moles of nitroglycerin.

[Math Processing Error]

Q3.43b

What is the enthalpy change from the formation of 5 grams of H_2CO_3 via $CO_{2(g)}$ + $H_2O_{(g)}$ à$H_2CO_{3(g)}$ $H_2CO_{3\,(g)}$ via $CO_{2\,(g)}$ + $H_2O_{\,(g)}$ → $H_2CO_{3\,(g)}$? The change in enthalpy associated with this reaction is +360.19 kJ/mol.

S3.43b

The enthalpy change from this reaction is given by the molar enthalpy change times the number of moles of product formed. Thus:

m_{co2} = 44.01 g mol^{-1} ;

n_{co2} = 5g /44.01 g mol^{-1} = 0.1136 mol

ΔH =0.1136 mol * 360.19 kJ/mol = 40.9kJ

Q3.43c

The following reaction was carried out at standard temperature and pressure:

[Math Processing Error]

If -148.16 KJ of heat was released during this reaction, how many grams of Ethane were formed?

S3.43c

For any reaction:

[Math Processing Error]

This can be rearranged as

[Math Processing Error]

The molar mass of ethane is

[Math Processing Error]

The mass of ethane produced, then, is

[Math Processing Error]

Q3.44a

When 2.3 g of calcium carbonate is decomposed under constant pressure, 178.3 kJ of heat were released. What is the [Math Processing Error] for this reaction?

[Math Processing Error]

S3.44a

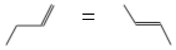
[Math Processing Error]

Q3.44b

In a high school chemistry experiment, 10 grams of methane were combusted in the presence of excess oxygen under standard conditions. A calorimeter measured that 554.9 kJ of heat were released by the reaction to the surroundings. Assuming the calorimeter's measurement accounts for all heat changes associated with the reaction, write the reaction for the combustion of methane and calculate the change in enthalpy associated with it.

Q3.46

The isomerization process from 1-butene to 2-butene has a reaction enthalpy of -7.1 kJ/mol.



1-butene 2-butene

If the hydrogenation of 1 butene has a reaction enthalpy of -126.8 kJ/mol. How much energy would the hydrogenation of 2-butene takes? Keep in mind that both processes yield the same product.

Hint: Look at example problems of change of standard reaction enthalpy

S3.46

$$\text{1-butene} + 2H_2 \rightarrow \text{butane}\ \Delta_f H° = -126.8\ kJ/mol$$

$$1\text{-}butene \rightarrow 2\text{-}butene\ \Delta_f H° = -7.1\ kJ/mol$$

Reverse the 2nd reaction and combine the two reactions

$$\text{1-butene} + 2H_2 \rightarrow \text{butane}\ \Delta_f H° = -126.8\ kJ/mol$$

$$2\text{-}butene \rightarrow 1\text{-}butene\ \Delta_f H° = +7.1\ kJ/mol$$

$$\Delta_r H° = -126.8\ kJ/mol + 7.1\ kJ/mol$$

$$\Delta_r H° = -119.7\ kJ/mol$$

Q3.47a

From the reaction below, calculate the enthalpy of formation of methane gas.

[Math Processing Error]

S3.47a

Use the following equation:

[Math Processing Error]

Plug in appropriate values and solve. Change in enthalpy of oxygen is 0 because it is the reference form of a pure element.

[Math Processing Error]

[Math Processing Error]

Click here for more information on standard enthalpies.

Q3.47b

For the following combustion reaction:

[Math Processing Error]

Calculate the enthalpy of formation for 2-propanol, given the following enthalpies of formation

[Math Processing Error]

S3.47b

In general:

[Math Processing Error]

In general,

[Math Processing Error]

[Math Processing Error]

[Math Processing Error]

Q3.48

Diatomic fluorine gas has a Cp of 31.3 J/K*mol. What is its molar enthalpy of formation on the surface of the planet Venus (at standard pressure), where temperature is commonly 465 C?

S3.48

At constant pressure, the change in enthalpy with respect to temperature is given by Cp. By determining the change in temperature and multiplying it by Cp we can find the change in enthalpy.

ΔT = 465 C - 25 C = 440K

ΔH = 31.3 J/K*mol * 440K = 13.772 kJ/mol

Q3.50

The combustion of graphite is

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

Calculate the change in the enthalpy of combustion from 298 K to 398 K. The molar C_p values are (in J K^{-1} mol^{-1}): C(gr):8.52, O_2(g):29.4, and CO_2(g):37.1

Q3.53

What values are needed to calculate the change in standard enthalpy of a reaction?

Q3.54

Consider the following reactions:

C(graphite) + $O_{2\,(g)}$ → CO (s) Δ_rH = -110.5 kJ/mole

CO_2 (g) → Co (s) + $O_{2\,(g)}$ Δ_rH = 283.0 kJ/mole

Find the enthalpy of formation of carbon dioxide ($CO_{2)}$

S3.54

The *[Math Processing Error]* of the reaction is the sum of *[Math Processing Error]* and *[Math Processing Error]*

\[2C + O_2 \rightarrow 2CO \,\,, \Delta H_1 = -110.5 kJ/mol

\[2CO + O2 \rightarrow 2CO_2 \Delta H_2 = -283 kJ/mol

thus the *[Math Processing Error]* of reaction is (-110.5)+(-283.0) = -393.5 kJ/mol

Q3.55

What is $\Delta_r H^\circ$ of the following reaction? $\Delta_f H^\circ$ for O(g) is 249.4 kJ mol^{-1} and $\Delta_f H^\circ$ for O_3(g) is 142.7 kJ mol^{-1}

[Math Processing Error]

S3.55

[Math Processing Error]

[Math Processing Error]

[Math Processing Error]

[Math Processing Error]

Q3.60

Methane combusts, what is the enthalpy of combustion for this reaction?

Substance	Standard Molar Enthalpies of Formation at 25°C
CH_4(g)	-74.85 kj/mol
CO_2(g)	-393.5 kj/mol
H_2O(g)	-241.8 kj/mol
H_2O(l)	-285.8 kj/mol

S3.60

Write the balanced formula for this reaction to identify the coefficients

[Math Processing Error]

[Math Processing Error]

[Math Processing Error]

We do not include *[Math Processing Error]* because it is a standard state

[Math Processing Error]

[Math Processing Error]

Q3.62

Predict whether the values of q, w, ΔU, and ΔH are positive, zero, or negative for each of the following processes: (a) freezing of ice at 1 atm and 273 K, (b) melting of solid butanol at 1 atm and the normal melting point, (c) reversible isothermal compression of an ideal gas, and (d) reversible adiabatic compression of an ideal gas.

Q3.62

Predict whether the values of q, w, ΔU, and ΔH are positive, zero, or negative for each of the following processes: (a) freezing of ice at 1 atm and 273 K, (b) melting of solid butanol at 1 atm and the normal melting point, (c) reversible isothermal compression of an ideal gas, and (d) reversible adiabatic compression of an ideal gas.

Q3.63

The first law of thermodynamics states that energy is conserved. It cannot be destroyed nor created. Using Einstein's equation E= mc^2 explain how large amounts of energy are necessary to fuse atoms together. If energy is conserved where did all this energy go?

S3.63

When large amounts of energy are used to fuse atoms together (eg: fusion) we can observe that the mass of the atoms is very small compared to the amount of energy used. However, using Einstein's equation $E= mc^2$ we see that the mass is multiplied times the speed of light squared which will result in a very large number. The energy was not destroyed but rather stored in the chemical bonds of the atoms.

Q3.64

For the nuclear process we cannot apply the assumption that *[Math Processing Error]* for most stable elements because there are different components in the reactant and product sides. Explain this difference?

Q3.66

You eat 2 pounds of fries for lunch and the fuel value is approximately *[Math Processing Error]*. If you don't store any of the energy, calculate the amount of water (evaporated perspiration) needed to keep your body temperature constant.

S3.66

Step1: (Hint: Calculate the fuel value for 2 pound of fries)

[Math Processing Error]

Step 2: (Hint: Use *[Math Processing Error]* to calculate grams of *[Math Processing Error]*)

[Math Processing Error]

[Math Processing Error]

[Math Processing Error]

Q3.68

What is the final temperature of the following reaction:

[Math Processing Error]

Hint: first find *[Math Processing Error]*, then look up the standard molar heat capacities of the products.

S3.68

[Math Processing Error]

[Math Processing Error]

[Math Processing Error]

Q3.70

The reaction below is a oxidation of 2-propanol to make acetone

a) Calculate the change of enthalpy of reaction by using bond enthalpies

b) Compare the result with the reaction of the combustion 2-propanol that has an enthalpy of -1825.5 kJ/mol. What does this say about the two reactions. (Hint: Look at bond enthalpies).

S3.70

a)

Types of bonds formed	***#of bonds formed***	***Bond Enthalpy (kJ/mol)***	***Enthalpy change (kJ/mol)***
C-H	*6*	*414*	*2484*
C-C	*2*	*347*	*694*
C=O	*1*	*724*	*724*
O-H	*1*	*460*	*460*

[Math Processing Error]

b) According to the enthalpy values, the enthalpy of the oxidation of 2-propanol into ketone is positive while its combustion is largely negative. This tells that although oxygen is involved, the two reactions are different. The combustion releases heat where as the other process needs an absorption of energy in order for the reaction to take place. In this case is usually the help of another catalyst.

Q3.71a

The molar enthalpy of sublimation for an unknown organic substance is found to be 58.05 KJ/mol, and the molar enthalpy of vaporization is 37.12 KJ/mol. Using these values, provide an estimate for the molar enthalpy of fusion for this substance.

Hint: Sublimination is the transition from solid to gas phase. Fusion and Vaporization, respectively, are the the transition from solid to liquid, then liquid to gas.

S3.71a

In general,

[Math Processing Error]

[Math Processing Error]

Q3.71b

Calculate the standard enthalpy of sublimation of ethanol. $\Delta_{fus}H^{o}$ (ethanol) = 4.9 kJ mol^{-1} and $\Delta_{vap}H^{o}$ (ethanol) = 38.56 kJ mol^{-1}.

S3.71b

You can estimate the standard enthalpy of sublimation by adding up the standard enthalpies of fusion and vaporization since sublimation consists of two simultaneous phase changes. See here for more information on it.

$\Delta_{sub}H^{o}$ (ethanol) = 4.9+38.56 = 43.46 kJ mol^{-1}

Q3.72

Nitric acid is neutralized by hydroxide via the reaction HNO_3 (aq) + OH^-(aq) → H_2O(l) + NO_3^-(aq). The dissociation of water has an enthalpy change of 55.8 kJ/mol. What is the enthalpy change for the dissociation of nitric acid?

Chemical	HNO_3	OH^-	H_2O	NO_3^-
Δ_fH (kJ/mol)	-207.6	-229.6	-285.8	-206.6

S3.72

The dissociation of water is H_2O(l) -> H^+(aq) + OH^-(aq), which when added to the neutralization reaction above, gives the overall reaction

[Math Processing Error]

which is the dissociation reaction for nitric acid. The enthalpy change of the first reaction is given by the difference in the total enthalpies of formation of the products and reactants, i.e.

Δ_rH=(-206.6 kJ/mol -285.8 kJ/mol) - (-229.6 kJ/mol -207.6 kJ/mol) = -55.2 kJ/mol.

When added to the enthalpy change for the dissociation of water to obtain the enthalpy change for the dissociation of nitric acid, we have:

$\Delta_{net}H$=-55.2 kJ/mol + 55.8 kJ/mol = 0.6 kJ/mol

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CHAPTER OVERVIEW

4: The Second Law of Thermodynamics

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4.1: Spontaneous Processes

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4.2: Entropy

Entropy is a state function that is often erroneously referred to as the 'state of disorder' of a system. Qualitatively, entropy is simply a measure how much the energy of atoms and molecules become more spread out in a process and can be defined in terms of statistical probabilities of a system or in terms of the other thermodynamic quantities. Entropy is also the subject of the Second and Third laws of thermodynamics, which describe the changes in entropy of the universe with respect to the system and surroundings, and the entropy of substances, respectively.

Statistical Definition of Entropy

Entropy is a thermodynamic quantity that is generally used to describe the course of a process, that is, whether it is a spontaneous process and has a probability of occurring in a defined direction, or a non-spontaneous process and will not proceed in the defined direction, but in the reverse direction. To define entropy in a statistical manner, it helps to consider a simple system such as in Figure *[Math Processing Error]*. Two atoms of hydrogen gas are contained in a volume of *[Math Processing Error]*.

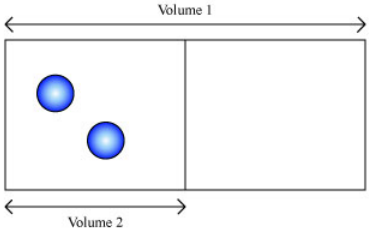

Figure *[Math Processing Error]*. Two hydrogen atoms in a volume *[Math Processing Error]*

Since all the hydrogen atoms are contained within this volume, the probability of finding any one hydrogen atom in *[Math Processing Error]* is 1. However, if we consider half the volume of this box and call it *[Math Processing Error]*,the probability of finding any one atom in this new volume is *[Math Processing Error]*, since it could either be in *[Math Processing Error]* or outside. If we consider the two atoms, finding both in *[Math Processing Error]*, using the multiplication rule of probabilities, is

[Math Processing Error]

For finding four atoms in *[Math Processing Error]* would be

[Math Processing Error]

Therefore, the probability of finding N number of atoms in this volume is *[Math Processing Error]*. Notice that the probability decreases as we increase the number of atoms.

If we started with volume *[Math Processing Error]* and expanded the box to volume *[Math Processing Error]*, the atoms would eventually distribute themselves evenly because this is the most probable state. In this way, we can define our direction of spontaneous change from the lowest to the highest state of probability. Therefore, entropy *[Math Processing Error]* can be expressed as

[Math Processing Error]

where *[Math Processing Error]* is the probability and *[Math Processing Error]* is a proportionality constant. This makes sense because entropy is an extensive property and relies on the number of molecules, when *[Math Processing Error]* increases to *[Math Processing Error]*, S should increase to 2S. Doubling the number of molecules doubles the entropy.

So far, we have been considering one system for which to calculate the entropy. If we have a process, however, we wish to calculate the change in entropy of that process from an initial state to a final state. If our initial state 1 is *[Math Processing Error]* and the final state 2 is *[Math Processing Error]*,

[Math Processing Error]

using the rule for subtracting logarithms. However, we wish to define *[Math Processing Error]* in terms of a measurable quantity. Considering the system of expanding a volume of gas molecules from above, we know that the probability is proportional to the volume raised to the number of atoms (or molecules), *[Math Processing Error]*. Therefore,

[Math Processing Error]

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We can define this in terms of moles of gas and not molecules by setting the *[Math Processing Error]* or Boltzmann constant equal to *[Math Processing Error]*, where R is the gas constant and *[Math Processing Error]* is Avogadro's number. So for a expansion of an ideal gas and holding the temperature constant,

[Math Processing Error]

because *[Math Processing Error]*, the number of moles. This is only defined for constant temperature because entropy can change with temperature. Furthermore, since S is a state function, we do not need to specify whether this process is reversible or irreversible.

Thermodynamic Definition of Entropy

Using the statistical definition of entropy is very helpful to visualize how processes occur. However, calculating probabilities like *[Math Processing Error]* can be very difficult. Fortunately, entropy can also be derived from thermodynamic quantities that are easier to measure. Recalling the concept of work from the first law of thermodynamics, the heat (q) absorbed by an ideal gas in a reversible, isothermal expansion is

[Math Processing Error]

If we divide by T, we can obtain the same equation we derived above for *[Math Processing Error]*:

[Math Processing Error]

We must restrict this to a reversible process because entropy is a state function, however the heat absorbed is path dependent. An irreversible expansion would result in less heat being absorbed, but the entropy change would stay the same. Then, we are left with

[Math Processing Error]

for an irreversible process because

[Math Processing Error]

This apparent discrepancy in the entropy change between an irreversible and a reversible process becomes clear when considering the changes in entropy of the surrounding and system, as described in the second law of thermodynamics.

It is evident from our experience that ice melts, iron rusts, and gases mix together. However, the entropic quantity we have defined is very useful in defining whether a given reaction will occur. Remember that the rate of a reaction is independent of spontaneity. A reaction can be spontaneous but the rate so slow that we effectively will not see that reaction happen, such as diamond converting to graphite, which is a spontaneous process.

The Second Law as Energy Dispersion

Energy of all types -- in chemistry, most frequently the kinetic energy of molecules (but also including the phase change/potential energy of molecules in fusion and vaporization, as well as radiation) changes from being localized to becoming more *dispersed* in space if that energy is not constrained from doing so. The simplest example stereotypical is the expansion illustrated in Figure 1.

The initial motional/kinetic energy (and potential energy) of the molecules in the first bulb is unchanged in such an isothermal process, but it becomes **more widely distributed** in the final larger volume. Further, this concept of energy dispersal equally applies to heating a system: a spreading of molecular energy from the volume of greater-motional energy (“warmer”) molecules in the surroundings to include the **additional** volume of a system that initially had “cooler” molecules. It is not obvious, but true, that this distribution of energy in greater space is implicit in the Gibbs free energy equation and thus in chemical reactions.

“Entropy change is the measure of *how more widely a specific quantity of molecular energy is dispersed in a process*, whether isothermal gas expansion, gas or liquid mixing, reversible heating and phase change, or chemical reactions.” There are two requisites for entropy change.

1. It is enabled by the above-described increased distribution of molecular energy.
2. It is actualized if the process makes available a larger number of arrangements for the system’s energy, i.e., a final state that involves the most probable distribution of that energy under the new constraints.

Thus, “information probability” is only one of the two requisites for entropy change. Some current approaches regarding “information entropy” are either misleading or truly fallacious, if they do not include explicit statements about the essential inclusion of molecular kinetic energy in their treatment of chemical reactions.

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References

1. This literal greater spreading of molecular energy in 3-D space in an isothermal process is accompanied by occupancy of more quantum states ("energy levels") within each microstate and thus more microstates for the final macrostate (i.e., a larger *[Math Processing Error]* in R\ln{W}). Similarly, in any thermal process higher energy quantum states can be significantly occupied – thereby increasing the number of microstates in the product macrostate as measured by the Boltzmann relationship.
2. I. N. Levine, Physical Chemistry, 6th ed. 2009, p. 101, toward the end of "What Is Entropy?"
3. Chang, Raymond. Physical Chemistry for the Biosciences. Sausalito, California: University Science Books, 2005.

Contributors and Attributions

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Carnot Cycle

In the early 19th century, steam engines came to play an increasingly important role in industry and transportation. However, a systematic set of theories of the conversion of thermal energy to motive power by steam engines had not yet been developed. Nicolas Léonard Sadi Carnot (1796-1832), a French military engineer, published *Reflections on the Motive Power of Fire* in 1824. The book proposed a generalized theory of heat engines, as well as an idealized model of a thermodynamic system for a heat engine that is now known as the Carnot cycle. Carnot developed the foundation of the second law of thermodynamics, and is often described as the "Father of thermodynamics."

The Carnot Cycle

The Carnot cycle consists of the following four processes:

I. A reversible isothermal gas expansion process. In this process, the ideal gas in the system absorbs *[Math Processing Error]* amount heat from a heat source at a high temperature *[Math Processing Error]*, expands and does work on surroundings.
II. A reversible adiabatic gas expansion process. In this process, the system is thermally insulated. The gas continues to expand and do work on surroundings, which causes the system to cool to a lower temperature, *[Math Processing Error]*.
III. A reversible isothermal gas compression process. In this process, surroundings do work to the gas at *[Math Processing Error]*, and causes a loss of heat, *[Math Processing Error]*.
IV. A reversible adiabatic gas compression process. In this process, the system is thermally insulated. Surroundings continue to do work to the gas, which causes the temperature to rise back to *[Math Processing Error]*.

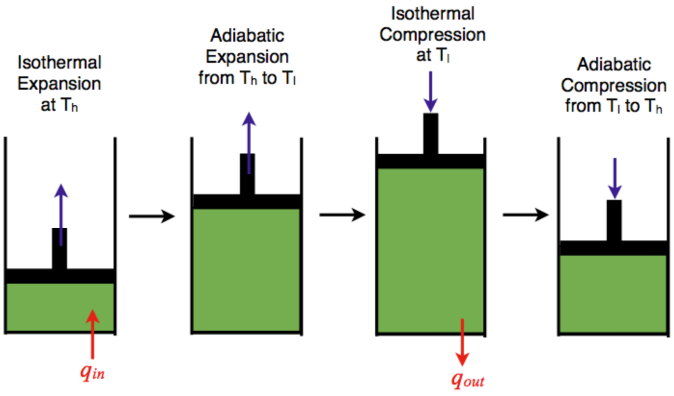

Figure *[Math Processing Error]*: An ideal gas-piston model of the Carnot cycle. (CC BY 4.0; XiSen Hou via Hope College)

P-V Diagram

The P-V diagram of the Carnot cycle is shown in Figure *[Math Processing Error]*. In isothermal processes I and III, ΔU=0 because ΔT=0. In adiabatic processes II and IV, q=0. Work, heat, ΔU, and ΔH of each process in the Carnot cycle are summarized in Table *[Math Processing Error]*.

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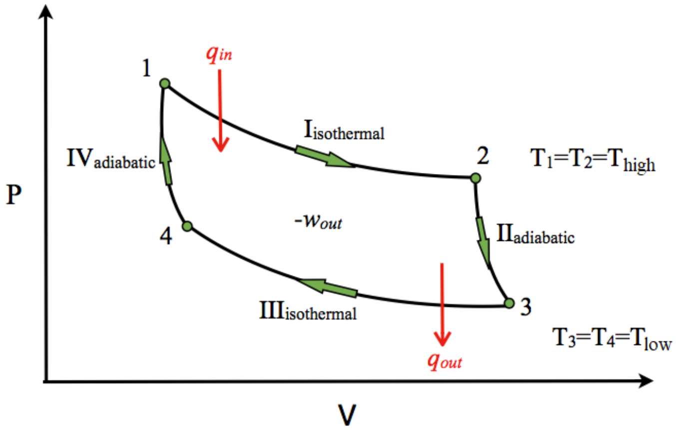

Figure *[Math Processing Error]*: A P-V diagram of the Carnot Cycle.

Table *[Math Processing Error]*: Work, heat, ΔU, and ΔH in the P-V diagram of the Carnot Cycle.

Process	*w*	*q*	ΔU	ΔH
I	*[Math Processing Error]*	*[Math Processing Error]*	0	0
II	*[Math Processing Error]*	0	*[Math Processing Error]*	*[Math Processing Error]*
III	*[Math Processing Error]*	*[Math Processing Error]*	0	0
IV	*[Math Processing Error]*	0	*[Math Processing Error]*	*[Math Processing Error]*
Full Cycle	*[Math Processing Error]*	*[Math Processing Error]*	0	0

T-S Diagram

The T-S diagram of the Carnot cycle is shown in Figure *[Math Processing Error]*. In isothermal processes I and III, ΔT=0. In adiabatic processes II and IV, ΔS=0 because dq=0. ΔT and ΔS of each process in the Carnot cycle are shown in Table *[Math Processing Error]*.

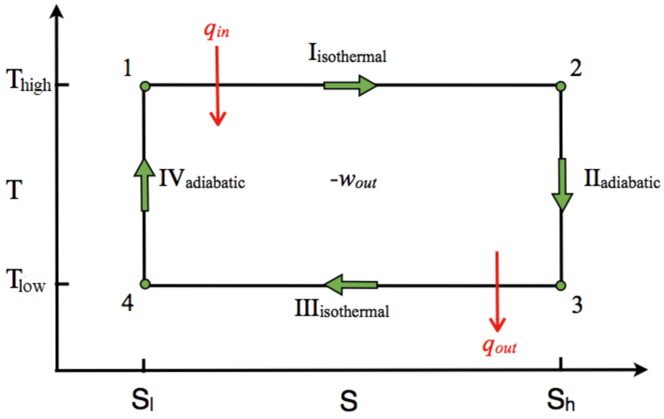

Figure *[Math Processing Error]*: A T-S diagram of the Carnot Cycle. (CC BY 4.0; XiSen Hou via Hope College)

Table *[Math Processing Error]*: Work, heat, and ΔU in the T-S diagram of the Carnot Cycle.

Process	**ΔT**	**ΔS**
I	0	*[Math Processing Error]*
II	*[Math Processing Error]*	0
III	0	*[Math Processing Error]*
IV	*[Math Processing Error]*	0

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Process	ΔT	ΔS
Full Cycle	0	0

Efficiency

The Carnot cycle is the most efficient engine possible based on the assumption of the absence of incidental wasteful processes such as friction, and the assumption of no conduction of heat between different parts of the engine at different temperatures. The efficiency of the carnot engine is defined as the ratio of the energy output to the energy input.

[Math Processing Error]

Since processes II (2-3) and IV (4-1) are adiabatic,

[Math Processing Error]

and

[Math Processing Error]

And since $T_1 = T_2$ and $T_3 = T_4$,

[Math Processing Error]

Therefore,

[Math Processing Error]

[Math Processing Error]

Summary

The Carnot cycle has the greatest efficiency possible of an engine (although other cycles have the same efficiency) based on the assumption of the absence of incidental wasteful processes such as friction, and the assumption of no conduction of heat between different parts of the engine at different temperatures.

Problems

1. You are now operating a Carnot engine at 40% efficiency, which exhausts heat into a heat sink at 298 K. If you want to increase the efficiency of the engine to 65%, to what temperature would you have to raise the heat reservoir?
2. A Carnot engine absorbed 1.0 kJ of heat at 300 K, and exhausted 400 J of heat at the end of the cycle. What is the temperature at the end of the cycle?
3. An indoor heater operating on the Carnot cycle is warming the house up at a rate of 30 kJ/s to maintain the indoor temperature at 72 ºF. What is the power operating the heater if the outdoor temperature is 30 ºF?

References

1. Goldstein, M. *J. Chem. Educ.*, **1980**, *57*, 114-116
2. Bader, M. *J. Chem. Educ.*, **1973**, *50*, 834
3. W. F. Luder. *J. Chem. Educ.*, **1944**, *21*, 600-601
4. Salter, C. *J. Chem. Educ.*, **2000**, 77, 1027-1030

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4.3: The Second Law of Thermodynamics

The Second Law of Thermodynamics states that the state of entropy of the entire universe, as an isolated system, will always increase over time. The second law also states that the changes in the entropy in the universe can never be negative.

Introduction

Why is it that when you leave an ice cube at room temperature, it begins to melt? Why do we get older and never younger? And, why is it whenever rooms are cleaned, they become messy again in the future? Certain things happen in one direction and not the other, this is called the "arrow of time" and it encompasses every area of science. The thermodynamic arrow of time (entropy) is the measurement of disorder within a system. Denoted as *[Math Processing Error]*, the change of entropy suggests that time itself is asymmetric with respect to order of an isolated system, meaning: a system will become more disordered, as time increases.

Major players in developing the Second Law

- Nicolas Léonard Sadi Carnot was a French physicist, who is considered to be the "father of thermodynamics," for he is responsible for the origins of the Second Law of Thermodynamics, as well as various other concepts. The current form of the second law uses entropy rather than caloric, which is what Sadi Carnot used to describe the law. Caloric relates to heat and Sadi Carnot came to realize that some caloric is always lost in the motion cycle. Thus, the thermodynamic reversibility concept was proven wrong, proving that irreversibility is the result of every system involving work.
- Rudolf Clausius was a German physicist, and he developed the Clausius statement, which says "Heat generally **cannot flow spontaneously** from a material at a lower temperature to a material at a higher temperature."
- William Thompson, also known as Lord Kelvin, formulated the Kelvin statement, which states "It is **impossible** to convert heat completely in a cyclic process." This means that there is no way for one to convert all the energy of a system into work, without losing energy.
- Constantin Carathéodory, a Greek mathematician, created his own statement of the second law arguing that "In the neighborhood of any initial state, there are states which **cannot** be approached arbitrarily close through adiabatic changes of state."

Sadi Carnot.jpeg

Figure *[Math Processing Error]*: Sade Carnot(Louis-LéopoldBoilly public domain)

Rudolf Clausius 01.jpg

Figure *[Math Processing Error]*: Rudolf Clausiius (Theo Schafgans, public domain)

William Thomson, 1st Baron Kelvin - Wikipedia

Figure *[Math Processing Error]*: Lord Kelvin (Smithsonian Institution, public domain)

Caratheodory (cropped).jpg

Figure *[Math Processing Error]*: Constantin Carathéodory (Public Domain

To understand why entropy increases and decreases, it is important to recognize that two changes in entropy have to considered at all times. The entropy change of the surroundings and the entropy change of the system itself. Given the entropy change of the universe is equivalent to the sums of the changes in entropy of the system and surroundings:

[Math Processing Error]

In an isothermal reversible expansion, the heat q absorbed by the system from the surroundings is

[Math Processing Error]

Since the heat absorbed by the system is the amount lost by the surroundings, *[Math Processing Error]*.Therefore, for a truly reversible process, the entropy change is

[Math Processing Error]

If the process is irreversible however, the entropy change is

[Math Processing Error]

If we put the two equations for *[Math Processing Error]*together for both types of processes, we are left with the second law of thermodynamics,

[Math Processing Error]

where *[Math Processing Error]* equals zero for a truly reversible process and is greater than zero for an irreversible process. In reality, however, truly reversible processes never happen (or will take an infinitely long time to happen), so it is safe to say all thermodynamic processes we encounter everyday are irreversible in the direction they occur.

> The second law of thermodynamics can also be stated that "all **spontaneous** processes produce an **increase** in the entropy of the universe".

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4.4: The Third Law of Thermodynamics

Learning Objectives

- The *absolute entropy* of a pure substance at a given temperature is the sum of all the entropy it would acquire on warming from absolute zero (where *[Math Processing Error]*) to the particular temperature.
- Calculate entropy changes for phase transitions and chemical reactions under standard conditions

The atoms, molecules, or ions that compose a chemical system can undergo several types of molecular motion, including translation, rotation, and vibration (Figure *[Math Processing Error]*). The greater the molecular motion of a system, the greater the number of possible microstates and the higher the entropy. A perfectly ordered system with only a single microstate available to it would have an entropy of zero. The only system that meets this criterion is a perfect crystal at a temperature of absolute zero (0 K), in which each component atom, molecule, or ion is fixed in place within a crystal lattice and exhibits no motion (ignoring quantum *zero point motion*).

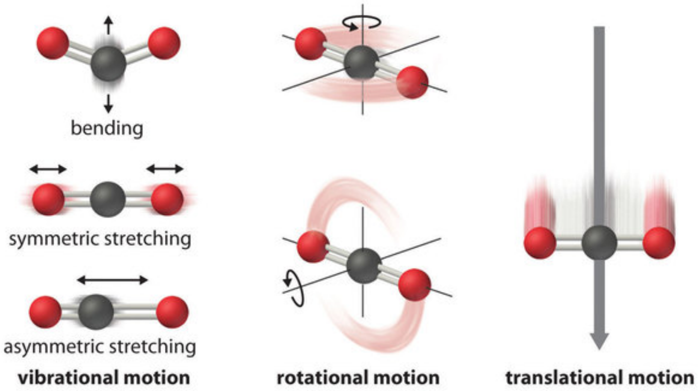

Figure *[Math Processing Error]*: Molecular Motions. Vibrational, rotational, and translational motions of a carbon dioxide molecule are illustrated here. Only a perfectly ordered, crystalline substance at absolute zero would exhibit no molecular motion (classically; there will always be motion quantum mechanically) and have zero entropy. In practice, this is an unattainable ideal. (CC BY-SA-NC; Anonymous by request)

This system may be described by a single microstate, as its purity, perfect crystallinity and complete lack of motion (at least classically, quantum mechanics argues for constant motion) means there is but one possible location for each identical atom or molecule comprising the crystal (*[Math Processing Error]*). According to the Boltzmann equation, the entropy of this system is zero.

[Math Processing Error]

In practice, absolute zero is an ideal temperature that is unobtainable, and a perfect single crystal is also an ideal that cannot be achieved. Nonetheless, the combination of these two ideals constitutes the basis for the third law of thermodynamics: the entropy of any perfectly ordered, crystalline substance at absolute zero is zero.

Definition: Third Law of Thermodynamics

The entropy of a pure, perfect crystalline substance at 0 K is zero.

The third law of thermodynamics has two important consequences: it defines the sign of the entropy of any substance at temperatures above absolute zero as positive, and it provides a fixed reference point that allows us to measure the absolute entropy of any substance at any temperature. In this section, we examine two different ways to calculate ΔS for a reaction or a physical change. The first, based on the definition of absolute entropy provided by the third law of thermodynamics, uses tabulated values of absolute entropies of substances. The second, based on the fact that entropy is a state function, uses a thermodynamic cycle similar to those discussed previously.

Standard-State Entropies

One way of calculating *[Math Processing Error]* for a reaction is to use tabulated values of the standard molar entropy (*[Math Processing Error]*), which is the entropy of 1 mol of a substance under standard pressure (1 bar). Often the standard molar entropy is given at 298 K and is often demarked as *[Math Processing Error]*. The units of *[Math Processing Error]* are J/(mol•K). Unlike enthalpy or internal energy, it is possible to obtain absolute entropy values by measuring the entropy change that occurs between the reference point of 0 K (corresponding to *[Math Processing Error]*) and 298 K (Tables T1 and T2).

As shown in Table *[Math Processing Error]*, for substances with approximately the same molar mass and number of atoms, *[Math Processing Error]* values fall in the order

[Math Processing Error]

For instance, *[Math Processing Error]* for liquid water is 70.0 J/(mol•K), whereas *[Math Processing Error]* for water vapor is 188.8 J/(mol•K). Likewise, *[Math Processing Error]* is 260.7 J/(mol•K) for gaseous *[Math Processing Error]* and 116.1 J/(mol•K) for solid *[Math Processing Error]*. This order makes qualitative sense based on the kinds and extents of motion available to atoms and molecules in the three phases (Figure *[Math Processing Error]*). The correlation between physical state and absolute entropy is illustrated in Figure *[Math Processing Error]*, which is a generalized plot of the entropy of a substance versus temperature.

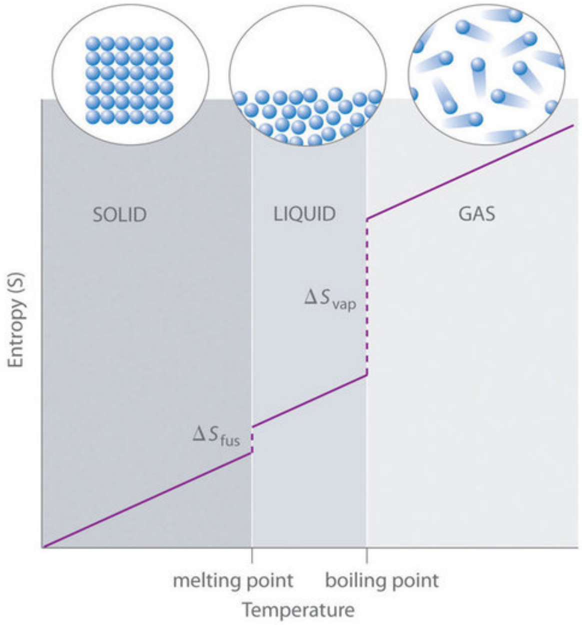

Figure *[Math Processing Error]*: A Generalized Plot of Entropy versus Temperature for a Single Substance. Absolute entropy increases steadily with increasing temperature until the melting point is reached, where it jumps suddenly as the substance undergoes a phase change from a highly ordered solid to a disordered liquid (ΔS_{fus}). The entropy again increases steadily with increasing temperature until the boiling point is reached, where it jumps suddenly as the liquid undergoes a phase change to a highly disordered gas (ΔS_{vap}). (CC BY-SA-NC; anonymous).

The Third Law Lets us Calculate Absolute Entropies

The *absolute entropy* of a substance at any temperature above 0 K must be determined by calculating the increments of heat *[Math Processing Error]* required to bring the substance from 0 K to the temperature of interest, and then summing the ratios *[Math Processing Error]*. Two kinds of experimental measurements are needed:

1. The enthalpies associated with any **phase changes** the substance may undergo within the temperature range of interest. Melting of a solid and vaporization of a liquid correspond to sizeable increases in the number of microstates available to accept thermal energy, so as these processes occur, energy will flow into a system, filling these new microstates to the extent required to maintain a constant temperature (the freezing or boiling point); these inflows of thermal energy correspond to the heats of fusion and vaporization. The entropy increase associated with transition at temperature *[Math Processing Error]* is *[Math Processing Error]*
2. The **heat capacity** *[Math Processing Error]* of a phase expresses the quantity of heat required to change the temperature by a small amount *[Math Processing Error]*, or more precisely, by an infinitesimal amount *[Math Processing Error]*. Thus the

entropy increase brought about by warming a substance over a range of temperatures that does not encompass a phase transition is given by the sum of the quantities *[Math Processing Error]* for each increment of temperature *[Math Processing Error]*. This is of course just the integral

[Math Processing Error]

Because the heat capacity is itself slightly temperature dependent, the most precise determinations of absolute entropies require that the functional dependence of *[Math Processing Error]* on *[Math Processing Error]* be used in the integral in Equation *[Math Processing Error]*, i.e.,:

[Math Processing Error]

When this is not known, one can take a series of heat capacity measurements over narrow temperature increments *[Math Processing Error]* and measure the area under each section of the curve. The area under each section of the plot represents the entropy change associated with heating the substance through an interval *[Math Processing Error]*. To this must be added the enthalpies of melting, vaporization, and of any solid-solid phase changes.

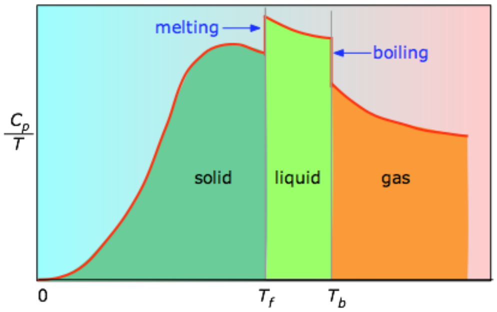

Figure *[Math Processing Error]*: Heat capacity/temperature as a function of temperature. (CC BY; Stephan Lower)

Values of *[Math Processing Error]* for temperatures near zero are not measured directly, but can be estimated from quantum theory. The cumulative areas from 0 K to any given temperature (Figure *[Math Processing Error]*) are then plotted as a function of *[Math Processing Error]*, and any phase-change entropies such as

[Math Processing Error]

are added to obtain the absolute entropy at temperature *[Math Processing Error]*. As shown in Figure *[Math Processing Error]* above, the entropy of a substance increases with temperature, and it does so for two reasons:

- As the temperature rises, more microstates become accessible, allowing thermal energy to be more widely dispersed. This is reflected in the gradual increase of entropy with temperature.
- The molecules of solids, liquids, and gases have increasingly greater freedom to move around, facilitating the spreading and sharing of thermal energy. Phase changes are therefore accompanied by massive and discontinuous increase in the entropy.

Calculating *[Math Processing Error]*

We can make careful calorimetric measurements to determine the temperature dependence of a substance's entropy and to derive absolute entropy values under specific conditions. Standard entropies are given the label *[Math Processing Error]* for values determined for one mole of substance at a pressure of 1 bar and a temperature of 298 K. The standard entropy change (*[Math Processing Error]*) for any process may be computed from the standard entropies of its reactant and product species like the following:

[Math Processing Error]

Here, *[Math Processing Error]* represents stoichiometric coefficients in the balanced equation representing the process. For example, *[Math Processing Error]* for the following reaction at room temperature

[Math Processing Error]

is computed as the following:

[Math Processing Error]

Table *[Math Processing Error]* lists some standard entropies at 298.15 K. You can find additional standard entropies in Tables T1 and T2

Table *[Math Processing Error]*: Standard Molar Entropy Values of Selected Substances at 25°C

Gases		**Liquids**		**Solids**	
Substance	*[Math Processing Error] [J/(mol•K)]*	*Substance*	*[Math Processing Error] [J/(mol•K)]*	*Substance*	*[Math Processing Error] [J/(mol•K)]*
He	126.2	H_2O	70.0	C (diamond)	2.4
H_2	130.7	CH_3OH	126.8	C (graphite)	5.7
Ne	146.3	Br_2	152.2	LiF	35.7
Ar	154.8	CH_3CH_2OH	160.7	SiO_2 (quartz)	41.5
Kr	164.1	C_6H_6	173.4	Ca	41.6
Xe	169.7	CH_3COCl	200.8	Na	51.3
H_2O	188.8	C_6H_{12} (cyclohexane)	204.4	MgF_2	57.2
N_2	191.6	C_8H_{18} (isooctane)	329.3	K	64.7
O_2	205.2			NaCl	72.1
CO_2	213.8			KCl	82.6
I_2	260.7			I_2	116.1

A closer examination of Table *[Math Processing Error]* also reveals that substances with similar molecular structures tend to have similar *[Math Processing Error]* values. Among crystalline materials, those with the lowest entropies tend to be rigid crystals composed of small atoms linked by strong, highly directional bonds, such as diamond (*[Math Processing Error]*). In contrast, graphite, the softer, less rigid allotrope of carbon, has a higher *[Math Processing Error]* (5.7 J/(mol•K)) due to more ~~disorder~~ (microstates) in the crystal. Soft crystalline substances and those with larger atoms tend to have higher entropies because of increased molecular motion and disorder. Similarly, the absolute entropy of a substance tends to increase with increasing molecular complexity because the number of available microstates increases with molecular complexity. For example, compare the *[Math Processing Error]* values for $CH_3OH(l)$ and $CH_3CH_2OH(l)$. Finally, substances with strong hydrogen bonds have lower values of *[Math Processing Error]*, which reflects a more ordered structure.

> *Entropy increases with softer, less rigid solids, solids that contain larger atoms, and solids with complex molecular structures.*

To calculate *[Math Processing Error]* for a chemical reaction from standard molar entropies, we use the familiar "products minus reactants" rule, in which the absolute entropy of each reactant and product is multiplied by its stoichiometric coefficient in the balanced chemical equation. Example *[Math Processing Error]* illustrates this procedure for the combustion of the liquid hydrocarbon isooctane (*[Math Processing Error]*; 2,2,4-trimethylpentane).

✓ Example *[Math Processing Error]*

Use the data in Table *[Math Processing Error]* to calculate *[Math Processing Error]* for the reaction of liquid isooctane with *[Math Processing Error]* to give *[Math Processing Error]* and *[Math Processing Error]* at 298 K.

Given: standard molar entropies, reactants, and products

Asked for: ΔS°

Strategy:

Write the balanced chemical equation for the reaction and identify the appropriate quantities in Table *[Math Processing Error]*. Subtract the sum of the absolute entropies of the reactants from the sum of the absolute entropies of the products, each multiplied by their appropriate stoichiometric coefficients, to obtain *[Math Processing Error]* for the reaction.

Solution:

The balanced chemical equation for the complete combustion of isooctane (*[Math Processing Error]*) is as follows:

[Math Processing Error]

We calculate *[Math Processing Error]* for the reaction using the “products minus reactants” rule, where m and n are the stoichiometric coefficients of each product and each reactant:

[Math Processing Error]

[Math Processing Error] is positive, as expected for a combustion reaction in which one large hydrocarbon molecule is converted to many molecules of gaseous products.

? Exercise *[Math Processing Error]*

Use the data in Table *[Math Processing Error]* to calculate *[Math Processing Error]* for the reaction of *[Math Processing Error]* with liquid benzene (*[Math Processing Error]*) to give cyclohexane (*[Math Processing Error]*) at 298 K.

Answer

-361.1 J/K

✓ Example *[Math Processing Error]*: Determination of ΔS°

Calculate the standard entropy change for the following process at 298 K:

[Math Processing Error]

Solution

The value of the standard entropy change at room temperature, *[Math Processing Error]*, is the difference between the standard entropy of the product, $H_2O(l)$, and the standard entropy of the reactant, $H_2O(g)$.

[Math Processing Error]

The value for *[Math Processing Error]* is negative, as expected for this phase transition (condensation), which the previous section discussed.

? Exercise *[Math Processing Error]*

Calculate the standard entropy change for the following process at 298 K:

[Math Processing Error]

Answer

$-120.6\ \mathrm{J\ mol^{-1}\ K^{-1}}$

✓ Example *[Math Processing Error]*: Determination of ΔS°

Calculate the standard entropy change for the combustion of methanol, CH_3OH at 298 K:

[Math Processing Error]

Solution

The value of the standard entropy change is equal to the difference between the standard entropies of the products and the entropies of the reactants scaled by their stoichiometric coefficients. The standard entropy of formations are found in Table

[Math Processing Error].

[Math Processing Error]

Exercise [Math Processing Error]

Calculate the standard entropy change for the following reaction at 298 K:

[Math Processing Error]

Answer

24.7 J/mol•K

Summary

Energy values, as you know, are all relative, and must be defined on a scale that is completely arbitrary; there is no such thing as the absolute energy of a substance, so we can arbitrarily define the enthalpy or internal energy of an element in its most stable form at 298 K and 1 atm pressure as zero. The same is *not* true of the entropy; since entropy is a measure of the “dilution” of thermal energy, it follows that the less thermal energy available to spread through a system (that is, the lower the temperature), the smaller will be its entropy. In other words, as the absolute temperature of a substance approaches zero, so does its entropy. This principle is the basis of the *Third law of thermodynamics*, which states that the entropy of a perfectly-ordered solid at 0 K is zero.

In practice, chemists determine the absolute entropy of a substance by measuring the molar heat capacity ([Math Processing Error]) as a function of temperature and then plotting the quantity [Math Processing Error] versus [Math Processing Error]. The area under the curve between 0 K and any temperature T is the absolute entropy of the substance at [Math Processing Error]. In contrast, other thermodynamic properties, such as internal energy and enthalpy, can be evaluated in only relative terms, not absolute terms.

The second law of thermodynamics states that a spontaneous process increases the entropy of the universe, $S_{\text{univ}} > 0$. If $\Delta S_{\text{univ}} < 0$, the process is nonspontaneous, and if $\Delta S_{\text{univ}} = 0$, the system is at equilibrium. The third law of thermodynamics establishes the zero for entropy as that of a perfect, pure crystalline solid at 0 K. With only one possible microstate, the entropy is zero. We may compute the standard entropy change for a process by using standard entropy values for the reactants and products involved in the process.

Contributors and Attributions

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- Stephen Lower, Professor Emeritus (Simon Fraser U.) Chem1 Virtual Textbook

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4.5: Evaluating Entropy and Entropy Changes

Learning Objectives

- To use thermodynamic cycles to calculate changes in entropy.

The atoms, molecules, or ions that compose a chemical system can undergo several types of molecular motion, including translation, rotation, and vibration (Figure *[Math Processing Error]*). The greater the molecular motion of a system, the greater the number of possible microstates and the higher the entropy. A perfectly ordered system with only a single microstate available to it would have an entropy of zero. The only system that meets this criterion is a perfect crystal at a temperature of absolute zero (0 K), in which each component atom, molecule, or ion is fixed in place within a crystal lattice and exhibits no motion (ignoring quantum effects). Such a state of perfect order (or, conversely, zero disorder) corresponds to zero entropy. In practice, absolute zero is an ideal temperature that is unobtainable, and a perfect single crystal is also an ideal that cannot be achieved. Nonetheless, the combination of these two ideals constitutes the basis for the third law of thermodynamics: the entropy of any perfectly ordered, crystalline substance at absolute zero is zero.

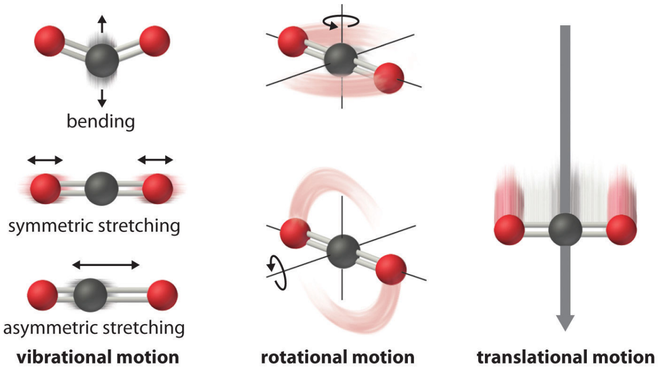

Figure *[Math Processing Error]*: Molecular Motions. Vibrational, rotational, and translational motions of a carbon dioxide molecule are illustrated here. Only a perfectly ordered, crystalline substance at absolute zero would exhibit no molecular motion and have zero entropy. In practice, this is an unattainable ideal.

Third Law of Thermodynamics

The entropy of any perfectly ordered, crystalline substance at absolute zero is *zero*.

The third law of thermodynamics has two important consequences: it defines the sign of the entropy of any substance at temperatures above absolute zero as positive, and it provides a fixed reference point that allows us to measure the absolute entropy of any substance at any temperature.In practice, chemists determine the absolute entropy of a substance by measuring the molar heat capacity (C_p) as a function of temperature and then plotting the quantity C_p/T versus T. The area under the curve between 0 K and any temperature T is the absolute entropy of the substance at T. In contrast, other thermodynamic properties, such as internal energy and enthalpy, can be evaluated in only relative terms, not absolute terms. In this section, we examine two different ways to calculate ΔS for a reaction or a physical change. The first, based on the definition of absolute entropy provided by the third law of thermodynamics, uses tabulated values of absolute entropies of substances. The second, based on the fact that entropy is a state function, uses a thermodynamic cycle similar to those discussed previously.

Calculating ΔS from Standard Molar Entropy Values

One way of calculating ΔS for a reaction is to use tabulated values of the standard molar entropy (S°), which is the entropy of 1 mol of a substance at a standard temperature of 298 K; the units of S° are J/(mol•K). Unlike enthalpy or internal energy, it is possible to obtain absolute entropy values by measuring the entropy change that occurs between the reference point of 0 K [corresponding to S = 0 J/(mol•K)] and 298 K.

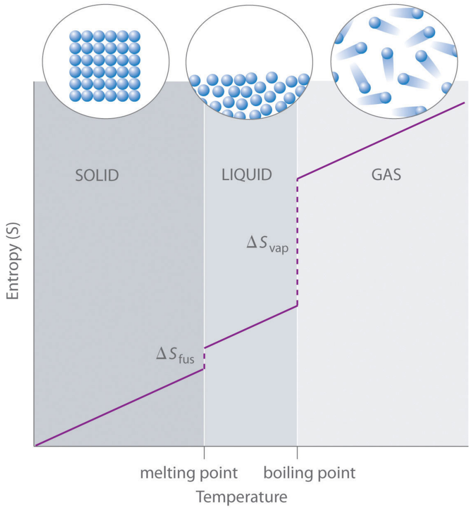

Figure [Math Processing Error]: A Generalized Plot of Entropy versus Temperature for a Single Substance. Absolute entropy increases steadily with increasing temperature until the melting point is reached, where it jumps suddenly as the substance undergoes a phase change from a highly ordered solid to a disordered liquid (ΔS_{fus}). The entropy again increases steadily with increasing temperature until the boiling point is reached, where it jumps suddenly as the liquid undergoes a phase change to a highly disordered gas (ΔS_{vap}).

As shown in Table [Math Processing Error], for substances with approximately the same molar mass and number of atoms, S° values fall in the order S°(gas) > S°(liquid) > S°(solid). For instance, S° for liquid water is 70.0 J/(mol•K), whereas S° for water vapor is 188.8 J/(mol•K). Likewise, S° is 260.7 J/(mol•K) for gaseous I_2 and 116.1 J/(mol•K) for solid I2. This order makes qualitative sense based on the kinds and extents of motion available to atoms and molecules in the three phases. The correlation between physical state and absolute entropy is illustrated in Figure [Math Processing Error], which is a generalized plot of the entropy of a substance versus temperature.

Table [Math Processing Error]: Standard Molar Entropy Values of Selected Substances at 25°C

Gases		**Liquids**		**Solids**	
Substance	*S° [J/(mol•K)]*	*Substance*	*S° [J/(mol•K)]*	*Substance*	*S° [J/(mol•K)]*
He	126.2	H_2O	70.0	C (diamond)	2.4
H_2	130.7	CH_3OH	126.8	C (graphite)	5.7
Ne	146.3	Br_2	152.2	LiF	35.7
Ar	154.8	CH_3CH_2OH	160.7	SiO_2 (quartz)	41.5
Kr	164.1	C_6H_6	173.4	Ca	41.6
Xe	169.7	CH_3COCl	200.8	Na	51.3
H_2O	188.8	C_6H_{12} (cyclohexane)	204.4	MgF_2	57.2
N_2	191.6	C_8H_{18} (isooctane)	329.3	K	64.7
O_2	205.2			NaCl	72.1
CO_2	213.8			KCl	82.6
I_2	260.7			I_2	116.1

Note

Entropy increases with softer, less rigid solids, solids that contain larger atoms, and solids with complex molecular structures.

A closer examination of Table *[Math Processing Error]* also reveals that substances with similar molecular structures tend to have similar S° values. Among crystalline materials, those with the lowest entropies tend to be rigid crystals composed of small atoms linked by strong, highly directional bonds, such as diamond [S° = 2.4 J/(mol•K)]. In contrast, graphite, the softer, less rigid allotrope of carbon, has a higher S° [5.7 J/(mol•K)] due to more disorder in the crystal. Soft crystalline substances and those with larger atoms tend to have higher entropies because of increased molecular motion and disorder. Similarly, the absolute entropy of a substance tends to increase with increasing molecular complexity because the number of available microstates increases with molecular complexity. For example, compare the S° values for $CH_3OH(l)$ and $CH_3CH_2OH(l)$. Finally, substances with strong hydrogen bonds have lower values of S°, which reflects a more ordered structure.

Note

ΔS° for a reaction can be calculated from absolute entropy values using the same “products minus reactants” rule used to calculate ΔH°.

To calculate ΔS° for a chemical reaction from standard molar entropies, we use the familiar “products minus reactants” rule, in which the absolute entropy of each reactant and product is multiplied by its stoichiometric coefficient in the balanced chemical equation. Example *[Math Processing Error]* illustrates this procedure for the combustion of the liquid hydrocarbon isooctane (C_8H_{18}; 2,2,4-trimethylpentane).

Example *[Math Processing Error]*

Use the data in Table *[Math Processing Error]* to calculate ΔS° for the reaction of liquid isooctane with $O_2(g)$ to give $CO_2(g)$ and $H_2O(g)$ at 298 K.

Given: standard molar entropies, reactants, and products

Asked for: ΔS°

Strategy:

Write the balanced chemical equation for the reaction and identify the appropriate quantities in Table *[Math Processing Error]*. Subtract the sum of the absolute entropies of the reactants from the sum of the absolute entropies of the products, each multiplied by their appropriate stoichiometric coefficients, to obtain ΔS° for the reaction.

Solution:

The balanced chemical equation for the complete combustion of isooctane (C_8H_{18}) is as follows:

[Math Processing Error]

We calculate ΔS° for the reaction using the “products minus reactants” rule, where m and n are the stoichiometric coefficients of each product and each reactant:

[Math Processing Error]

ΔS° is positive, as expected for a combustion reaction in which one large hydrocarbon molecule is converted to many molecules of gaseous products.

Exercise *[Math Processing Error]*

Use the data in Table *[Math Processing Error]* to calculate ΔS° for the reaction of $H_2(g)$ with liquid benzene (C_6H_6) to give cyclohexane (C_6H_{12}).

Answer: −361.1 J/K

Calculating ΔS from Thermodynamic Cycles

We can also calculate a change in entropy using a thermodynamic cycle. As you learned previously, the molar heat capacity (C_p) is the amount of heat needed to raise the temperature of 1 mol of a substance by 1°C at constant pressure. Similarly, C_v is the amount of heat needed to raise the temperature of 1 mol of a substance by 1°C at constant volume. The increase in entropy with increasing temperature in Figure *[Math Processing Error]* is approximately proportional to the heat capacity of the substance.

Recall that the entropy change (ΔS) is related to heat flow (q_{rev}) by $\Delta S = q_{rev}/T$. Because $q_{rev} = nC_p\Delta T$ at constant pressure or $nC_v\Delta T$ at constant volume, where n is the number of moles of substance present, the change in entropy for a substance whose temperature changes from T_1 to T_2 is as follows:

[Math Processing Error]

As you will discover in more advanced math courses than is required here, it can be shown that this is equal to the following:For a review of natural logarithms, see Essential Skills 6 in Chapter 11.

[Math Processing Error]

Similarly,

[Math Processing Error]

Thus we can use a combination of heat capacity measurements (Equation 18.20 or Equation 18.21) and experimentally measured values of enthalpies of fusion or vaporization if a phase change is involved (Equation 18.18) to calculate the entropy change corresponding to a change in the temperature of a sample.

We can use a thermodynamic cycle to calculate the entropy change when the phase change for a substance such as sulfur cannot be measured directly. As noted in the exercise in Example 6, elemental sulfur exists in two forms (part (a) in Figure *[Math Processing Error]*): an orthorhombic form with a highly ordered structure (S_α) and a less-ordered monoclinic form (S_β). The orthorhombic (α) form is more stable at room temperature but undergoes a phase transition to the monoclinic (β) form at temperatures greater than 95.3°C (368.5 K). The transition from S_α to S_β can be described by the thermodynamic cycle shown in part (b) in Figure *[Math Processing Error]*, in which liquid sulfur is an intermediate. The change in entropy that accompanies the conversion of liquid sulfur to S_β ($-\Delta S_{fus(\beta)} = \Delta S_3$ in the cycle) cannot be measured directly. Because entropy is a state function, however, ΔS_3 can be calculated from the overall entropy change (ΔS_t) for the S_α–S_β transition, which equals the sum of the ΔS values for the steps in the thermodynamic cycle, using Equation 18.20 and tabulated thermodynamic parameters (the heat capacities of S_α and S_β, $\Delta H_{fus(\alpha)}$, and the melting point of S_α.)

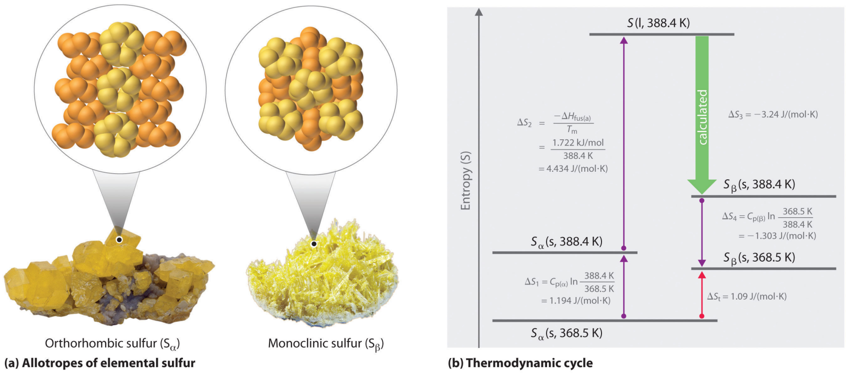

Figure *[Math Processing Error]*: Two Forms of Elemental Sulfur and a Thermodynamic Cycle Showing the Transition from One to the Other(a) Orthorhombic sulfur (S_α) has a highly ordered structure in which the S_8 rings are stacked in a “crankshaft” arrangement. Monoclinic sulfur (S_β) is also composed of S_8 rings but has a less-ordered structure. (b) At 368.5 K, S_α undergoes a phase transition to S_β. Although ΔS_3 cannot be measured directly, it can be calculated using the values shown in this thermodynamic cycle.

If we know the melting point of S_α (T_m = 115.2°C = 388.4 K) and ΔS_t for the overall phase transition [calculated to be 1.09 J/(mol•K) in the exercise in Example 6], we can calculate ΔS_3 from the values given in part (b) in Figure *[Math Processing Error]* where $C_{p(\alpha)}$ = 22.70 J/mol•K and $C_{p(\beta)}$ = 24.77 J/mol•K (subscripts on ΔS refer to steps in the cycle):

[Math Processing Error]

Solving for ΔS_3 gives a value of −3.24 J/(mol•K). As expected for the conversion of a less ordered state (a liquid) to a more ordered one (a crystal), ΔS_3 is negative.

How are Entropies Measured

The *absolute entropy* of a substance at any temperature above 0 K must be determined by calculating the increments of heat *q* required to bring the substance from 0 K to the temperature of interest, and then summing the ratios *q*/*T*. Two kinds of experimental measurements are needed:

1. The enthalpies associated with any **phase changes** the substance may undergo within the temperature range of interest. Melting of a solid and vaporization of a liquid correspond to sizeable increases in the number of microstates available to accept thermal energy, so as these processes occur, energy will flow into a system, filling these new microstates to the extent required to maintain a constant temperature (the freezing or boiling point); these inflows of thermal energy correspond to the heats of fusion and vaporization. The entropy increase associated with melting, for example, is just $\Delta H_{fusion}/T_m$.
2. The **heat capacity** C of a phase expresses the quantity of heat required to change the temperature by a small amount ΔT , or more precisely, by an infinitesimal amount dT . Thus the entropy increase brought about by warming a substance over a range of temperatures that does not encompass a phase transition is given by the sum of the quantities $C\ dT/T$ for each increment of temperature dT . This is of course just the integral

[Math Processing Error]

Because the heat capacity is itself slightly temperature dependent, the most precise determinations of absolute entropies require that the functional dependence of C on T be used in the above integral in place of a constant C.

[Math Processing Error]

When this is not known, one can take a series of heat capacity measurements over narrow temperature increments ΔT and measure the area under each section of the curve.

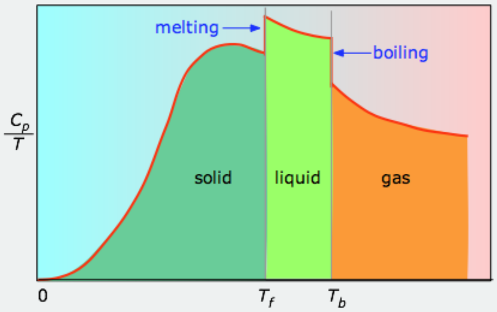

Figure *[Math Processing Error]*: Heat capitity/temperature as a function of temperature

The area under each section of the plot represents the entropy change associated with heating the substance through an interval ΔT. To this must be added the enthalpies of melting, vaporization, and of any solid-solid phase changes. Values of C_p for temperatures near zero are not measured directly, but can be estimated from quantum theory.

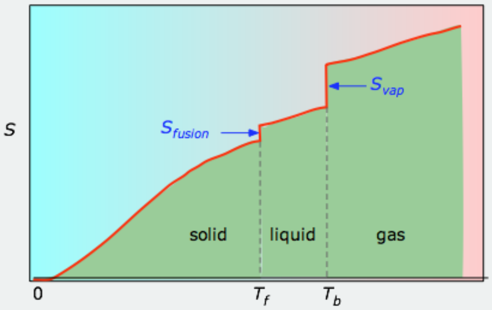

Figure *[Math Processing Error]*: Molar entropy as a function of temperature

The cumulative areas from 0 K to any given temperature (taken from the experimental plot on the left) are then plotted as a function of T, and any phase-change entropies such as $S_{vap} = H_{vap} / T_b$ are added to obtain the absolute entropy at temperature T.

Summary

- Entropy changes can be calculated using the “products minus reactants” rule or from a combination of heat capacity measurements and measured values of enthalpies of fusion or vaporization.

The third law of thermodynamics states that the entropy of any perfectly ordered, crystalline substance at absolute zero is zero. At temperatures greater than absolute zero, entropy has a positive value, which allows us to measure the absolute entropy of a substance. Measurements of the heat capacity of a substance and the enthalpies of fusion or vaporization can be used to calculate the changes in entropy that accompany a physical change. The entropy of 1 mol of a substance at a standard temperature of 298 K is its standard molar entropy (S°). We can use the “products minus reactants” rule to calculate the standard entropy change (ΔS°) for a reaction using tabulated values of S° for the reactants and the products.

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4.6: Gibbs Energy

Gibbs energy is the energy of a chemical reaction that can be used to do non-mechanical work. Gibbs Energy is described as

[Math Processing Error]

Where H is enthalpy, T is temperature, and S is entropy. ΔG is used to predict spontaneity within a system by

[Math Processing Error]

Gibbs energy was developed in the 1870's by Josiah Willard Gibbs. He originally termed this energy as the "available energy" in a system. His paper published in 1873, "Graphical Methods in the Thermodynamics of Fluids," outlined how his equation could predict the behavior of systems when they are combined.

At a constant temperature and pressure, the Gibbs Energy of a system can be described as

[Math Processing Error]

This equation can be used to determine the spontaneity of the process.

- If $\Delta G_{sys} \leq 0$, the process is spontaneous.
- If $\Delta G_{sys} = 0$, the system is at equilibrium.
- If $\Delta G_{sys} > 0$, the process is not spontaneous.

Furthermore,

- If $\Delta G_{sys} < 0$, the process is *exergonic*
- If $\Delta G_{sys} > 0$, the process is *endergonic*.

Gibbs Energy is a useful tool to describe in what manner the reaction is conducted. If ΔH >> TΔS, the reaction is enthalpy driven. However, if TΔS >> ΔH, the reaction is driven by entropy. The Clausius-Clapeyron Equation is an application derived from Gibb's energy:

[Math Processing Error]

Another important application of Gibb's energy is the Maxwell relations (also available in a link at the end of the wiki page.)

Temperature & Pressure Dependence

When the pressure & temperature of a reaction are not held constant,

[Math Processing Error]

For an infinitesimal process,

[Math Processing Error]

[Math Processing Error]

For a reaction where temperature is held constant,

[Math Processing Error]

From the First Law of Thermodynamics, we know

[Math Processing Error]

[Math Processing Error]

Since

[Math Processing Error]

We find that

[Math Processing Error]

showing the obvious dependence of ΔG on temperature and pressure. To observe the change in Gibbs energy due to temperature change alone (pressure held constant) the equation becomes

[Math Processing Error]

Solving for S and plugging it into Eq. (1), the Gibbs-Helmholtz Equation is found:

[Math Processing Error]

The Gibbs-Helmholtz Equation is very important because it relates the change in Gibbs energy to its temperature dependence, and the position of equilibrium to change in enthalpy.

To observe the change in Gibbs energy due to pressure change alone (temperature held constant) the equation becomes

[Math Processing Error]

If the gas is assumed to be ideal then

[Math Processing Error]

for an initial and final pressure (P1 and P2) at a constant T.

Standard-State Free Energy of Formation

Gibbs Energy is defined as a state function (a property that depends only on conditions describing the system, not how the change occurs as in a path function.) This is because each component of the equation (H,T, and S) are all state functions. Therefore, we can know the change in Gibbs energy without knowing every detail of the process. In a process that takes place at constant temperature and pressure (298 K, 1 atm) the standard molar free energy of formation can be determined by the change in free energy from the reactants and products. Using predetermined values, Eqn. (17) can be used

[Math Processing Error]

Standard-State Free Energy of Reaction

Gibbs Energy can be found at standard-state conditions using

[Math Processing Error]

ΔH° and ΔS° values can be found in the appendix of any general chemistry textbook, or using this link.

Free Energy of Reaction

Gibbs energy can be found at any conditions by relating it to the standard-state free energy of reaction, using

[Math Processing Error]

Where Q is the reaction quotient. Very rarely does chemistry actually occur at the given "standard-state" conditions. Using the above equation and standard-state values, chemists can determine the overall Gibb's energy for the system, regardless of the conditions.

References

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Problems

1. Calculate the standard-state free energy of formation for the $H_2O_2(l)$ from H_2 and O_2, given the following values:
   $\Delta_f G$ (H_2): 0 kJ/mol
   $\Delta_f G$ (O_2): 0 kJ/mol
   $\Delta_f G$ ($H_2O_2(l)$): -120.4 kJ/mol

   Hint: (product*coefficient) - [(Reactant1*coefficient)+(Reactant2*coefficient)]
2. Consider the following reaction: *[Math Processing Error]*
   At what temperature will this reaction become favorable? Note: Assume $\Delta H_r°$and $\Delta S_r°$ are temperature independent.
   Given values:

Substance	$\Delta H_f°$	$S_f°$

Substance	ΔH_f°	S_f°
$CaCO_3$	-1206.9 kJ/mol	92.9 J/K mol
CaO	-635.6 kJ/mol	39.8 J/K mol
CO_2	-393.5 kJ/mol	213.6 J/K mol

Hint: At what value of ΔG does a reaction become spontaneous, and therefore favorable? Next, find the ΔH value for the reaction (products-reactants) and the ΔS values for the reaction (products-reactants.) Solve for T.

3. Is the above decomposition of calcium carbonate enthalpy driven or entropy driven?

   Hint: Is ΔH >> TΔS, or TΔS >> ΔH?

Anwers to Problems

1. -120.4 kJ/mol
2. 1107.8 K
3. Enthalpy

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4.7: Standard Molar Gibbs Energy of Formation

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4.8: Dependence of Gibbs Energy on Temperature and Pressure

Learning Objectives

- To get an overview of Gibbs energy and its general uses in chemistry.
    - Understand how Gibbs energy pertains to reactions properties
    - Understand how Gibbs energy pertains to equilibria properties
    - Understand how Gibbs energy pertains to electrochemical properties

Gibbs free energy, denoted *[Math Processing Error]*, combines enthalpy and entropy into a single value. The change in free energy, *[Math Processing Error]*, is equal to the sum of the enthalpy plus the product of the temperature and entropy of the system. *[Math Processing Error]* can predict the direction of the chemical reaction under two conditions:

1. constant temperature and
2. constant pressure.

If *[Math Processing Error]* is positive, then the reaction is nonspontaneous (i.e., an the input of external energy is necessary for the reaction to occur) and if it is negative, then it is spontaneous (occurs without external energy input).

Introduction

Gibbs energy was developed in the 1870's by Josiah Willard Gibbs. He originally termed this energy as the "available energy" in a system. His paper published in 1873, "Graphical Methods in the Thermodynamics of Fluids," outlined how his equation could predict the behavior of systems when they are combined. This quantity is the energy associated with a chemical reaction that can be used to work, and is the sum of its enthalpy (H) and the product of the temperature and the entropy (S) of the system. This quantity is defined as follows:

[Math Processing Error]

or more completely as

[Math Processing Error]

where

- *[Math Processing Error]* is internal energy (SI unit: joule)
- *[Math Processing Error]* is pressure (SI unit: pascal)
- *[Math Processing Error]* is volume (SI unit: *[Math Processing Error]*)
- *[Math Processing Error]*is temperature (SI unit: kelvin)
- *[Math Processing Error]* is entropy (SI unit: joule/kelvin)
- *[Math Processing Error]* is the enthalpy (SI unit: joule)

Gibbs Energy in Reactions

Spontaneous - is a reaction that is consider to be natural because it is a reaction that occurs by itself without any external action towards it. Non spontaneous - needs constant external energy applied to it in order for the process to continue and once you stop the external action the process will cease. When solving for the equation, if change of G is negative, then it's spontaneous. If change of G if positive, then it's non spontaneous. The symbol that is commonly used for FREE ENERGY is G. can be more properly consider as "standard free energy change"

In chemical reactions involving the changes in thermodynamic quantities, a variation on this equation is often encountered:

[Math Processing Error]

Example 1.1

Calculate ΔG at 290 K for the following reaction:

[Math Processing Error]

Given

- ΔH = -120 kJ
- ΔS = -150 JK^{-1}

Solution

now all you have to do is plug in all the given numbers into Equation 3 above. Remember to divide *[Math Processing Error]* by 1000 *[Math Processing Error]* so that after you multiply by temperature, *[Math Processing Error]*, it will have the same units, *[Math Processing Error]*, as *[Math Processing Error]*.

[Math Processing Error]

and substituting into Equation 3:

[Math Processing Error]

? Exercise 1.1: The Haber Process

What is the *[Math Processing Error]* for this formation of ammonia from nitrogen and hydrogen gas.

[Math Processing Error]

The Standard free energy formations: NH_3 =-16.45 H_2=0 N_2=0

Answer

[Math Processing Error]

Since the changes of entropy of chemical reaction are not measured readily, thus, entropy is not typically used as a criterion. To obviate this difficulty, we can use *[Math Processing Error]*. The sign of ΔG indicates the direction of a chemical reaction and determine if a reaction is spontaneous or not.

- *[Math Processing Error]*: reaction is spontaneous in the direction written (i.e., the reaciton is **exergonic**)
- *[Math Processing Error]*: the system is at equilibrium and there is no net change either in forward or reverse direction.
- *[Math Processing Error]*: reaction is not spontaneous and the process proceeds spontaneously in the reserve direction. To drive such a reaction, we need to have input of free energy (i.e., the reaction is **endergonic**)

The factors affect *[Math Processing Error]* of a reaction (assume *[Math Processing Error]* and *[Math Processing Error]* are independent of temperature):

[Math Processing Error]	*[Math Processing Error]*	*[Math Processing Error]*	Example
+	+	at low temperature: + , at high temperature: -	$2HgO(s) \rightarrow 2Hg(l) + O_2(g)$
+	-	at all temperature: +	$3O_2(g) \rightarrow 2O_3(g)$
-	+	at all temperature: -	$2H_2O_2(l) \rightarrow 2H_2O(l) + O_2(g)$
-	-	at low temperature: - , at high temperature: +	$NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$

Note:

1. *[Math Processing Error]* depends only on the difference in free energy of products and reactants (or final state and initial state). *[Math Processing Error]* is independent of the path of the transformation and is unaffected by the mechanism of a reaction.
2. *[Math Processing Error]* cannot tell us anything about the rate of a reaction.

The standard Gibbs energy change *[Math Processing Error]* (at which reactants are converted to products at 1 bar) for:

[Math Processing Error]

[Math Processing Error]

[Math Processing Error]

The standard-state free energy of reaction (*[Math Processing Error]*) is defined as the free energy of reaction at standard state conditions:

[Math Processing Error]

Note

- If *[Math Processing Error]*: the reaction is *enthalpy-driven*
- If *[Math Processing Error]* << *[Math Processing Error]*: the *reaction is entropy-driven*

Standard-State Free Energy of Formation

- The partial pressure of any gas involved in the reaction is 0.1 MPa.
- The concentrations of all aqueous solutions are 1 M.
- Measurements are generally taken at a temperature of 25° C (298 K).

The standard-state free energy of formation is the change in free energy that occurs when a compound is formed from its elements in their most thermodynamically stable states at standard-state conditions. In other words, it is the difference between the free energy of a substance and the free energies of its constituent elements at standard-state conditions:

[Math Processing Error]

Example 1.2

Used the below information to determine if *[Math Processing Error]* will dissolve in water at room temperature.

Compound	*[Math Processing Error]*	*[Math Processing Error]*
[Math Processing Error]	-365.56	151.08
[Math Processing Error]	-132.51	113.4
[Math Processing Error]	205.0	146.4

Solution

This question is essentially asking if the following reaction is spontaneous at room temperature.

[Math Processing Error]

This would normally only require calculating *[Math Processing Error]* and evaluating its sign. However, the *[Math Processing Error]* values are not tabulated, so they must be calculated manually from calculated *[Math Processing Error]* and *[Math Processing Error]* values for the reaction.

- *Calculate [Math Processing Error]:*

[Math Processing Error]

[Math Processing Error]

[Math Processing Error]

[Math Processing Error]

- *Calculate [Math Processing Error]:*

[Math Processing Error]

[Math Processing Error]

[Math Processing Error]

[Math Processing Error]

- *Calculate [Math Processing Error]:*

These values can be substituted into the free energy equation

[Math Processing Error]

[Math Processing Error]

[Math Processing Error]

Plug in [Math Processing Error], [Math Processing Error] and [Math Processing Error] into Equation 1.7

[Math Processing Error]

[Math Processing Error]

[Math Processing Error]

[Math Processing Error]

This reaction is spontaneous at room temperature since [Math Processing Error] is negative. Therefore [Math Processing Error] will dissolve in water at room temperature.

✓ Example 1.3

Calculate [Math Processing Error] for the following reaction at [Math Processing Error]. Will the reaction occur spontaneously?

[Math Processing Error]

given for the reaction

- [Math Processing Error]
- [Math Processing Error]

Solution

calculate [Math Processing Error] from the formula

[Math Processing Error]

but first we need to convert the units for [Math Processing Error] into kJ/K (or convert [Math Processing Error] into J) and temperature into Kelvin

- [Math Processing Error]
- [Math Processing Error]

The definition of Gibbs energy can then be used directly

[Math Processing Error]

[Math Processing Error]

[Math Processing Error]

[Math Processing Error]

Yes, this reaction is spontaneous at room temperature since [Math Processing Error] is negative.

Gibbs Energy in Equilibria

Let's consider the following reversible reaction:

[Math Processing Error]

The following equation relates the standard-state free energy of reaction with the free energy at any point in a given reaction (not necessarily at standard-state conditions):

[Math Processing Error]

- [Math Processing Error] = free energy at any moment
- [Math Processing Error] = standard-state free energy
- R is the ideal gas constant = 8.314 J/mol-K

- T is the absolute temperature (Kelvin)
- *[Math Processing Error]* is natural logarithm of the **reaction quotient**

At equilibrium, ΔG = 0 and Q=K. Thus the equation can be arranged into:

[Math Processing Error]

with

- *[Math Processing Error]* = standard free energy change
- *[Math Processing Error]* = gas constant = 1.98 * 10^{-3} kcal mol^{-1} deg^{-10}
- *[Math Processing Error]* = is usually room temperature = 298 K
- *[Math Processing Error]*

The Gibbs free energy *[Math Processing Error]* depends primarily on the reactants' nature and concentrations (expressed in the *[Math Processing Error]* term and the logarithmic term of Equation 1.11, respectively).

At equilibrium, *[Math Processing Error]*: no driving force remains

[Math Processing Error]

[Math Processing Error]

The equilibrium constant is defined as

[Math Processing Error]

When *[Math Processing Error]* is large, almost all reactants are converted to products. Substituting *[Math Processing Error]* into Equation 1.14, we have:

[Math Processing Error]

or

[Math Processing Error]

Rearrange,

[Math Processing Error]

This equation is particularly interesting as it relates the free energy difference under standard conditions to the properties of a system at equilibrium (which is rarely at standard conditions).

Table 1.1: Converting *[Math Processing Error]* to *[Math Processing Error]*

[Math Processing Error]	*[Math Processing Error]*
[Math Processing Error]	6.82
[Math Processing Error]	5.46
[Math Processing Error]	4.09
[Math Processing Error]	2.73
[Math Processing Error]	1.36
1	0
[Math Processing Error]	-1.36
[Math Processing Error]	-2.73
[Math Processing Error]	-4.09
[Math Processing Error]	-5.46
[Math Processing Error]	-6.82

Example 1.4

What is [Math Processing Error] for isomerization of dihydroxyacetone phosphate to glyceraldehyde 3-phosphate?

If at equilibrium, we have [Math Processing Error] at 298 K and pH 7. We can calculate:

[Math Processing Error]

Given:

- The initial concentration of dihydroxyacetone phosphate = [Math Processing Error]
- The initial concentration of glyceraldehyde 3-phosphate = [Math Processing Error]

Solution

From equation 2:

[Math Processing Error] = 1.8 kcal/mol + 2.303 RT $\log_{10}(3*10^{-6}$ M/$2*10^{-4}$ M) = -0.7 kcal/mol

Note

Under non-standard conditions (which is essential all reactions), the spontaneity of reaction is determined by [Math Processing Error], not [Math Processing Error].

Gibbs Energy in Electrochemistry

The Nernst equation relates the standard-state cell potential with the cell potential of the cell at any moment in time:

[Math Processing Error]

with

- [Math Processing Error] = cell potential in volts (joules per coulomb)
- [Math Processing Error] = moles of electrons
- [Math Processing Error] = Faraday's constant: 96,485 coulombs per mole of electrons

By rearranging this equation we obtain:

[Math Processing Error]

multiply the entire equation by [Math Processing Error]

[Math Processing Error]

which is similar to:

[Math Processing Error]

By juxtaposing these two equations:

[Math Processing Error]

[Math Processing Error]

it can be concluded that:

[Math Processing Error]

Therefore,

[Math Processing Error]

Some remarks on the Gibbs "Free" Energy

- **Free Energy is not necessarily "free"**: The appellation “free energy” for G has led to so much confusion that many scientists now refer to it simply as the Gibbs energy. The “free” part of the older name reflects the steam-engine origins of thermodynamics with its interest in converting heat into work: ΔG is the maximum amount of energy which can be “freed” from the system to perform useful work. By "useful", we mean work other than that which is associated with the expansion of the system. This is most commonly in the form of electrical work (moving electric charge through a potential difference), but other forms of work (osmotic work, increase in surface area) are also possible.

- **Free Energy is not energy**: A much more serious difficulty with the Gibbs function, particularly in the context of chemistry, is that although G has the units of energy (joules, or in its intensive form, J mol^{-1}), it lacks one of the most important attributes of energy in that it is not conserved. Thus although the free energy always falls when a gas expands or a chemical reaction takes place spontaneously, there need be no compensating increase in energy anywhere else. Referring to G as an energy also reinforces the false but widespread notion that a fall in energy must accompany any change. But if we accept that energy is conserved, it is apparent that the only necessary condition for change (whether the dropping of a weight, expansion of a gas, or a chemical reaction) is the redistribution of energy.The quantity –ΔG associated with a process represents the quantity of energy that is “shared and spread”, which as we have already explained is the meaning of the increase in the entropy. The quotient –ΔG/T is in fact identical with ΔStotal, the entropy change of the world, whose increase is the primary criterion for any kind of change.
- **Free Energy is not even "real"**: G differs from the thermodynamic quantities H and S in another significant way: it has no physical reality as a property of matter, whereas H and S can be related to the quantity and distribution of energy in a collection of molecules (e.g., the third law of thermodynamics). The free energy is simply a useful construct that serves as a criterion for change and makes calculations easier.

References

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4.9: Phase Equilibria

Learning Objectives

- To know how and why the vapor pressure of a liquid varies with temperature.
- To understand that the equilibrium vapor pressure of a liquid depends on the temperature and the intermolecular forces present.
- To understand that the relationship between pressure, enthalpy of vaporization, and temperature is given by the Clausius-Clapeyron equation.

Nearly all of us have heated a pan of water with the lid in place and shortly thereafter heard the sounds of the lid rattling and hot water spilling onto the stovetop. When a liquid is heated, its molecules obtain sufficient kinetic energy to overcome the forces holding them in the liquid and they escape into the gaseous phase. By doing so, they generate a population of molecules in the vapor phase above the liquid that produces a pressure—the vapor pressure of the liquid. In the situation we described, enough pressure was generated to move the lid, which allowed the vapor to escape. If the vapor is contained in a sealed vessel, however, such as an unvented flask, and the vapor pressure becomes too high, the flask will explode (as many students have unfortunately discovered). In this section, we describe vapor pressure in more detail and explain how to quantitatively determine the vapor pressure of a liquid.

Evaporation and Condensation

Because the molecules of a liquid are in constant motion, we can plot the fraction of molecules with a given kinetic energy (KE) against their kinetic energy to obtain the kinetic energy distribution of the molecules in the liquid (Figure *[Math Processing Error]*), just as we did for a gas. As for gases, increasing the temperature increases both the average kinetic energy of the particles in a liquid and the range of kinetic energy of the individual molecules. If we assume that a minimum amount of energy (*[Math Processing Error]*) is needed to overcome the intermolecular attractive forces that hold a liquid together, then some fraction of molecules in the liquid always has a kinetic energy greater than *[Math Processing Error]*. The fraction of molecules with a kinetic energy greater than this minimum value increases with increasing temperature. Any molecule with a kinetic energy greater than *[Math Processing Error]* has enough energy to overcome the forces holding it in the liquid and escape into the vapor phase. Before it can do so, however, a molecule must also be at the surface of the liquid, where it is physically possible for it to leave the liquid surface; that is, only molecules at the surface can undergo evaporation (or vaporization), where molecules gain sufficient energy to enter a gaseous state above a liquid's surface, thereby creating a vapor pressure.

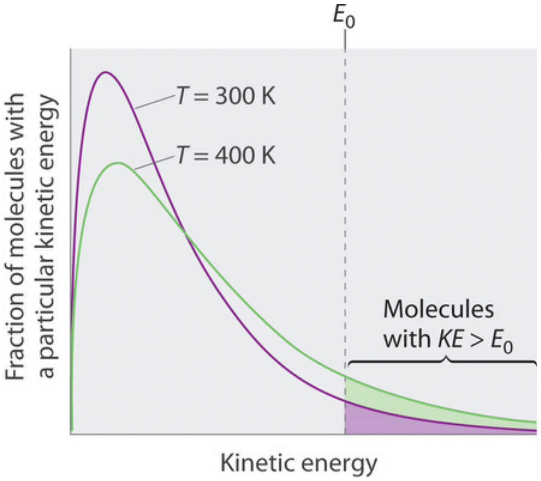

Figure *[Math Processing Error]*: The Distribution of the Kinetic Energies of the Molecules of a Liquid at Two Temperatures. Just as with gases, increasing the temperature shifts the peak to a higher energy and broadens the curve. Only molecules with a kinetic energy greater than E_0 can escape from the liquid to enter the vapor phase, and the proportion of molecules with $KE > E_0$ is greater at the higher temperature. (CC BY-SA-NC; Anonymous by request)

Graph of fraction of molecules with a particular kinetic energy against kinetic energy. Green line is temperature at 400 kelvin, purple line is temperature at 300 kelvin.

To understand the causes of vapor pressure, consider the apparatus shown in Figure *[Math Processing Error]*. When a liquid is introduced into an evacuated chamber (part (a) in Figure *[Math Processing Error]*), the initial pressure above the liquid is approximately zero because there are as yet no molecules in the vapor phase. Some molecules at the surface, however, will have sufficient kinetic energy to escape from the liquid and form a vapor, thus increasing the pressure inside the container. As long as the temperature of the liquid is held constant, the fraction of molecules with *[Math Processing Error]* will not change, and the rate at which molecules escape from the liquid into the vapor phase will depend only on the surface area of the liquid phase.

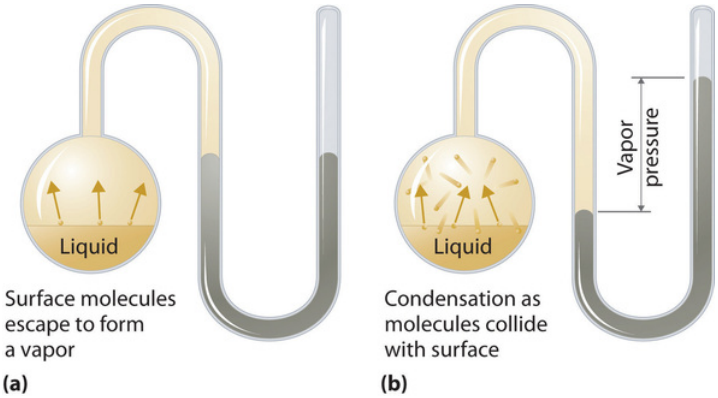

Figure *[Math Processing Error]*: Vapor Pressure. (a) When a liquid is introduced into an evacuated chamber, molecules with sufficient kinetic energy escape from the surface and enter the vapor phase, causing the pressure in the chamber to increase. (b) When sufficient molecules are in the vapor phase for a given temperature, the rate of condensation equals the rate of evaporation (a steady state is reached), and the pressure in the container becomes constant. (CC BY-SA-NC; Anonymous by request)

As soon as some vapor has formed, a fraction of the molecules in the vapor phase will collide with the surface of the liquid and reenter the liquid phase in a process known as condensation (part (b) in Figure *[Math Processing Error]*). As the number of molecules in the vapor phase increases, the number of collisions between vapor-phase molecules and the surface will also increase. Eventually, a *steady state* will be reached in which exactly as many molecules per unit time leave the surface of the liquid (vaporize) as collide with it (condense). At this point, the pressure over the liquid stops increasing and remains constant at a particular value that is characteristic of the liquid at a given temperature. The rates of evaporation and condensation over time for a system such as this are shown graphically in Figure *[Math Processing Error]*.

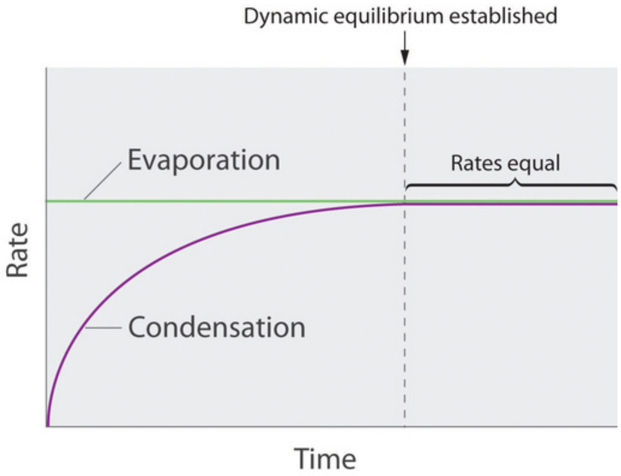

Figure *[Math Processing Error]*: The Relative Rates of Evaporation and Condensation as a Function of Time after a Liquid Is Introduced into a Sealed Chamber. The rate of evaporation depends only on the surface area of the liquid and is essentially constant. The rate of condensation depends on the number of molecules in the vapor phase and increases steadily until it equals the rate of evaporation. (CC BY-SA-NC; Anonymous by request)

Graph of rate against time. The green line is evaporation while the pruple line is condensation. Dynamic equilibrium is established when the evaporation and condensation rates are equal.

Equilibrium Vapor Pressure

Two opposing processes (such as evaporation and condensation) that occur at the same rate and thus produce no *net* change in a system, constitute a dynamic equilibrium. In the case of a liquid enclosed in a chamber, the molecules continuously evaporate and condense, but the amounts of liquid and vapor do not change with time. The pressure exerted by a vapor in dynamic equilibrium with a liquid is the equilibrium vapor pressure of the liquid.

If a liquid is in an *open* container, however, most of the molecules that escape into the vapor phase will *not* collide with the surface of the liquid and return to the liquid phase. Instead, they will diffuse through the gas phase away from the container, and an equilibrium will never be established. Under these conditions, the liquid will continue to evaporate until it has "disappeared." The speed with which this occurs depends on the vapor pressure of the liquid and the temperature. Volatile liquids have relatively high vapor pressures and tend to evaporate readily; nonvolatile liquids have low vapor pressures and evaporate more slowly. Although the dividing line between volatile and nonvolatile liquids is not clear-cut, as a general guideline, we can say that substances with vapor pressures greater than that of water (Figure *[Math Processing Error]*) are relatively volatile, whereas those with vapor pressures less than that of water are relatively nonvolatile. Thus diethyl ether (ethyl ether), acetone, and gasoline are volatile, but mercury, ethylene glycol, and motor oil are nonvolatile.

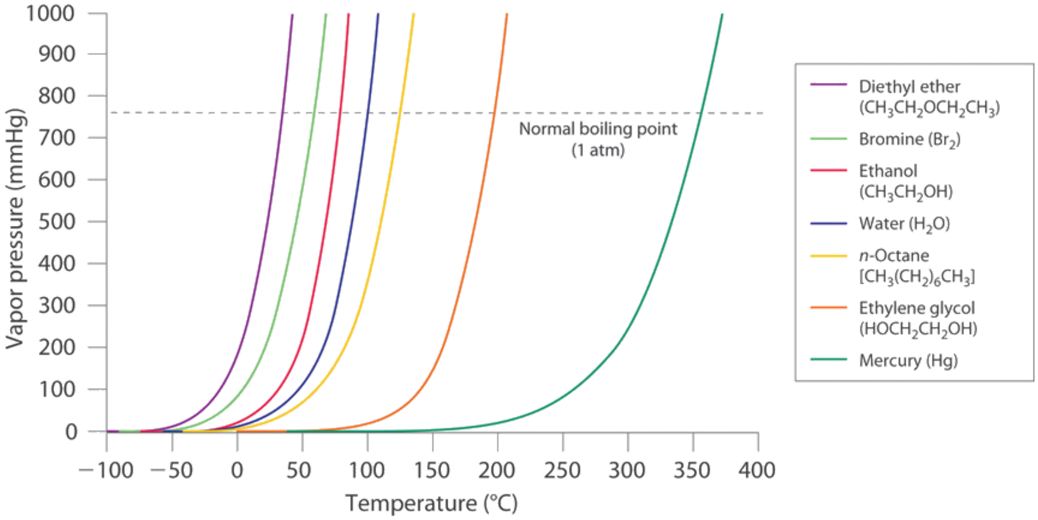

Figure *[Math Processing Error]*: The Vapor Pressures of Several Liquids as a Function of Temperature. The point at which the vapor pressure curve crosses the P = 1 atm line (dashed) is the normal boiling point of the liquid. (CC BY-SA-NC; Anonymous by request)

The equilibrium vapor pressure of a substance at a particular temperature is a characteristic of the material, like its molecular mass, melting point, and boiling point. It does *not* depend on the amount of liquid as long as at least a tiny amount of liquid is present in equilibrium with the vapor. The equilibrium vapor pressure does, however, depend very strongly on the temperature and the intermolecular forces present, as shown for several substances in Figure *[Math Processing Error]*. Molecules that can hydrogen bond, such as ethylene glycol, have a much lower equilibrium vapor pressure than those that cannot, such as octane. The nonlinear increase in vapor pressure with increasing temperature is *much* steeper than the increase in pressure expected for an ideal gas over the corresponding temperature range. The temperature dependence is so strong because the vapor pressure depends on the fraction of molecules that have a kinetic energy greater than that needed to escape from the liquid, and this fraction increases exponentially with temperature. As a result, sealed containers of volatile liquids are potential bombs if subjected to large increases in temperature. The gas tanks on automobiles are vented, for example, so that a car won't explode when parked in the sun. Similarly, the small cans (1–5 gallons) used to transport gasoline are required by law to have a pop-off pressure release.

> *Volatile substances have low boiling points and relatively weak intermolecular interactions; nonvolatile substances have high boiling points and relatively strong intermolecular interactions.*

A Video Discussing Vapor Pressure and Boiling Points. Video Source: Vapor Pressure & Boiling Point(opens in new window) [youtu.be]

The exponential rise in vapor pressure with increasing temperature in Figure *[Math Processing Error]* allows us to use natural logarithms to express the nonlinear relationship as a linear one.

[Math Processing Error]

where

- *[Math Processing Error]* is the natural logarithm of the vapor pressure,
- *[Math Processing Error]* is the enthalpy of vaporization,
- *[Math Processing Error]* is the universal gas constant [8.314 J/(mol•K)],
- *[Math Processing Error]* is the temperature in kelvins, and
- *[Math Processing Error]* is the y-intercept, which is a constant for any given line.

Plotting *[Math Processing Error]* versus the inverse of the absolute temperature (*[Math Processing Error]*) is a straight line with a slope of $-\Delta H_{vap}/R$. Equation *[Math Processing Error]*, called the Clausius–Clapeyron Equation, can be used to calculate the *[Math Processing Error]* of a liquid from its measured vapor pressure at two or more temperatures. The simplest way to determine *[Math Processing Error]* is to measure the vapor pressure of a liquid at **two** temperatures and insert the values of *[Math Processing Error]* and *[Math Processing Error]* for these points into Equation *[Math Processing Error]*, which is derived from the Clausius–Clapeyron equation:

[Math Processing Error]

Conversely, if we know ΔH_{vap} and the vapor pressure *[Math Processing Error]* at any temperature *[Math Processing Error]*, we can use Equation *[Math Processing Error]* to calculate the vapor pressure *[Math Processing Error]* at any other temperature *[Math Processing Error]*, as shown in Example *[Math Processing Error]*.

A Video Discussing the Clausius-Clapeyron Equation. Video Link: The Clausius-Clapeyron Equation(opens in new window) [youtu.be]

✓ Example [Math Processing Error]: Vapor Pressure of Mercury

The experimentally measured vapor pressures of liquid Hg at four temperatures are listed in the following table:

experimentally measured vapor pressures of liquid Hg at four temperatures

T (°C)	80.0	100	120	140
P (torr)	0.0888	0.2729	0.7457	1.845

From these data, calculate the enthalpy of vaporization (ΔH_{vap}) of mercury and predict the vapor pressure of the liquid at 160°C. (Safety note: mercury is highly toxic; when it is spilled, its vapor pressure generates hazardous levels of mercury vapor.)

Given: vapor pressures at four temperatures

Asked for: ΔH_{vap} of mercury and vapor pressure at 160°C

Strategy:

A. Use Equation *[Math Processing Error]* to obtain ΔH_{vap} directly from two pairs of values in the table, making sure to convert all values to the appropriate units.
B. Substitute the calculated value of ΔH_{vap} into Equation *[Math Processing Error]* to obtain the unknown pressure (P_2).

Solution:

A The table gives the measured vapor pressures of liquid Hg for four temperatures. Although one way to proceed would be to plot the data using Equation *[Math Processing Error]* and find the value of ΔH_{vap} from the slope of the line, an alternative approach is to use Equation *[Math Processing Error]* to obtain ΔH_{vap} directly from two pairs of values listed in the table, assuming no errors in our measurement. We therefore select two sets of values from the table and convert the temperatures from degrees Celsius to kelvin because the equation requires absolute temperatures. Substituting the values measured at 80.0°C (T_1) and 120.0°C (T_2) into Equation *[Math Processing Error]* gives

[Math Processing Error]

B We can now use this value of ΔH_{vap} to calculate the vapor pressure of the liquid (P_2) at 160.0°C (T_2):

[Math Processing Error]

Using the relationship *[Math Processing Error]*, we have

[Math Processing Error]

At 160°C, liquid Hg has a vapor pressure of 4.21 torr, substantially greater than the pressure at 80.0°C, as we would expect.

? Exercise [Math Processing Error]: Vapor Pressure of Nickel

The vapor pressure of liquid nickel at 1606°C is 0.100 torr, whereas at 1805°C, its vapor pressure is 1.000 torr. At what temperature does the liquid have a vapor pressure of 2.500 torr?

Answer

1896°C

Boiling Points

As the temperature of a liquid increases, the vapor pressure of the liquid increases until it equals the external pressure, or the atmospheric pressure in the case of an open container. Bubbles of vapor begin to form throughout the liquid, and the liquid begins to boil. The temperature at which a liquid boils at exactly 1 atm pressure is the normal boiling point of the liquid. For water, the normal boiling point is exactly 100°C. The normal boiling points of the other liquids in Figure *[Math Processing Error]* are represented by the points at which the vapor pressure curves cross the line corresponding to a pressure of 1 atm. Although we usually cite the normal boiling point of a liquid, the *actual* boiling point depends on the pressure. At a pressure greater than 1 atm, water boils at a temperature greater than 100°C because the increased pressure forces vapor molecules above the surface to condense. Hence the molecules must have greater kinetic energy to escape from the surface. Conversely, at pressures less than 1 atm, water boils below 100°C.

Table *[Math Processing Error]*: The Boiling Points of Water at Various Locations on Earth

Place	Altitude above Sea Level (ft)	Atmospheric Pressure (mmHg)	Boiling Point of Water (°C)
Mt. Everest, Nepal/Tibet	29,028	240	70
Bogota, Colombia	11,490	495	88
Denver, Colorado	5280	633	95
Washington, DC	25	759	100
Dead Sea, Israel/Jordan	−1312	799	101.4

Typical variations in atmospheric pressure at sea level are relatively small, causing only minor changes in the boiling point of water. For example, the highest recorded atmospheric pressure at sea level is 813 mmHg, recorded during a Siberian winter; the lowest sea-level pressure ever measured was 658 mmHg in a Pacific typhoon. At these pressures, the boiling point of water changes minimally, to 102°C and 96°C, respectively. At high altitudes, on the other hand, the dependence of the boiling point of water on pressure becomes significant. Table *[Math Processing Error]* lists the boiling points of water at several locations with different altitudes. At an elevation of only 5000 ft, for example, the boiling point of water is already lower than the lowest ever recorded at sea level. The lower boiling point of water has major consequences for cooking everything from soft-boiled eggs (a "three-minute egg" may well take four or more minutes in the Rockies and even longer in the Himalayas) to cakes (cake mixes are often sold with separate high-altitude instructions). Conversely, pressure cookers, which have a seal that allows the pressure inside them to exceed 1 atm, are used to cook food more rapidly by raising the boiling point of water and thus the temperature at which the food is being cooked.

> *As pressure increases, the boiling point of a liquid increases and vice versa.*

✓ Example *[Math Processing Error]*: Boiling Mercury

Use Figure *[Math Processing Error]* to estimate the following.

a. the boiling point of water in a pressure cooker operating at 1000 mmHg
b. the pressure required for mercury to boil at 250°C

Mercury boils at 356 °C at room pressure. To see video go to www.youtube.com/watch?v=0iizsbXWYoo

Given: Data in Figure *[Math Processing Error]*, pressure, and boiling point

Asked for: corresponding boiling point and pressure

Strategy:

A. To estimate the boiling point of water at 1000 mmHg, refer to Figure *[Math Processing Error]* and find the point where the vapor pressure curve of water intersects the line corresponding to a pressure of 1000 mmHg.
B. To estimate the pressure required for mercury to boil at 250°C, find the point where the vapor pressure curve of mercury intersects the line corresponding to a temperature of 250°C.

Solution:

a. **A** The vapor pressure curve of water intersects the P = 1000 mmHg line at about 110°C; this is therefore the boiling point of water at 1000 mmHg.
b. **B** The vertical line corresponding to 250°C intersects the vapor pressure curve of mercury at $P \approx 75$ mmHg. Hence this is the pressure required for mercury to boil at 250°C.

? Exercise *[Math Processing Error]*: Boiling Ethlyene Glycol

Ethylene glycol is an organic compound primarily used as a raw material in the manufacture of polyester fibers and fabric industry, and polyethylene terephthalate resins (PET) used in bottling. Use the data in Figure *[Math Processing Error]* to estimate the following.

a. the normal boiling point of ethylene glycol
b. the pressure required for diethyl ether to boil at 20°C.

Answer a

200°C

Answer b

450 mmHg

Summary

Because the molecules of a liquid are in constant motion and possess a wide range of kinetic energies, at any moment some fraction of them has enough energy to escape from the surface of the liquid to enter the gas or vapor phase. This process, called **vaporization** or **evaporation**, generates a **vapor pressure** above the liquid. Molecules in the gas phase can collide with the liquid surface and reenter the liquid via **condensation**. Eventually, a *steady state* is reached in which the number of molecules evaporating and condensing per unit time is the same, and the system is in a state of **dynamic equilibrium**. Under these conditions, a liquid exhibits a characteristic **equilibrium vapor pressure** that depends only on the temperature. We can express the nonlinear relationship between vapor pressure and temperature as a linear relationship using the **Clausius–Clapeyron equation**. This equation can be used to calculate the enthalpy of vaporization of a liquid from its measured vapor pressure at two or more temperatures. **Volatile liquids** are liquids with high vapor pressures, which tend to evaporate readily from an open container; **nonvolatile liquids** have low vapor pressures. When the vapor pressure equals the external pressure, bubbles of vapor form within the liquid, and it boils. The temperature at which a substance boils at a pressure of 1 atm is its **normal boiling point**.

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4.E: Exercises

Q4.9

What is the entropy changed when 10.2 moles of diatomic gas is cooled from a temperature of 25 °C to 10 °C at constant pressure?

Q4.9

Determine the value of ΔS while reversibly heating 5 moles of an ideal gas from 25 °C to 73 °C at constant volume.

S4.9

At constant volume, $dq_{rev} = C_V dT$.

$$\Delta S = \int \frac{dq_{rev}}{T} = \int \frac{C_V dT}{T} = C_V \ln \frac{T_2}{T_1} = \frac{3}{2} nR \ln \frac{T_2}{T_1}$$

$$= \frac{3}{2}(5.0\text{mol})(8.314\text{JK}^{-1}\text{mol}^{-1})\ln \frac{346\text{K}}{298\text{K}}$$

$$= 9.3\text{JK}^{-1}$$

Q4.10

If 1.50 moles of an ideal gas were compressed isothermally from 6.6 L to 2.5 L:

a. What is $\triangle S_{sys}$ when compressed irreversibly?
b. $\triangle S_{sys}$ when done reversibly?
c. What do the values mean for the overall process?

S4.10

a. *[Math Processing Error]*
b. The change in entropy of the system is the same whether an irreversible or reversible process is being carried out.
c. The negative value means that the reaction that was carried out was unfavorable. Entropy increases as molecules become more disordered.

Q4.13

Nitrogen gas is reversibly heated at constant pressure of 101.3 kPa. The molar heat capacity of nitrogen gas is:

$C_p = A + BT + CT^2$, where A = 27.4 J/mol-K, B = 5.23 x 10^{-3} J/mol-K^2, and C = -0.0300 x 10^{-7} J/mol-K^3.

Assuming N_2 is an ideal gas, calculate the change in entropy when 42 g of $N_2(g)$ is heated from 250 K to 350 K.

Q4.21

Imagine you are to carry out the isothermal and reversible gas expansion with an ideal gas. You have 0.5 moles of the gas at 280K. You wish to expand this gas from its initial volume of 2 liters to a new volume of 8 liters. What would your values for heat, work, change in entropy, and change in internal energy have to be? What if you wanted to instead carry his experiment out as isothermal and irreversible with 2.0 atm of external pressure?

Q4.22

Consider 0.50 moles of an ideal gas at 30^{o}C. It expands from a pressure of 4.5 atm to a pressure of 2.0 atm at the same temperature.

a. For a reversible process, find the entropy change for the surrounding.
b. For an irreversible process, calculate the entropy change for the universe which against a constant external pressure of 2.0 atm.

S4.22

a) Reversible process:

delta S of system =(\dfrac{q}{T}\)=(\dfrac{-W}{T}\)=(\dfrac{-1}{T}*(-nRT\ln\dfrac{V2}{V1})\)=(\nR\ln\dfrac{P1}{P}\)

q_{sys}/T = - W_{sys}/T = -1/T *(-nRT\ln (V_2/V_1) = nR\ln (P1/P2)

= 0.5 moles * 8.3145 $Jmol^{-1}K^{-1}$ * \ln(4.5/2)

= 3.37 J/K

delta S of surrounding = -3.37 J/K

b) Irreversible process:

delta S of system is 3.37 J/K

Delta S(surrouding)=(\dfrac{-1}{T}*P2*V2*(1-\dfrac{V1}{V2})\)= (\-nR(1-\dfrac{P2}{P1})\)

delta S of surrounding = -1/T * P2*V2*(1 - V1/V2) = -nR(1 - P2/P1)

=-0.5 * 8.3145 *(1-2/4.5)=2.31 J/K

delta of the universe is : 3.37 J/K +2.31J/K=5.68 J/K

Q4.23

Calculate ΔS_{sys} for the heating of 2.00 moles of nitrogen from 25°C to 200°C. The heat capacity of oxygen is:

$C_p = (3.268 + 0.00325T)\ J\ K^{-1}\ mol^{-1}$

S4.23

[Math Processing Error]

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[Math Processing Error]

Q4.27

The value of $\overline{S}^{\circ}$ ($CO_2(aq)$) is less than that of $\overline{S}^{\circ}$ ($CO_2(g)$) at 298 K. (Note: Refer to table below). Would this be the case at a temperature of 0 K as well?

Substance	$\overline{S}^{\circ}$ / J K^{-1} mol^{-1}
$CO_2(g)$	213.6
$CO_2(aq)$	117.6

S4.27

Since the gaseous form of a compound always has a greater enthalpy than the more ordered liquid or aqueous form, this would still be the case at a temperature of 0 K as well.

Q4.27

Is the standard entropy of $CO_2(g)$ higher than the standard entropy of $CO_2(s)$ at 298 K? What about at 0 K?

Q4.28

You have an ideal gas that expands 3.56 L with the initial volume at 22 L. All you know is that you have 0.45 moles and that the temperature is 22 ºC. What is the change in Gibbs free energy for this system?

S4.28

$$\Delta G = nRTln(\frac{P_2}{P_1})$$

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

$$= (0.45mol)(8.314\frac{J}{molK})(22 + 273.15)Kln\frac{22 + 3.56}{22}$$

=167.3

Q4.28

0.70 moles of an ideal gas expands adiabatically from 1.0 atm to 2.5 atm at a temperature of 30°C. Calculate the values of q, w, $\triangle U$, $\triangle S$, and $\triangle G$.

S4.28

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[Math Processing Error]

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Q4.30

Use the values listed listed below to calculate the value of $_{\Delta_r}G°$ for the following reaction:

$$\text{pyruvate(aq)} \rightarrow 2 \text{ lactate ion(aq)} + 2H^+\text{(aq)}$$

($\Delta_f G°$[pyruvate(aq)] = -472.4 kJ mol^{-1}, $\Delta_f G°$[lactate ion] = -516.7 kJ mol^{-1}). Is pyruvate or the lactate ion favored under standard conditions? Explain.

Q4.30

Use the values listed listed below to calculate the value of $_{\Delta_r}G°$ for the following reaction:

$$\text{pyruvate(aq)} \rightarrow 2 \text{ lactate ion(aq)} + 2H^+\text{(aq)}$$

($\Delta_f G°$[pyruvate(aq)] = -472.4 kJ mol^{-1}, $\Delta_f G°$[lactate ion] = -516.7 kJ mol^{-1})

Q4.31

A scientist measures studies the thermodynamics of a protein of interest. He interested in finding the Free Energy of unfolding in the quaternary structure of protein at a concentration of 5µM. He finds that the Gibbs free energy of the reaction -0.84 Kcal/mol. Why does the scientist want to know the value of (\Delta G\) Explain how the reaction proceeds.

S4.31

The value of (\Delta G\) of the reaction will let the scientist know how likely the reaction of the unfolding of the protein is to occur. If (\Delta G\) is negative the reaction will go forward, towards the unfolded state. In this case (\Delta G\) is negative so the reaction goes forward to the unfolding of the protein.

Q4.32

For the reaction

[Math Processing Error]

Using the formula $\Delta_r G = \Delta_f G$ (products)-$\Delta_f G$ (reactants) to compute the Gibbs energy of the reaction?

Q4.34

Consider the conversion of graphite carbon into diamond

[Math Processing Error]

a. Determine *[Math Processing Error]* and *[Math Processing Error]* for the reaction. Is the conversion spontaneous at any temperature?
b. The molar volume of graphite is *[Math Processing Error]* greater than diamond in density.
c. If you apply pressure on graphite at *[Math Processing Error]*, can you convert graphite to diamond? If so, determine the required pressure to make the process spontaneous.

S4.34

(a)

$$\Delta rH^{o}=\Delta _f\bar{H}^{o}[C_{(diamond)}]-\Delta _f\bar{H}^{o}[C_{(graphite)}]$$

$$=1.90Kjmol^{-1}-0kjmol^{-1}$$

$$=1.90kj\,mol^{-1}$$

$$\Delta rS^{o}=\Delta S^{o}[C_{(diamond)}]-\Delta S^{o}[C_{(graphite)}]$$

$$=2.4J\,K^{-1}mol^{-1}-5.7JK^{-1}mol^{-1}$$

$$=-3.3J\,K^{-1}mol^{-1}$$

At *[Math Processing Error]*,

$$\Delta rG^{o}=\Delta rH^o-(273K)\Delta rS^{o}$$

$$=(1.90kj\,mol^{-1})-(273K)(-3.3\times10^{-3}kj\,K^{-1}mol^{-1})$$

$$=2.8834kj\,mol^{-1}$$

(b)

Step 1:

$$G_2=G_1+V(P_2-P_1)$$

Step 2: (Hint: Apply molar quantities)

$$\bar{G}_2=\bar{G}_1+\bar{V}\Delta P$$

Step 3: (Hint: Apply the equation to diamond and graphite)

$$\bar{G}_2[Graphite]=\bar{G}_1[graphite]+\bar{V}[graphite]\Delta P$$

$$\bar{G}_2[diamond]=\bar{G}_1[diamond]+\bar{V}[diamond]\Delta P$$

Step 4: (Hint: Combine the equations)

$$\Delta rG_2=\Delta rG_1+[\bar{V}[diamond]-\bar{V}[graphite]]\Delta P$$

Step 5: (Hint: At *[Math Processing Error]*)

$$\Delta rG_2=2.883kj\,mol^{-1}+(-2.1cm^3mol^{-1})\Delta P(\dfrac{1L}{1000cm^{3}})(\dfrac{1atm}{1.01 bar})(\dfrac{101.3J}{1L\,atm})(\dfrac{1kj}{1000J})$$

$$\Delta rG_2=2.883kj\,mol^{-1}-2.1\times10^{-4}\Delta P\,kj\,bar^{-1}mol^{-1}$$

Step 6: (Hint: To make the process spontaneous)

$$\Delta rG_2=2.883kj\,mol^{-1}-2.1\times10^{-4}\Delta P\,kj\,bar^{-1}mol^{-1}\lt0$$

$$2.883kj\,mol^{-1}\lt2.1\times10^{-4}\Delta P\,kj\,bar^{-1}mol^{-1}$$

$$\Delta P\lt\dfrac{2.883kj\,mol^{-1}}{2.1\times10^{-4}}=1.4\times10^{4} bar$$

Q4.36

Predict the signs of *[Math Processing Error]* and *[Math Processing Error]* of the system for the following processes at 1atm:

a. Ice melt at 200 K
b. Ice melt at 273.15 K
c. Ice melt at 300 K

S4.36

[Math Processing Error] is positive for all because melting is endothermic. *[Math Processing Error]* is positive for all because going from solid to liquid is becoming more disordered. *[Math Processing Error]* for (a) is positive because reaction is not spontaneous when melting at below the melting point, *[Math Processing Error]* for (b) is 0 because reaction is in equilibrium at the melting point, *[Math Processing Error]* for (c) is negative because reaction is spontaneous when melting at above the melting point.

	(a)	(b)	(c)
[Math Processing Error]	+	+	+
[Math Processing Error]	+	+	+
[Math Processing Error]	+	0	-

Q4.37

Crystals of AgCl(s) form spontaneously when aqueous solutions of silver(I)nitrate and sodium chloride are combined. What can you deduce about the signs of the changes in enthalpy and entropy?

Q4.38

The formation reaction to form magnesium oxide is as follow:

[Math Processing Error]

Verify the equation $\Delta G° = \Delta H° + TS°$ using values from Appendix

Hint: Gibbs free definition above is free energy of the whole reaction, not free energy of formation

S4.38

[Math Processing Error]

[Math Processing Error]

[Math Processing Error]

[Math Processing Error]

The answers agree therefore the equation is true.

Q4.39a

At 49°C, a particular reaction is spontaneous. What would be the smallest possible value of $\Delta_r S$ for the reaction if $\Delta_r H$ was 10 kJ?

S4.39a

Use the following equation

[Math Processing Error]

Since the process is spontaneous:

Note: Don't forget to flip the inequality when dividing by a negative number.

[Math Processing Error]

Thus the minimum value is the closest number above 0.031 kJ K^{-1}.

Click here for more information on Gibb's free energy.

Q4.39b

Calculate the minimum change in entropy of reaction for a spontaneous process at 340K with an enthalpy change of reaction equal to 800 J. Your answer must be in KJ/K and have 2 significant figures.

Q4.39c

The entropy change for a reaction is found to be 47.50 J/K. The enthalpy change for the reaction is 21.25 KJ. At what temperature is this reaction spontaneous?

S4.39c

[Math Processing Error]

Because we want to find the temperature at equilibrium we set the Gibbs Free Energy equal to 0. Thus:

[Math Processing Error]

[Math Processing Error]

Q4.40a

The standard Gibbs energy change, $\Delta_r G^o$, for the reaction is +108 kJ. What can you deduce about the state of reaction when the reactants are mixed together?

S4.40a

When the two gases are mixed, there is no interaction between them. So, the products would not form.

Q4.40b

A scientist mixes together a set of reagents which are known to undergo a reaction with a negative change in Gibbs' free energy in a beaker. When the scientist comes back in a few hours, they find by looking at the beaker that the reaction does not appear to have proceeded. What are two reasons that the scientist would not observe a change after two hours?

S4.40b

The Gibbs' free energy is an indicator of a reaction's favorability, but does not indicate that that reaction will proceed quickly. If the rate constant for the reaction is low, or the concentration of one or more of the reagents is low, the reaction might not proceed at a pace that the scientist would observe over a few hours or even longer.

Q4.41

If water changes from a liquid to a gas at 50°C and 0.123 bar, what must the pressure be to convert water from a liquid to a gas at 75°C? The molar enthalpy of vaporization for water ($\Delta_{vap}H$) is 42.3 kJ mol^{-1}

S4.41

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Q4.42

What is the change in pressure when ice melts ast room temperature if the density of ice is 0.919 g/ml and the $\Delta_{fus}H$ = 6.01 KJ/mol?

Q4.42

Calculate the freezing point depression of ice if a pressure of 450 atm is exerted on it by a car that weighs 1500-kg. Note: The molar volumes are as follows: molar volume of liquid water is 18.03 mL mol^{-1} and the molar volume of ice is 19.65 mL mol^{-1}.

S4.42

Use the slope of the S-L curve from the phase diagram:

$$\frac{dP}{dT}=\frac{\Delta\overline{H}}{T\Delta\overline{V}}=\frac{(6.01\times10^{3}\text{J mol}^{-1})(\frac{1\text{Latm}}{101.3\text{J}})}{(273.2\text{K})(18.03\text{mLmol}^{-1}-19.65\text{mLmol}^{-1})(\frac{1\text{mL}}{1000\text{L}})}$$

$$=-135.7\text{atmK}^{-1}$$

$$dP=-135.7\text{atmK}^{-1}dT$$

$$\int_{1\text{atm}}^{450\text{atm}}dP=-135.7\text{atmK}^{-1}\int_{273.15\text{K}}^{T\text{K}}dT$$

$$449\text{atm}=-135.7\text{atmK}^{-1}\Delta T$$

$$\Delta T=\frac{449\text{atm}}{-135.7\text{atmK}^{-1}}=-3.31\text{K}$$

This means that the freezing point depression determined for when 450 atm of pressure is applied to ice by a car is 3.30 K.

Q4.43

Here is a phase diagram for carbon.

a. What phase will carbon be if temperature is increased at constant pressure from the triple point between the vapor, liquid, and graphite?
b. At 1.0 GPa and 5000 K, what phase will carbon be in?

File:Carbon basic phase diagram.png

$Image from Wikimedia Commons$

S4.43

a. Carbon will be in its vapor phase if the temperature is increased from the lower triple point.
b. At 1.0 GPa and 5000 K, carbon will be in the liquid phase.

Q4.46

Look at the phase diagram of water. Which phase is more dense, liquid or solid? How can you tell by just looking at the graph?

The link below contains a phase diagram of water:

http://chemwiki.ucdavis.edu/Wikitext...Phase_Diagrams

S4.46

Through looking at the phase diagram, we can see that the liquid phase is more dense. You can see this because the line separating the two phases is negative.

Q4.48

Explain what happens to Δ_{vap}H as the temperature increases significantly.

Q4.49

You go on an adventure and find yourself stranded on the top of a mountain where the air pressure is 0.68 atm. You find water but you want to make sure is safe to drink so you want to boil the water. At what temperature would you expect the water to start boiling? Hint: The molar heat of vaporization of H_2O is 41.0 kJ mol^{-1}

Q4.50

At higher altitude, water is boiled faster than at lower altitude. The reason is because the pressure is smaller. Given the heat of vaporization of water at 100°C is 42.0 KJ/mol. Calculate the temperature to boil the water at a place where air pressure is 0.7 atm?

Q4.52

The equations are as follows

a. *[Math Processing Error]*
b. *[Math Processing Error]*
c. *[Math Processing Error]*
d. *[Math Processing Error]*

Determine the conditions needed for each equation.

S4.52

a. Constant pressure
b. Constant pressure and temperature
c. Absolute 0, no residual entropy, pure crystalline
d. reversible process

Q4.54

Calculate the entropy change when nitrogen gas is heated from 25°C to 75°C while simultaneously allowed to expand from 0.562 L to 1.245 L. Assume ideal gas behavior.

S4.54

1. Find how many moles of gas we have: *[Math Processing Error]*

[Math Processing Error]

2. entropy change during expansion:

[Math Processing Error]

3. entropy change during heating at constant volume:

[Math Processing Error]

4. Combine 2&3:

[Math Processing Error]

Q4.54

A *[Math Processing Error]* moles sample of Xenon (Xe) is heated from 300 K to 400 K in a 1 L container at 1.5 atm. What will be the change in entropy if Xe is able to expand to twice the volume of the container?

Q4.55

Photosynthesis depends upon the absorption of visible light. However, the infrared radiation can not be used for photosynthesis. Explain why.

S4.55

The infrared light : Cells do absorb the photon of infrared radiation, but it could not provide enough energy to do work in a biological system.

Whereas, for the visible light, each photon of visible light contains just enough energy to excite the electrons of molecules.

Photosynthesis is carried out by using the visible light.

Q4.56a

An amount of ideal diatomic gas is expanded from 4.8 atm to 1.7 atm while experiencing the change of temperature from 35°C to 128ºC. The change in entropy of the gas expansion process is 15.0 J/K. Determine the ΔU, ΔH, and ΔS of the entire process. Assume the temperature is not enough to unleash the rotational and vibrational energy of the gas.

Hint: Break the problem into 2 processes (isothermic and isobaric)

S4.56a

Step 1: Consider the isothermal process of the ideal gas (expanding from 4.8 atm to 1.7atm at constant temperature of 35°C

ΔU = 0, ΔH = 0, ΔS = 15.0 J/K

[Math Processing Error]

[Math Processing Error]

Step 2: Consider the change in temperature at constant pressure of 1.7 atm

[Math Processing Error]

[Math Processing Error]

[Math Processing Error]

For the entire process

[Math Processing Error]

[Math Processing Error]

[Math Processing Error]

Q4.56b

Calculate the ΔU, ΔH, and ΔS of 3.00 moles of an ideal monatomic gas that are compressed from 7.00 L to 1.00 L while being heated from 25 $^{\circ}$C to 100 $^{\circ}$C.

S4.56b

Break the process down into two steps: isothermal compression from 7 L to 1 L at 298 K and heating at a constant pressure from 298 K to 373 K.

a. Compression:

Because the compressions is isothermal, ΔU=0 & ΔH=0 for this step

[Math Processing Error]

[Math Processing Error]

b. Heating:

[Math Processing Error]

[Math Processing Error]

[Math Processing Error]

[Math Processing Error]

[Math Processing Error]

[Math Processing Error]

c. For entire process

[Math Processing Error]

[Math Processing Error]

[Math Processing Error]

Q4.57a

Briefly provide examples and descriptions for each of the three laws of thermodynamics.

S4.57a

- The first law is the conservation of mass and energy. Basically you can't create anything out of thin air and perpetual motion machines are impossible.
- The second law states how entropy is always increasing and the entropy of the universe can never become negative. In other words things will always attempt to go to equilibrium. This is seen commonly when batteries run out. You never see a battery charge itself spontaneously because that would violate the second law.
- The third law states how a pure crystalline structure at 0 K will essentially have 0 entropy. The third law is visualized by knowing how frozen and solid materials have less entropy because the molecules within can only vibrate.

Q4.57b

The three laws of thermodynamics are often generally stated to be:

1. Energy and matter cannot be created or destroyed.
2. The entropy of the universe is always increasing.
3. At absolute zero, the entropy of a system is zero.

With this knowledge, which of the three laws of thermodynamics apply to the examples below? There may be more than one.

a.) A graduate student in UC davis claims to have created the world's first perpetual motion engine. This machine produces no heat and can be used, (he claims), to power the campus for the next decade! This is not possible.

b.) $\Delta S = \left(\frac{q_p}{T_F}\right)$

If T_F becomes 0, entropy becomes undefined. Hence, it is not possible to reach absolute zero.

c.) In an adiabatic gas expansion where:

[Math Processing Error]

No thermal energy or matter is exchanged. Hence:

[Math Processing Error]

d.) In an imperfect crystal of CO, carbon monoxide, there are multiple energy states at 0K. Thus, it experiences residual entropy and, quite unusually, follows:

[Math Processing Error]

S4.57b

a.) first and second laws; The existence of the perpetual motion machine violates the first and second laws of thermodynamics. Because

[Math Processing Error]

and heat is a form of entropy, a perpetual motion machine does not increase the entropy of the universe. By definition, a machine which does work must do less work than it has internal energy.

b.) second and third law; In order for absolute zero to be reached, the system would have to be removed from the universe. Because

[Math Processing Error]

and entropy must always increase, a system within the universe would always be at a temperature lower than its surroundings and hence could experience heat transfer which would mitigate the absolute zero condition.

c.) first law; Energy which is "lost" from the system due to lack of heat transfer is compensated by the system doing more work.

d.) third law; In a perfect crystal, where there is only one energy state, there is no residual entropy at 0K

Q4.58

The standard enthalpy of formation of ice is -291.83 kJ/mol and its standard molar entropy is 41.0 J/(mol K). The standard enthalpy of formation of liquid water is -285.83 kJ/mol and its standard molar entropy is 69.95 J/(mol K). Estimate the melting point of water based on this information. What would you expect the value be? Do your values match? What assumptions made during this calculation could be responsible for the difference?

Q4.61

In a reversible adiabatic expansion, what do you expect to happen to the volume? What about the temperature?

S4.61

We expect both volume and temperature to increase.

Q4.63

Aniline can hydrogen bond, whereas benzene is nonpolar. Explain why, contrary to our expectation, benzene melts at a higher temperature than aniline. Why is the boiling point of aniline higher than that of benzene?

Q4.64

Molar Gibbs energies of solid, liquid and vapor depend on temperature and pressure. **(a)** Briefly explain how temperature affects molar Gibbs energy. **(b)** Explain how pressure changes affect molar Gibbs energy. Why is water an exemption?

S4.64

a. At a constant pressure the phase with the lowest molar Gibbs energy is the most stable phase at that temperature. At high temperatures the vapor phase has the lowest molar Gibbs energy, therefore it is the most stable. As temperature decreases, liquid becomes the stable phase, and at even lower temperatures, solid becomes the most stable phase.
b. From the equation *[Math Processing Error]* we observe that the molar volume affects the molar Gibbs energy depending on pressure. In this case the vapor phase has the greatest increase in molar Gibbs energy because the molar volume is much larger than that of liquids and solids. In general, an increase in external pressure will raise both the melting point and the boiling point of a substance. The exception to this, is water. This is because the molar volume of ice is actually greater than that of liquid water. Thus, for water an increase in pressure will lower the melting point.

Q4.65

When ice melts to liquid water, entropy is increasing and the the surrounding becomes cooler since ice absorbs heat. Explain the relationship between those two facts.

Q4.66

For any spontaneous endothermic process, what must be true about the entropy of the process?

Q4.67

For the following situation take a rubber band and stretch it quickly. It will feel warm. Next stretch it out for a few seconds and then release it. Consequently, it will feel cool. Why do you think this happens? Explain thermodynamically.

S4.67

[Math Processing Error]

The warming effect: Stretching the rubber band creates a nonspontaneous process *[Math Processing Error]* and *[Math Processing Error]*. The warming effect means that *[Math Processing Error]*. This makes *[Math Processing Error]* negative. T must be positive and *[Math Processing Error]* must be negative. This tells us that the rubber band under tension is more disordered in its natural state.

The cooling effect: If theres no tension and the rubber band snaps back to its natural state, *[Math Processing Error]* is negative and *[Math Processing Error]* is positive. Since it cools the *[Math Processing Error]* so *[Math Processing Error]* is positive. Entropy increases when the rubber band goes from stretched state to natural state.

Q4.69

Cold packs utilizes the chemical reaction of water and ammonium nitrate (or similar substances) to turn cold. Predict the signs of *[Math Processing Error]* and *[Math Processing Error]* for the reaction when the membrane that separates the two substances in a cold pack breaks.

S4.69

The reaction is spontaneous so *[Math Processing Error]* is negative; the cold pack feels cold because it's taking in heat so *[Math Processing Error]* is positive; *[Math Processing Error]* is positive because disorder increases as ammonium nitrate breaks down to ammonium ion and nitrate ion.

Q4.71

At what temperature will toluene have a vapor pressure of 517 torr. The normal boiling point of toluene is 110.6°C with the molar enthalpy of vaporization being 35.2 kJ/mol. (Hint: Use Clausius-Clapeyron equation).

S4.71

[Math Processing Error]

[Math Processing Error]

[Math Processing Error]

Q4.72a

You have discovered a way to create a new organic compound of the formula *[Math Processing Error]*. What measurements would you need to take to find out values for the following:properties:

[Math Processing Error]

S4.72a

For enthalpy, you need to take measurements of the change of enthalpy of one mole of the unknown compound. Thus you would need to take measurements for the molar heat capacity and how much temperature changes in for formation of one mole. See here and here.

For entropy of formation you would need to divide enthalpy by the temperature at which the formation takes place because the change in entropy can equate to enthalpy divided by temperature. See here.

For Gibb's free energy of formation, you simply need the enthalpy and entropy of formation along with the temperature where one mole of the substance is formed. See here.

[Math Processing Error]

Q4.72b

You are given hexane, C_6H_{14}, and a constant pressure calorimeter. What steps would you take to determine standard gibbs free energy of formation, $\Delta_f\bar{G}^\circ$ for this substance?

Hint: $\Delta_f\bar{H}^\circ$of hexane can be found using a measurement obtained by the calorimeter

S4.72b

An equation for the complete combustion of hexane can be written as follows:

[Math Processing Error]

The calorimeter would then be used to find the heat released by this reaction by the following rule:

[Math Processing Error]

after which the standard heat of formation for hexane could be calculated using the known heat of formation for H_2O, O_2, and CO_2.

Under the 3rd law of dynamics, the standard entropy would then be calculated by

[Math Processing Error]

where T=298K

From this, standard entropy for the formation of hexane should be obtained from the known standard entropies of H_2O, O_2, and CO_2, through the following reaction for the formation of hexane from elemental reactants:

[Math Processing Error]

The standard gibbs free energy of formation, $\Delta_f \bar{G}^\circ$ for this substance is then determined through the relationship:

[Math Processing Error]

Q4.73

A 93.5 Liter drum at 65 C houses 20g of water. How many moles of water are in the vapor phase, and what mole fraction is in the vapor phase? The vapor pressure of water at 65C is 187.54 mmhg.

S4.73

[Math Processing Error]

- n_{tot} = 20g/18.02 g mol^{-1}= 1.11 mol
- n_{vap} = (187.54 mmhg 93.5 L)/(8.314 L atm mol^{-1} K^{-1}* 338 K * 710 mmhg atm^{-1}) = 8.79 *10^{-3} mol
- x_{vap}= 8.79 *10^{-3} mol / 1.11 mol = 7.92*10^{-3}

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CHAPTER OVERVIEW

5: Solutions

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5.3: The Thermodynamics of Mixing

When solids, liquids or gases are combined, the thermodynamic quantities of the system experience a change as a result of the mixing. This module will discuss the effect that mixing has on a solution's Gibbs energy, enthalpy, and entropy, with a specific focus on the mixing of two gases.

Introduction

A solution is created when two or more components mix homogeneously to form a single phase. Studying solutions is important because most chemical and biological life processes occur in systems with multiple components. Understanding the thermodynamic behavior of mixtures is integral to the study of any system involving either ideal or non-ideal solutions because it provides valuable information on the molecular properties of the system.

Most real gases behave like ideal gases at standard temperature and pressure. This allows us to combine our knowledge of ideal systems and solutions with standard state thermodynamics in order to derive a set of equations that quantitatively describe the effect that mixing has on a given gas-phase solution's thermodynamic quantities.

Gibbs Free Energy of Mixing

Unlike the extensive properties of a one-component system, which rely only on the amount of the system present, the extensive properties of a solution depend on its temperature, pressure and composition. This means that a mixture must be described in terms of the partial molar quantities of its components. The total Gibbs free energy of a two-component solution is given by the expression

$$G = n_1\overline{G}_1 + n_2\overline{G}_2 \tag{5.3.1}$$

where

- G is the total Gibbs energy of the system,
- n_i is the number of moles of component *i*,and
- $\overline{G}_i$ is the partial molar Gibbs energy of component *i*.

The molar Gibbs energy of an ideal gas can be found using the equation

$$\overline{G} = \overline{G}^{\circ} + RT\ln\frac{P}{1bar} \tag{5.3.2}$$

where $\overline{G}^{\circ}$ is the standard molar Gibbs energy of the gas at 1 bar, and P is the pressure of the system. In a mixture of ideal gases, we find that the system's partial molar Gibbs energy is equivalent to its chemical potential, or that

$$\overline{G}_i = \mu_i \tag{5.3.3}$$

This means that for a solution of ideal gases, Equation 5.3.2 can become

$$\overline{G}_i = \mu_i = \mu_i^{\circ} + RT\ln\frac{P_i}{1bar} \tag{5.3.4}$$

where

- μ_i is the chemical potential of the *i*th component,
- $\mu_i°$ is the standard chemical potential of component *i* at 1 bar, and
- P_i is the partial pressure of component *i*.

Now pretend we have two gases at the same temperature and pressure, gas 1 and gas 2. The Gibbs energy of the system before the gases are mixed is given by Equation 5.3.1, which can be combined with Equation 5.3.4 to give the expression

$$G_{initial} = n_1(\mu_1^{\circ} + RT\ln P) + n_2(\mu_2^{\circ} + RT\ln P) \tag{5.3.5}$$

If gas 1 and gas 2 are then mixed together, they will each exert a partial pressure on the total system, P_1 and P_2, so that $P_1 + P_2 = P$. This means that the final Gibbs energy of the final solution can be found using the equation

$$G_{final} = n_1(\mu_1^{\circ} + RT\ln P_1) + n_2(\mu_2^{\circ} + RT\ln P_2) \tag{5.3.6}$$

The Gibbs energy of mixing, $\Delta_{mix}G$, can then be found by subtracting $G_{initial}$ from G_{final}.

$$\Delta_{mix}G = G_{final} - G_{initial} \tag{5.3.7}$$

$$= n_1 RT \ln \frac{P_1}{P} + n_2 RT \ln \frac{P_2}{P} \tag{5.3.8}$$

$$= n_1 RT \ln \chi_1 + n_2 RT \ln \chi_2 \tag{5.3.9}$$

where

$$P_i = \chi_i P \tag{5.3.10}$$

and χ_i is the mole fraction of gas i. This equation can be simplified further by knowing that the mole fraction of a component is equal to the number of moles of that component over the total moles of the system, or

$$\chi_i = \frac{n_i}{n}. \tag{5.3.11}$$

Equation 5.3.9 then becomes

$$\Delta_{mix}G = nRT(\chi_1 \ln \chi_1 + \chi_2 \ln \chi_2) \tag{5.3.12}$$

This expression gives us the effect that mixing has on the Gibbs free energy of a solution. Since χ_1 and χ_2 are mole fractions that range from 0 to 1, we can conclude that $\Delta_{mix}G$ will be a negative number. This is consistent with the idea that gases mix spontaneously at constant pressure and temperature.

Entropy of mixing

Figure 5.3.1 shows that when two gases mix, it can really be seen as two gases expanding into twice their original volume. This greatly increases the number of available microstates, and so we would therefore expect the entropy of the system to increase as well.

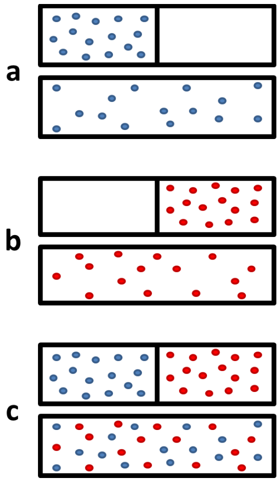

Figure 5.3.1: The mixing of two gases can be seen as two expansions. (a) Expansion of gas 1 alone when teh barrier is removed. The molecules have twice as many microstates in the open box. (b) Expansion of gas 2 along. (c) the simultaneous expansion of gases 1 and 2 is equivalent to mixing

Thermodynamic studies of an ideal gas's dependence of Gibbs free energy of temperature have shown that

$$\left(\frac{dG}{dT}\right)_P = -S \tag{5.3.13}$$

This means that differentiating Equation 5.3.12 at constant pressure with respect to temperature will give an expression for the effect that mixing has on the entropy of a solution. We see that

$$\left(\frac{dG_{mix}}{dT}\right)_P = nR(x_1 \ln x_1 + x_2 \ln x_2) \tag{5.3.14}$$

$$= -\Delta_{mix}S \tag{5.3.15}$$

$$\Delta_{mix} S = -nR(x_1 \ln x_1 + x_2 \ln x_2) \tag{5.3.16}$$

Since the mole fractions again lead to negative values for ln x_1 and ln x_2, the negative sign in front of the equation makes $\Delta_{mix}S$ positive, as expected. This agrees with the idea that mixing is a spontaneous process.

Enthalpy of mixing

We know that in an ideal system $\Delta G = \Delta H - T\Delta S$, but this equation can also be applied to the thermodynamics of mixing and solved for the enthalpy of mixing so that it reads

$$\Delta_{mix} H = \Delta_{mix} G + T\Delta_{mix} S \tag{5.3.17}$$

Plugging in our expressions for $\Delta_{mix} G$ (Equation 5.3.12) and $\Delta_{mix} S$ (Equation 5.3.16) , we get

$$\Delta_{mix} H = nRT(x_1 \ln x_1 + x_2 \ln x_2) + T\left[-nR(x_1 \ln x_1 + x_2 \ln x_2)\right] = 0 \tag{5.3.18}$$

This result makes sense when considering the system. The molecules of ideal gas are spread out enough that they do not interact with one another when mixed, which implies that no heat is absorbed or produced and results in a $\Delta_{mix} H$ of zero. Figure 5.3.2 illustrates how $T\Delta_{mix} S$ and $\Delta_{mix} G$ change as a function of the mole fraction so that $\Delta_{mix} H$ of a solution will always be equal to zero (this is for the mixing of two ideal gasses).

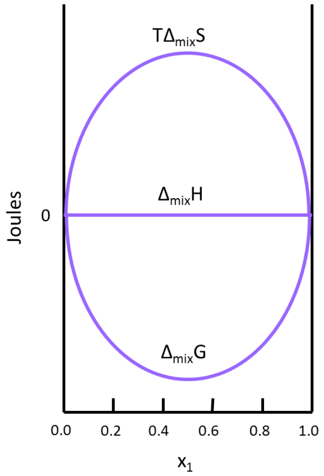

Figure 5.3.2: A graph of $T\Delta_{mix} S$, $T\Delta_{mix} H$, and $T\Delta_{mix} G$ as a function of x_1 for the mixing of two ideal gases.

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2. Meyer, E.F. (1987). Theromodynamics of “Mixing” of Ideal Gases. J. Chem. Educ. 64, 676-677.

Outside Links

- Satter, S. (2000). Thermodynamics of Mixing Real Gases. J. Chem. Educ. 77, 1361-1365.
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Problems

1. Use Figure 2 to find the x_1 that has the largest impact on the thermodynamic quantities of the final solution. Explain why this is true.
2. Calculate the effect that mixing 2 moles of nitrogen and 3 moles of oxygen has on the entropy of the final solution.
3. Another way to find the entropy of a system is using the equation $\Delta S = nR\ln(V_2/V_1)$. Use this equation and the fact that volume is directly proportional to the number of moles of gas at constant temperature and pressure to derive the final expression for $T\Delta_{mix} S$. (Hint: Use the derivation of $T\Delta_{mix} G$ as a guide).

Answers

1. x_1= 0.5
2. Increases the entropy of the system by 27.98 J/molK

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5.4: Binary Mixtures of Volatile Liquids

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5.5: Real Solutions

A non-ideal solution is a solution that does not abide to the rules of an ideal solution where the interactions between the molecules are identical (or very close) to the interactions between molecules of different components. That is, there is no forces acting between the components: no Van-der-Waals nor any Coulomb forces. We assume ideal properties for dilute solutions.

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5.6: Colligative Properties

Learning Objectives

- Express concentrations of solution components using mole fraction and molality
- Describe the effect of solute concentration on various solution properties (vapor pressure, boiling point, freezing point, and osmotic pressure)
- Perform calculations using the mathematical equations that describe these various colligative effects
- Describe the process of distillation and its practical applications
- Explain the process of osmosis and describe how it is applied industrially and in nature

The properties of a solution are different from those of either the pure solute(s) or solvent. Many solution properties are dependent upon the chemical identity of the solute. Compared to pure water, a solution of hydrogen chloride is more acidic, a solution of ammonia is more basic, a solution of sodium chloride is more dense, and a solution of sucrose is more viscous. There are a few solution properties, however, that depend *only* upon the total concentration of solute species, regardless of their identities. These colligative properties include vapor pressure lowering, boiling point elevation, freezing point depression, and osmotic pressure. This small set of properties is of central importance to many natural phenomena and technological applications, as will be described in this module.

Mole Fraction and Molality

Several units commonly used to express the concentrations of solution components were introduced in an earlier chapter of this text, each providing certain benefits for use in different applications. For example, molarity (M) is a convenient unit for use in stoichiometric calculations, since it is defined in terms of the molar amounts of solute species:

[Math Processing Error]

Because solution volumes vary with temperature, molar concentrations will likewise vary. When expressed as molarity, the concentration of a solution with identical numbers of solute and solvent species will be different at different temperatures, due to the contraction/expansion of the solution. More appropriate for calculations involving many colligative properties are mole-based concentration units whose values are not dependent on temperature. Two such units are *mole fraction* (introduced in the previous chapter on gases) and *molality*.

The mole fraction, *[Math Processing Error]*, of a component is the ratio of its molar amount to the total number of moles of all solution components:

[Math Processing Error]

Molality is a concentration unit defined as the ratio of the numbers of moles of solute to the mass of the solvent in kilograms:

[Math Processing Error]

Since these units are computed using only masses and molar amounts, they do not vary with temperature and, thus, are better suited for applications requiring temperature-independent concentrations, including several colligative properties, as will be described in this chapter module.

✓ Example *[Math Processing Error]*: Calculating Mole Fraction and Molality

The antifreeze in most automobile radiators is a mixture of equal volumes of ethylene glycol and water, with minor amounts of other additives that prevent corrosion. What are the (a) mole fraction and (b) molality of ethylene glycol, $C_2H_4(OH)_2$, in a solution prepared from *[Math Processing Error]* of ethylene glycol and *[Math Processing Error]* of water (approximately 2 L of glycol and 2 L of water)?

Solution

(a) The mole fraction of ethylene glycol may be computed by first deriving molar amounts of both solution components and then substituting these amounts into the unit definition.

[Math Processing Error]

[Math Processing Error]

[Math Processing Error]

Notice that mole fraction is a dimensionless property, being the ratio of properties with identical units (moles).

(b) To find molality, we need to know the moles of the solute and the mass of the solvent (in kg).

First, use the given mass of ethylene glycol and its molar mass to find the moles of solute:

[Math Processing Error]

Then, convert the mass of the water from grams to kilograms:

[Math Processing Error]

Finally, calculate molarity per its definition:

[Math Processing Error]

? Exercise [Math Processing Error]

What are the mole fraction and molality of a solution that contains 0.850 g of ammonia, NH_3, dissolved in 125 g of water?

Answer

7.14×10^{-3}; 0.399 *m*

✓ Example [Math Processing Error]: Converting Mole Fraction and Molal Concentrations

Calculate the mole fraction of solute and solvent in a 3.0 *m* solution of sodium chloride.

Solution

Converting from one concentration unit to another is accomplished by first comparing the two unit definitions. In this case, both units have the same numerator (moles of solute) but different denominators. The provided molal concentration may be written as:

[Math Processing Error]

The numerator for this solution's mole fraction is, therefore, 3.0 mol NaCl. The denominator may be computed by deriving the molar amount of water corresponding to 1.0 kg

[Math Processing Error]

and then substituting these molar amounts into the definition for mole fraction.

[Math Processing Error]

? Exercise [Math Processing Error]

The mole fraction of iodine, [Math Processing Error], dissolved in dichloromethane, [Math Processing Error], is 0.115. What is the molal concentration, *m*, of iodine in this solution?

Answer

1.50 *m*

Vapor Pressure Lowering

As described in the chapter on liquids and solids, the equilibrium vapor pressure of a liquid is the pressure exerted by its gaseous phase when vaporization and condensation are occurring at equal rates:

[Math Processing Error]

Dissolving a nonvolatile substance in a volatile liquid results in a lowering of the liquid's vapor pressure. This phenomenon can be rationalized by considering the effect of added solute molecules on the liquid's vaporization and condensation processes. To vaporize, solvent molecules must be present at the surface of the solution. The presence of solute decreases the surface area available to solvent molecules and thereby reduces the rate of solvent vaporization. Since the rate of condensation is unaffected by the presence of solute, the net result is that the vaporization-condensation equilibrium is achieved with fewer solvent molecules in the vapor phase (i.e., at a lower vapor pressure) (Figure *[Math Processing Error]*). While this kinetic interpretation is useful, it does not account for several important aspects of the colligative nature of vapor pressure lowering. A more rigorous explanation involves the property of *entropy*, a topic of discussion in a later text chapter on thermodynamics. For purposes of understanding the lowering of a liquid's vapor pressure, it is adequate to note that the greater entropy of a solution in comparison to its separate solvent and solute serves to effectively stabilize the solvent molecules and hinder their vaporization. A lower vapor pressure results, and a correspondingly higher boiling point as described in the next section of this module.

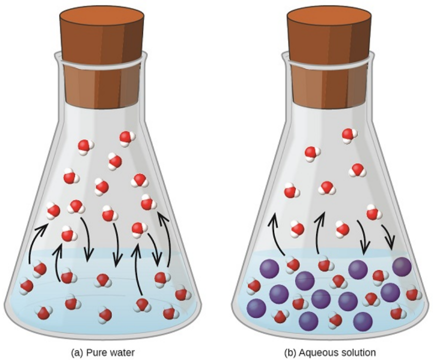


Figure *[Math Processing Error]*: The presence of nonvolatile solutes lowers the vapor pressure of a solution by impeding the evaporation of solvent molecules.

This figure contains two images. Figure a is labeled "pure water." It shows a beaker half-filled with liquid. In the liquid, eleven molecules are evenly dispersed in the liquid each consisting of one central red sphere and two slightly smaller white spheres are shown. Four molecules near the surface of the liquid have curved arrows drawn from them pointing to the space above the liquid in the beaker. Above the liquid, twelve molecules are shown, with arrows pointing from three of them into the liquid below. Figure b is labeled "Aqueous solution." It is similar to figure a except that eleven blue spheres, slightly larger in size than the molecules, are dispersed evenly in the liquid. Only four curved arrows appear in this diagram with two from the molecules in the liquid pointing to the space above and two from molecules in the space above the liquid pointing into the liquid below.

The relationship between the vapor pressures of solution components and the concentrations of those components is described by Raoult's law: *The partial pressure exerted by any component of an ideal solution is equal to the vapor pressure of the pure component multiplied by its mole fraction in the solution.*

[Math Processing Error]

where P_A is the partial pressure exerted by component A in the solution, *[Math Processing Error]* is the vapor pressure of pure A, and X_A is the mole fraction of A in the solution. (Mole fraction is a concentration unit introduced in the chapter on gases.)

Recalling that the total pressure of a gaseous mixture is equal to the sum of partial pressures for all its components (Dalton's law of partial pressures), the total vapor pressure exerted by a solution containing *i* components is

[Math Processing Error]

A nonvolatile substance is one whose vapor pressure is negligible ($P° \approx 0$), and so the vapor pressure above a solution containing only nonvolatile solutes is due only to the solvent:

[Math Processing Error]

✓ Example *[Math Processing Error]*: Calculation of a Vapor Pressure

Compute the vapor pressure of an ideal solution containing 92.1 g of glycerin, $C_3H_5(OH)_3$, and 184.4 g of ethanol, C_2H_5OH, at 40 °C. The vapor pressure of pure ethanol is 0.178 atm at 40 °C. Glycerin is essentially nonvolatile at this temperature.

Solution

Since the solvent is the only volatile component of this solution, its vapor pressure may be computed per Raoult's law as:

[Math Processing Error]

First, calculate the molar amounts of each solution component using the provided mass data.

[Math Processing Error]

[Math Processing Error]

Next, calculate the mole fraction of the solvent (ethanol) and use Raoult's law to compute the solution's vapor pressure.

[Math Processing Error]

[Math Processing Error]

Exercise *[Math Processing Error]*

A solution contains 5.00 g of urea, $CO(NH_2)_2$ (a nonvolatile solute) and 0.100 kg of water. If the vapor pressure of pure water at 25 °C is 23.7 torr, what is the vapor pressure of the solution?

Answer

23.4 torr

Elevation of the Boiling Point of a Solvent

As described in the chapter on liquids and solids, the *boiling point* of a liquid is the temperature at which its vapor pressure is equal to ambient atmospheric pressure. Since the vapor pressure of a solution is lowered due to the presence of nonvolatile solutes, it stands to reason that the solution's boiling point will subsequently be increased. Compared to pure solvent, a solution, therefore, will require a higher temperature to achieve any given vapor pressure, including one equivalent to that of the surrounding atmosphere. The increase in boiling point observed when nonvolatile solute is dissolved in a solvent, *[Math Processing Error]*, is called boiling point elevation and is directly proportional to the molal concentration of solute species:

[Math Processing Error]

where

- *[Math Processing Error]* is the boiling point elevation constant, or the *ebullioscopic constant* and
- *[Math Processing Error]* is the molal concentration (molality) of all solute species.

Boiling point elevation constants are characteristic properties that depend on the identity of the solvent. Values of K_b for several solvents are listed in Table *[Math Processing Error]*.

Table *[Math Processing Error]*: Boiling Point Elevation and Freezing Point Depression Constants for Several Solvents

Solvent	Boiling Point (°C at 1 atm)	K_b (Cm^{-1})	Freezing Point (°C at 1 atm)	K_f (Cm^{-1})
water	100.0	0.512	0.0	1.86
hydrogen acetate	118.1	3.07	16.6	3.9
benzene	80.1	2.53	5.5	5.12
chloroform	61.26	3.63	−63.5	4.68
nitrobenzene	210.9	5.24	5.67	8.1

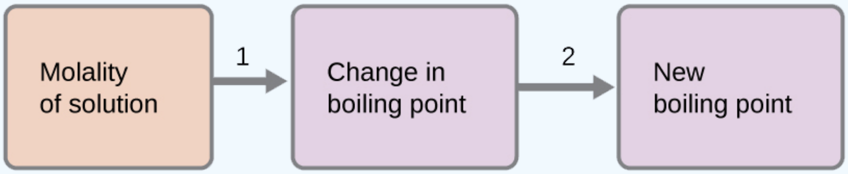
The extent to which the vapor pressure of a solvent is lowered and the boiling point is elevated depends on the total number of solute particles present in a given amount of solvent, not on the mass or size or chemical identities of the particles. A 1 *m* aqueous solution of sucrose (342 g/mol) and a 1 *m* aqueous solution of ethylene glycol (62 g/mol) will exhibit the same boiling point because each solution has one mole of solute particles (molecules) per kilogram of solvent.

✓ Example [Math Processing Error]: Calculating the Boiling Point of a Solution

What is the boiling point of a 0.33 *m* solution of a nonvolatile solute in benzene?

Solution

Use the equation relating boiling point elevation to solute molality to solve this problem in two steps.



1. *Calculate the change in boiling point.*
   [Math Processing Error]

- *Add the boiling point elevation to the pure solvent's boiling point.*
  [Math Processing Error]

? Exercise [Math Processing Error]

What is the boiling point of the antifreeze described in Example [Math Processing Error]?

Answer

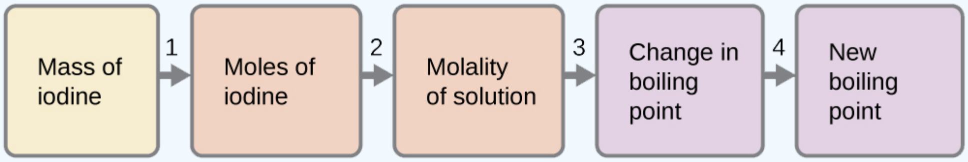
109.2 °C

✓ Example [Math Processing Error]: The Boiling Point of an Iodine Solution

Find the boiling point of a solution of 92.1 g of iodine, [Math Processing Error], in 800.0 g of chloroform, [Math Processing Error], assuming that the iodine is nonvolatile and that the solution is ideal.

Solution

We can solve this problem using four steps.



1. *Convert from grams to moles of [Math Processing Error] using the molar mass of [Math Processing Error] in the unit conversion factor.*

Result: 0.363 mol

Determine the molality of the solution from the number of moles of solute and the mass of solvent, in kilograms.

Result: 0.454 *m*

Use the direct proportionality between the change in boiling point and molal concentration to determine how much the boiling point changes.

Result: 1.65 °C

Determine the new boiling point from the boiling point of the pure solvent and the change.

Result: 62.91 °C

Check each result as a self-assessment.

? Exercise [Math Processing Error]: glycerin:Water Solution

What is the boiling point of a solution of 1.0 g of glycerin, [Math Processing Error], in 47.8 g of water? Assume an ideal solution.

Answer

100.12 °C

Distillation of Solutions

Distillation is a technique for separating the components of mixtures that is widely applied in both in the laboratory and in industrial settings. It is used to refine petroleum, to isolate fermentation products, and to purify water. This separation technique involves the controlled heating of a sample mixture to selectively vaporize, condense, and collect one or more components of interest. A typical apparatus for laboratory-scale distillations is shown in Figure [Math Processing Error].

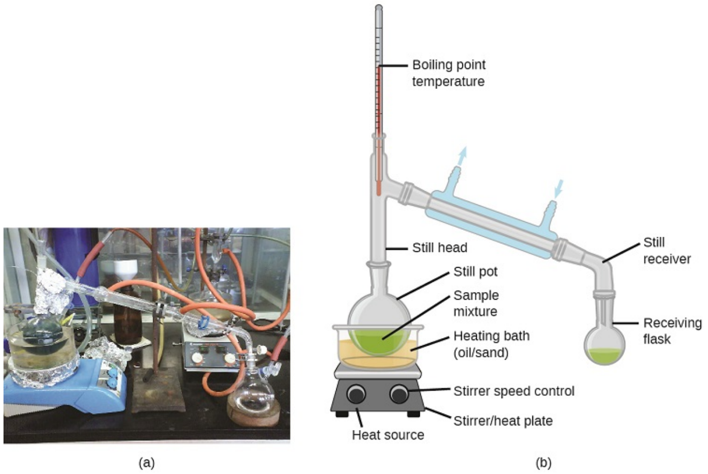


Figure [Math Processing Error]: A typical laboratory distillation unit is shown in (a) a photograph and (b) a schematic diagram of the components. (credit a: modification of work by “Rifleman82”/Wikimedia commons; credit b: modification of work by “Slashme”/Wikimedia Commons)

Figure a contains a photograph of a common laboratory distillation unit. Figure b provides a diagram labeling typical components of a laboratory distillation unit, including a stirrer/heat plate with heat and stirrer speed control, a heating bath of oil or sand, stirring means such as boiling chips, a still pot, a still head, a thermometer for boiling point temperature reading, a condenser with a cool water inlet and outlet, a still receiver with a vacuum or gas inlet, a receiving flask for holding distillate, and a cooling bath.

Oil refineries use large-scale *fractional distillation* to separate the components of crude oil. The crude oil is heated to high temperatures at the base of a tall *fractionating column*, vaporizing many of the components that rise within the column. As vaporized components reach adequately cool zones during their ascent, they condense and are collected. The collected liquids are simpler mixtures of hydrocarbons and other petroleum compounds that are of appropriate composition for various applications (e.g., diesel fuel, kerosene, gasoline), as depicted in Figure [Math Processing Error].

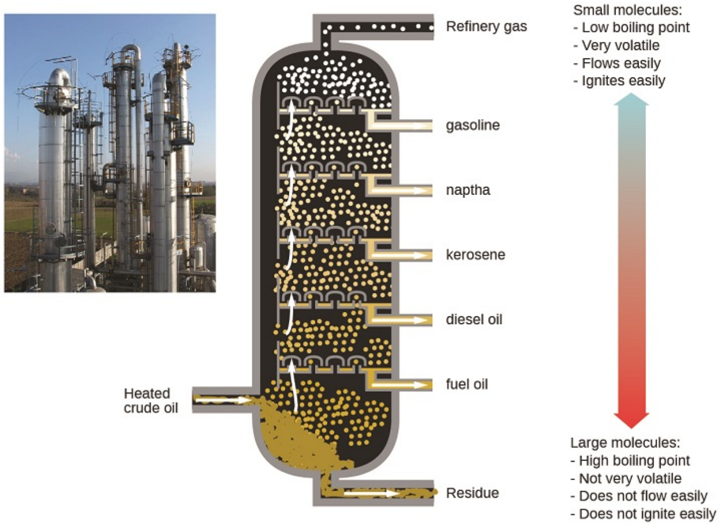


Figure *[Math Processing Error]*: Crude oil is a complex mixture that is separated by large-scale fractional distillation to isolate various simpler mixtures.

This figure contains a photo of a refinery, showing large columnar structures. A diagram of a fractional distillation column used in separating crude oil is also shown. Near the bottom of the column, an arrow pointing into the column shows a point of entry for heated crude oil. The column contains several layers at which different components are removed. At the very bottom, residue materials are removed as indicated by an arrow out of the column. At each successive level, different materials are removed proceeding from the bottom to the top of the column. The materials are fuel oil, followed by diesel oil, kerosene, naptha, gasoline, and refinery gas at the very top. To the right of the column diagram, a double sided arrow is shown that is blue at the top and gradually changes color to red moving downward. The blue top of the arrow is labeled, “small molecules: low boiling point, very volatile, flows easily, ignites easily.” The red bottom of the arrow is labeled, “large molecules: high boiling point, not very volatile, does not flow easily, does not ignite easily.”

Depression of the Freezing Point of a Solvent

Solutions freeze at lower temperatures than pure liquids. This phenomenon is exploited in “de-icing” schemes that use salt (Figure *[Math Processing Error]*), calcium chloride, or urea to melt ice on roads and sidewalks, and in the use of ethylene glycol as an “antifreeze” in automobile radiators. Seawater freezes at a lower temperature than fresh water, and so the Arctic and Antarctic oceans remain unfrozen even at temperatures below 0 °C (as do the body fluids of fish and other cold-blooded sea animals that live in these oceans).

Figure *[Math Processing Error]*: Rock salt (NaCl), calcium chloride ($CaCl_2$), or a mixture of the two are used to melt ice. (credit: modification of work by Eddie Welker)

The decrease in freezing point of a dilute solution compared to that of the pure solvent, ΔT_f, is called the freezing point depression and is directly proportional to the molal concentration of the solute

[Math Processing Error]

where

- *[Math Processing Error]* is the *molal* concentration of the solute in the solvent and
- *[Math Processing Error]* is called the freezing point depression constant (or *cryoscopic constant*).

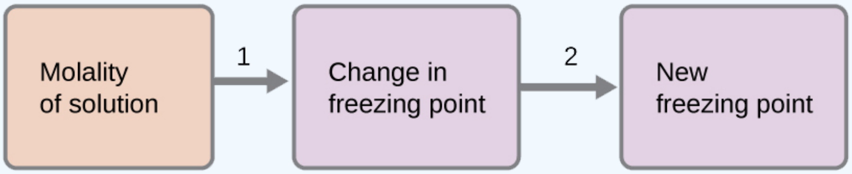
Just as for boiling point elevation constants, these are characteristic properties whose values depend on the chemical identity of the solvent. Values of K_f for several solvents are listed in Table *[Math Processing Error]*.

Example [Math Processing Error]: Calculation of the Freezing Point of a Solution

What is the freezing point of the 0.33 *m* solution of a nonvolatile nonelectrolyte solute in benzene described in Example *[Math Processing Error]*?

Solution

Use the equation relating freezing point depression to solute molality to solve this problem in two steps.



1. *Calculate the change in freezing point.* *[Math Processing Error]*
2. *Subtract the freezing point change observed from the pure solvent's freezing point.* *[Math Processing Error]*

Exercise [Math Processing Error]

What is the freezing point of a 1.85 *m* solution of a nonvolatile nonelectrolyte solute in nitrobenzene?

Answer

−9.3 °C

Colligative Properties and De-Icing

Sodium chloride and its group 2 analogs calcium and magnesium chloride are often used to de-ice roadways and sidewalks, due to the fact that a solution of any one of these salts will have a freezing point lower than 0 °C, the freezing point of pure water. The group 2 metal salts are frequently mixed with the cheaper and more readily available sodium chloride ("rock salt") for use on roads, since they tend to be somewhat less corrosive than the NaCl, and they provide a larger depression of the freezing point, since they dissociate to yield three particles per formula unit, rather than two particles like the sodium chloride.

Because these ionic compounds tend to hasten the corrosion of metal, they would not be a wise choice to use in antifreeze for the radiator in your car or to de-ice a plane prior to takeoff. For these applications, covalent compounds, such as ethylene or propylene glycol, are often used. The glycols used in radiator fluid not only lower the freezing point of the liquid, but they elevate the boiling point, making the fluid useful in both winter and summer. Heated glycols are often sprayed onto the surface of airplanes prior to takeoff in inclement weather in the winter to remove ice that has already formed and prevent the formation of more ice, which would be particularly dangerous if formed on the control surfaces of the aircraft (Video *[Math Processing Error]*).

Video [Math Processing Error]: *Freezing point depression is exploited to remove ice from the control surfaces of aircraft.*

Phase Diagram for an Aqueous Solution of a Nonelectrolyte

The colligative effects on vapor pressure, boiling point, and freezing point described in the previous section are conveniently summarized by comparing the phase diagrams for a pure liquid and a solution derived from that liquid. Phase diagrams for water and an aqueous solution are shown in Figure *[Math Processing Error]*.

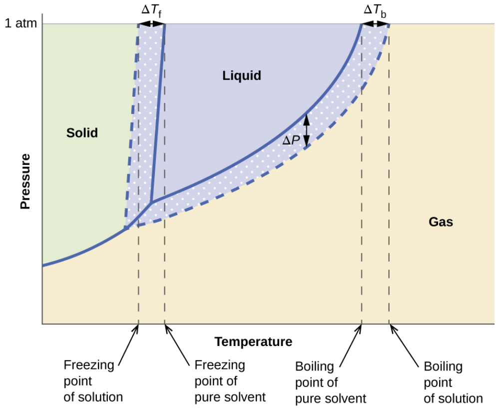


Figure *[Math Processing Error]*: These phase diagrams show water (solid curves) and an aqueous solution of nonelectrolyte (dashed curves).

This phase diagram indicates the pressure in atmospheres of water and a solution at various temperatures. The graph shows the freezing point of water and the freezing point of the solution, with the difference between these two values identified as delta T subscript f. The graph shows the boiling point of water and the boiling point of the solution, with the difference between these two values identified as delta T subscript b. Similarly, the difference in the pressure of water and the solution at the boiling point of water is shown and identified as delta P. This difference in pressure is labeled vapor pressure lowering. The lower level of the vapor pressure curve for the solution as opposed to that of pure water shows vapor pressure lowering in the solution. Background colors on the diagram indicate the presence of water and the solution in the solid state to the left, liquid state in the central upper region, and gas to the right.

The liquid-vapor curve for the solution is located *beneath* the corresponding curve for the solvent, depicting the vapor pressure *lowering*, ΔP, that results from the dissolution of nonvolatile solute. Consequently, at any given pressure, the solution's boiling point is observed at a higher temperature than that for the pure solvent, reflecting the boiling point elevation, ΔT_b, associated with the presence of nonvolatile solute. The solid-liquid curve for the solution is displaced left of that for the pure solvent, representing the freezing point depression, ΔTf, that accompanies solution formation. Finally, notice that the solid-gas curves for the solvent and its solution are identical. This is the case for many solutions comprising liquid solvents and nonvolatile solutes. Just as for vaporization, when a solution of this sort is frozen, it is actually just the *solvent* molecules that undergo the liquid-to-solid transition, forming pure solid solvent that excludes solute species. The solid and gaseous phases, therefore, are composed solvent only, and so transitions between these phases are not subject to colligative effects.

Osmosis and Osmotic Pressure of Solutions

A number of natural and synthetic materials exhibit *selective permeation*, meaning that only molecules or ions of a certain size, shape, polarity, charge, and so forth, are capable of passing through (permeating) the material. Biological cell membranes provide elegant examples of selective permeation in nature, while dialysis tubing used to remove metabolic wastes from blood is a more simplistic technological example. Regardless of how they may be fabricated, these materials are generally referred to as semipermeable membranes.

Consider the apparatus illustrated in Figure *[Math Processing Error]*, in which samples of pure solvent and a solution are separated by a membrane that only solvent molecules may permeate. Solvent molecules will diffuse across the membrane in both directions. Since the concentration of *solvent* is greater in the pure solvent than the solution, these molecules will diffuse from the solvent side of the membrane to the solution side at a faster rate than they will in the reverse direction. The result is a net transfer of solvent molecules from the pure solvent to the solution. Diffusion-driven transfer of solvent molecules through a semipermeable membrane is a process known as osmosis.

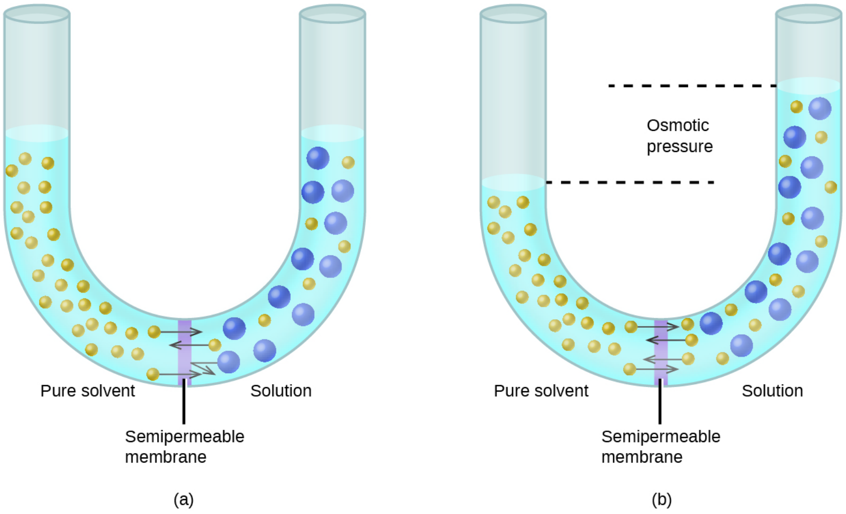


Figure *[Math Processing Error]*: Osmosis results in the transfer of solvent molecules from a sample of low (or zero) solute concentration to a sample of higher solute concentration.

The figure shows two U shaped tubes with a semi permeable membrane placed at the base of the U. In figure a, pure solvent is present and indicated by small yellow spheres to the left of the membrane. To the right, a solution exists with larger blue spheres intermingled with some small yellow spheres. At the membrane, arrows pointing from three small yellow spheres on both sides of the membrane cross over the membrane. An arrow drawn from one of the large blue spheres does not cross the membrane, but rather is reflected back from the surface of the membrane. The levels of liquid in both sides of the U shaped tube are equal. In figure b, arrows again point from small yellow spheres across the semipermeable membrane from both sides. This diagram shows the level of liquid in the left, pure solvent, side to be significantly lower than the liquid level on the right. Dashed lines are drawn from these two liquid levels into the middle of the U-shaped tube and between them is the term osmotic pressure.

When osmosis is carried out in an apparatus like that shown in Figure *[Math Processing Error]*, the volume of the solution increases as it becomes diluted by accumulation of solvent. This causes the level of the solution to rise, increasing its hydrostatic pressure (due to the weight of the column of solution in the tube) and resulting in a faster transfer of solvent molecules back to the pure solvent side. When the pressure reaches a value that yields a reverse solvent transfer rate equal to the osmosis rate, bulk transfer of solvent ceases. This pressure is called the osmotic pressure (*[Math Processing Error]*) of the solution. The osmotic pressure of a dilute solution is related to its solute molarity, M, and absolute temperature, T, according to the equation

[Math Processing Error]

where *[Math Processing Error]* is the universal gas constant.

✓ Example *[Math Processing Error]*: Calculation of Osmotic Pressure

What is the osmotic pressure (atm) of a 0.30 M solution of glucose in water that is used for intravenous infusion at body temperature, 37 °C?

Solution

We can find the osmotic pressure, \(*Π*\), using Equation *[Math Processing Error]*, where T is on the Kelvin scale (310 K) and the value of R is expressed in appropriate units (0.08206 L atm/mol K).

[Math Processing Error]

? Exercise *[Math Processing Error]*

What is the osmotic pressure (atm) a solution with a volume of 0.750 L that contains 5.0 g of methanol, CH_3OH, in water at 37 °C?

Answer

5.3 atm

If a solution is placed in an apparatus like the one shown in Figure *[Math Processing Error]*, applying pressure greater than the osmotic pressure of the solution reverses the osmosis and pushes solvent molecules from the solution into the pure solvent. This technique of reverse osmosis is used for large-scale desalination of seawater and on smaller scales to produce high-purity tap water for drinking.

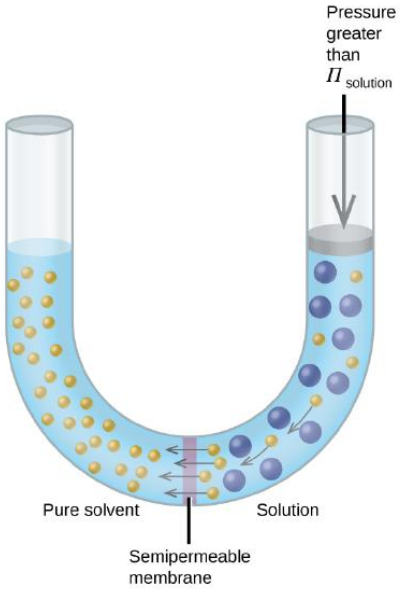


Figure *[Math Processing Error]*: Applying a pressure greater than the osmotic pressure of a solution will reverse osmosis. Solvent molecules from the solution are pushed into the pure solvent.

The figure shows a U shaped tube with a semi permeable membrane placed at the base of the U. Pure solvent is present and indicated by small yellow spheres to the left of the membrane. To the right, a solution exists with larger blue spheres intermingled with some small yellow spheres. At the membrane, arrows point from four small yellow spheres to the left of the membrane. On the right side of the U, there is a disk that is the same width of the tube and appears to block it. The disk is at the same level as the solution. An arrow points down from the top of the tube to the disk and is labeled, “Pressure greater than Π subscript solution.”

Examples of osmosis are evident in many biological systems because cells are surrounded by semipermeable membranes. Carrots and celery that have become limp because they have lost water can be made crisp again by placing them in water. Water moves into the carrot or celery cells by osmosis. A cucumber placed in a concentrated salt solution loses water by osmosis and absorbs some salt to become a pickle. Osmosis can also affect animal cells. Solute concentrations are particularly important when solutions are injected into the body. Solutes in body cell fluids and blood serum give these solutions an osmotic pressure of approximately 7.7 atm. Solutions injected into the body must have the same osmotic pressure as blood serum; that is, they should be isotonic with blood serum. If a less concentrated solution, a hypotonic solution, is injected in sufficient quantity to dilute the blood serum, water from the diluted serum passes into the blood cells by osmosis, causing the cells to expand and rupture. This process is called hemolysis. When a more concentrated solution, a hypertonic solution, is injected, the cells lose water to the more concentrated solution, shrivel, and possibly die in a process called *crenation* (Figure 11.5.8).

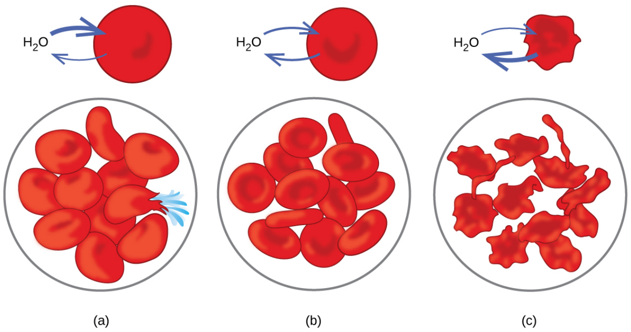


Figure *[Math Processing Error]*: Red blood cell membranes are water permeable and will (a) swell and possibly rupture in a hypotonic solution; (b) maintain normal volume and shape in an isotonic solution; and (c) shrivel and possibly die in a hypertonic solution. (credit a/b/c: modifications of work by "LadyofHats"/Wikimedia commons)

This figure shows three scenarios relating to red blood cell membranes. In a, H subscript 2 O has two arrows drawn from it pointing into a red disk. Beneath it in a circle are eleven similar disks with a bulging appearance, one of which appears to have burst with blue liquid erupting from it. In b, the image is similar except that rather than having two arrows pointing into the red disk, one points in and a second points out toward the H subscript 2 O. In the circle beneath, twelve of the red disks are present. In c, both arrows are drawn from a red shriveled disk toward the H subscript 2 O. In the circle below, twelve shriveled disks are shown.

Determination of Molar Masses

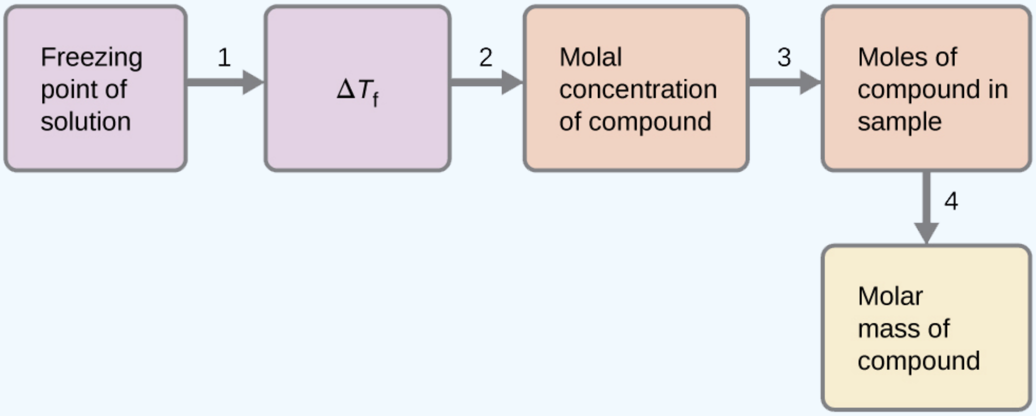
Osmotic pressure and changes in freezing point, boiling point, and vapor pressure are directly proportional to the concentration of solute present. Consequently, we can use a measurement of one of these properties to determine the molar mass of the solute from the measurements.

✓ Example *[Math Processing Error]*: Determining Molar Mass from Freezing Point Depression

A solution of 4.00 g of a nonelectrolyte dissolved in 55.0 g of benzene is found to freeze at 2.32 °C. What is the molar mass of this compound?

Solution

We can solve this problem using the following steps.



1. *Determine the change in freezing point from the observed freezing point and the freezing point of pure benzene* (Table 11.5.1).

[Math Processing Error]

1. *Determine the molal concentration from* K_f*, the freezing point depression constant for benzene* (Table 11.5.1), *and* ΔT_f.

\(ΔT_\ce{f}=K_\ce{f}m\)

[Math Processing Error]

1. *Determine the number of moles of compound in the solution from the molal concentration and the mass of solvent used to make the solution.*
   [Math Processing Error]
2. *Determine the molar mass from the mass of the solute and the number of moles in that mass.*

\(\mathrm{Molar\: mass=\dfrac{4.00\:g}{0.034\:mol}=1.2×10^2\:g/mol}\)

? Exercise *[Math Processing Error]*

A solution of 35.7 g of a nonelectrolyte in 220.0 g of chloroform has a boiling point of 64.5 °C. What is the molar mass of this compound?

Answer

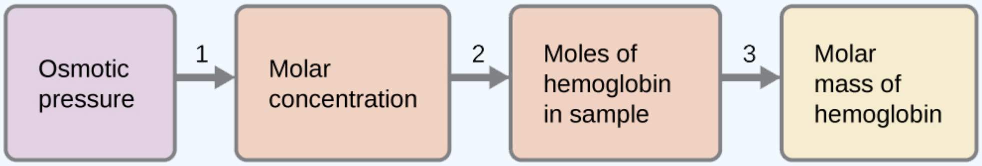
1.8×10^2 g/mol

✓ Example *[Math Processing Error]*: Determination of a Molar Mass from Osmotic Pressure

A 0.500 L sample of an aqueous solution containing 10.0 g of hemoglobin has an osmotic pressure of 5.9 torr at 22 °C. What is the molar mass of hemoglobin?

Solution

Here is one set of steps that can be used to solve the problem:



1. *[Math Processing Error]*

[Math Processing Error]

[Math Processing Error]

1. *[Math Processing Error]*
2. *Determine the molar mass from the mass of hemoglobin and the number of moles in that mass.*

[Math Processing Error]

? Exercise *[Math Processing Error]*

What is the molar mass of a protein if a solution of 0.02 g of the protein in 25.0 mL of solution has an osmotic pressure of 0.56 torr at 25 °C?

Answer

2.7×10^4 g/mol

Colligative Properties of Electrolytes

As noted previously in this module, the colligative properties of a solution depend only on the number, not on the kind, of solute species dissolved. For example, 1 mole of any nonelectrolyte dissolved in 1 kilogram of solvent produces the same lowering of the freezing point as does 1 mole of any other nonelectrolyte. However, 1 mole of sodium chloride (an electrolyte) forms *2 moles* of ions when dissolved in solution. Each individual ion produces the same effect on the freezing point as a single molecule does.

Example [Math Processing Error]: The Freezing Point of a Solution of an Electrolyte

The concentration of ions in seawater is approximately the same as that in a solution containing 4.2 g of NaCl dissolved in 125 g of water. Assume that each of the ions in the NaCl solution has the same effect on the freezing point of water as a nonelectrolyte molecule, and determine the freezing temperature the solution (which is approximately equal to the freezing temperature of seawater).

Solution

We can solve this problem using the following series of steps.

- Convert from grams to moles of NaCl using the molar mass of NaCl in the unit conversion factor. Result: 0.072 mol NaCl
- Determine the number of moles of ions present in the solution using the number of moles of ions in 1 mole of NaCl as the conversion factor (2 mol ions/1 mol NaCl). Result: 0.14 mol ions
- Determine the molality of the ions in the solution from the number of moles of ions and the mass of solvent, in kilograms. Result: 1.1 m
- Use the direct proportionality between the change in freezing point and molal concentration to determine how much the freezing point changes. Result: 2.0 °C
- Determine the new freezing point from the freezing point of the pure solvent and the change. Result: −2.0 °C

Check each result as a self-assessment.

Exercise [Math Processing Error]

Assume that each of the ions in calcium chloride, $CaCl_2$, has the same effect on the freezing point of water as a nonelectrolyte molecule. Calculate the freezing point of a solution of 0.724 g of $CaCl_2$ in 175 g of water.

Answer

−0.208 °C

Assuming complete dissociation, a 1.0 *m* aqueous solution of NaCl contains 2.0 mole of ions (1.0 mol Na^+ and 1.0 mol $Cl^−$) per each kilogram of water, and its freezing point depression is expected to be

[Math Processing Error]

When this solution is actually prepared and its freezing point depression measured, however, a value of 3.4 °C is obtained. Similar discrepancies are observed for other ionic compounds, and the differences between the measured and expected colligative property values typically become more significant as solute concentrations increase. These observations suggest that the ions of sodium chloride (and other strong electrolytes) are not completely dissociated in solution.

To account for this and avoid the errors accompanying the assumption of total dissociation, an experimentally measured parameter named in honor of Nobel Prize-winning German chemist Jacobus Henricus van't Hoff is used. The van't Hoff factor (*i*) is defined as the ratio of solute particles in solution to the number of formula units dissolved:

[Math Processing Error]

Values for measured van't Hoff factors for several solutes, along with predicted values assuming complete dissociation, are shown in Table *[Math Processing Error]*.

Table *[Math Processing Error]*: Expected and Observed van't Hoff Factors for Several 0.050 m Aqueous Electrolyte Solutions

Electrolyte	Particles in Solution	*i* (Predicted)	*i* (Measured)
HCl	H^+, $Cl^−$	2	1.9
NaCl	Na^+, $Cl^−$	2	1.9
$MgSO_4$	Mg^{2+}, *[Math Processing Error]*	2	1.3
$MgCl_2$	Mg^{2+}, $2Cl^−$	3	2.7
$FeCl_3$	Fe^{3+}, $3Cl^−$	4	3.4

Electrolyte	Particles in Solution	*i* (Predicted)	*i* (Measured)
glucose (a non-electrolyte)	$C_{12}H_{22}O_{11}$	1	1.0

In 1923, the chemists Peter Debye and Erich Hückel proposed a theory to explain the apparent incomplete ionization of strong electrolytes. They suggested that although interionic attraction in an aqueous solution is very greatly reduced by solvation of the ions and the insulating action of the polar solvent, it is not completely nullified. The residual attractions prevent the ions from behaving as totally independent particles (Figure *[Math Processing Error]*). In some cases, a positive and negative ion may actually touch, giving a solvated unit called an ion pair. Thus, the activity, or the effective concentration, of any particular kind of ion is less than that indicated by the actual concentration. Ions become more and more widely separated the more dilute the solution, and the residual interionic attractions become less and less. Thus, in extremely dilute solutions, the effective concentrations of the ions (their activities) are essentially equal to the actual concentrations. Note that the van't Hoff factors for the electrolytes in Table *[Math Processing Error]* are for 0.05 *m* solutions, at which concentration the value of *i* for NaCl is 1.9, as opposed to an ideal value of 2.

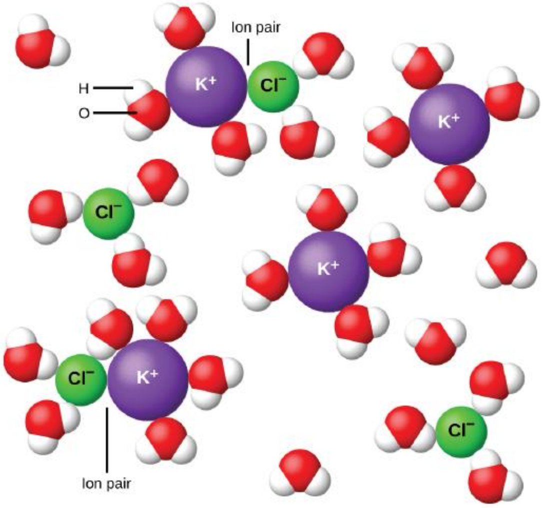


Figure *[Math Processing Error]*: Ions become more and more widely separated the more dilute the solution, and the residual interionic attractions become less.

The diagram shows four purple spheres labeled K superscript plus and four green spheres labeled C l superscript minus dispersed in H subscript 2 O as shown by clusters of single red spheres with two white spheres attached. Red spheres represent oxygen and white represent hydrogen. In two locations, the purple and green spheres are touching. In these two locations, the diagram is labeled ion pair. All red and green spheres are surrounded by the white and red H subscript 2 O clusters. The white spheres are attracted to the purple spheres and the red spheres are attracted to the green spheres.

Summary

Properties of a solution that depend only on the concentration of solute particles are called colligative properties. They include changes in the vapor pressure, boiling point, and freezing point of the solvent in the solution. The magnitudes of these properties depend only on the total concentration of solute particles in solution, not on the type of particles. The total concentration of solute particles in a solution also determines its osmotic pressure. This is the pressure that must be applied to the solution to prevent diffusion of molecules of pure solvent through a semipermeable membrane into the solution. Ionic compounds may not completely dissociate in solution due to activity effects, in which case observed colligative effects may be less than predicted.

Key Equations

- *[Math Processing Error]*
- *[Math Processing Error]*
- *[Math Processing Error]*
- $\Delta T_b = K_b m$
- $\Delta T_f = K_f m$
- $\Pi = MRT$

Footnotes

1. A nonelectrolyte shown for comparison.

Glossary

boiling point elevation

elevation of the boiling point of a liquid by addition of a solute

boiling point elevation constant

the proportionality constant in the equation relating boiling point elevation to solute molality; also known as the ebullioscopic constant

colligative property

property of a solution that depends only on the concentration of a solute species

crenation

process whereby biological cells become shriveled due to loss of water by osmosis

freezing point depression

lowering of the freezing point of a liquid by addition of a solute

freezing point depression constant

(also, cryoscopic constant) proportionality constant in the equation relating freezing point depression to solute molality

hemolysis

rupture of red blood cells due to the accumulation of excess water by osmosis

hypertonic

of greater osmotic pressure

hypotonic

of less osmotic pressure

ion pair

solvated anion/cation pair held together by moderate electrostatic attraction

isotonic

of equal osmotic pressure

molality (m)

a concentration unit defined as the ratio of the numbers of moles of solute to the mass of the solvent in kilograms

osmosis

diffusion of solvent molecules through a semipermeable membrane

osmotic pressure (Π)

opposing pressure required to prevent bulk transfer of solvent molecules through a semipermeable membrane

Raoult's law

the partial pressure exerted by a solution component is equal to the product of the component's mole fraction in the solution and its equilibrium vapor pressure in the pure state

semipermeable membrane

a membrane that selectively permits passage of certain ions or molecules

van’t Hoff factor (*i*)

the ratio of the number of moles of particles in a solution to the number of moles of formula units dissolved in the solution

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5.7: Electrolyte Solutions

An electrolyte solution is a solution that generally contains ions, atoms or molecules that have lost or gained electrons, and is electrically conductive. For this reason they are often called ionic solutions, however there are some cases where the electrolytes are not ions. For this discussion we will only consider solutions of ions. A basic principle of electrostatics is that opposite charges attract and like charges repel. It also takes a great deal of force to overcome this electrostatic attraction.

Introduction

The general form of Coulomb's law describes the force of attraction between charges:

$$F = k\frac{q_1 m q_2}{r^2} \tag{5.7.1}$$

However, we must make some changes to this physics formula to be able to use it for a solution of oppositely charged ions. In Coulomb's Law, the constant

$$k = \frac{1}{4\pi\varepsilon_0} \tag{5.7.2}$$

, where ε_0 is the permittivity of free space, such as in a vacuum. However, since we are looking at a solution, we must consider the effect that the medium (the solvent in this case) has on the electrostatic force, which is represented by the dielectric constant ε:

$$F = \frac{q_1 q_2}{4\pi\varepsilon_0\varepsilon r^2} \tag{5.7.3}$$

Polar substances such as water have a relatively high dielectric constant.

Standard Definitions of Enthalpy, Entropy, and Gibbs Energy for Ions

Ions are not stable on their own, and thus no ions can ever be studied separately. Particularly in biology, all ions in a certain cell or tissue have a counterion that balances this charge. Therefore, we cannot measure the enthalpy or entropy of a single ion as we can atoms of a pure element. So we define a reference point. The $\Delta_f\overline{H}^\circ$ of a hydrogen ion H^+ is equal to zero, as are the other thermodynamic quantities.

$$\Delta_f\overline{H}^\circ[H^+(aq)] = 0 \tag{5.7.4}$$

$$\Delta_f\overline{G}^\circ[H^+(aq)] = 0 \tag{5.7.5}$$

$$\overline{S}^\circ[H^+(aq)] = 0 \tag{5.7.6}$$

When studying the formation of ionic solutions, the most useful quantity to describe is chemical potential μ, defined as the partial molar Gibbs energy of the ith component in a substance:

$$\mu_i = \overline{G}_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j} = \mu_i^\circ + RT\ln x_i \tag{5.7.7}$$

where x_i can be any unit of concentration of the component: mole fraction, molality, or for gases, the partial pressure divided by the pressure of pure component.

Ionic Solutions

To express the chemical potential of an electrolyte in solution in terms of molality, let us use the example of a dissolved salt such as magnesium chloride, $MgCl_2$.

$$MgCl_2 \rightleftharpoons Mg^{2+} + 2Cl^- \tag{5.7.8}$$

We can now write a more general equation for a dissociated salt:

$$M_{\nu+}X_{\nu-} \rightleftharpoons \nu_+M^{z+} + \nu_-X^{z-} \tag{5.7.9}$$

where $\nu_\pm$ represents the stoichiometric coefficient of the cation or anion and $z_\pm$ represents the charge, and M and X are the metal and halide, respectively.

The total chemical potential for these anion-cation pair would be the sum of their individual potentials multiplied by their stoichiometric coefficients:

$$\mu = \nu_+\mu_+ + \nu_-\mu_- \tag{5.7.10}$$

The chemical potentials of the individual ions are:

$$\mu_+ = \mu_+^\circ + RT\ln m_+ \tag{5.7.11}$$

$$\mu_- = \mu_-^\circ + RT\ln m_- \tag{5.7.12}$$

And the molalities of the individual ions are related to the original molality of the salt m by their stoichiometric coefficients

$$m_+ = \nu_+ m \tag{5.7.13}$$

Substituting Equations 5.7.11 and 5.7.12 into Equation 5.7.10,

$$\mu = (\nu_+\mu_+^\circ + \nu_- mu_-^\circ) + RT\ln\left(m_+^{\nu+} m_-^{\nu-}\right) \tag{5.7.14}$$

since the total number of moles $\nu = \nu_+ + \nu_-$, we can define the mean ionic molality as the geometric average of the molarity of the two ions:

$$m_\pm = (m_+^{\nu+} m_-^{\nu-})^{\frac{1}{\nu}} \tag{5.7.15}$$

then Equation 5.7.14 becomes

$$\mu = (\nu_+\mu_+^\circ + \nu_-\mu_-^\circ) + \nu RT\ln m_\pm \tag{5.7.16}$$

We have derived this equation for a ideal solution, but ions in solution exert electrostatic forces on one another to deviate from ideal behavior, so instead of molarities we must use the activity a to represent how the ion is behaving in solution. Therefore the mean ionic activity is defined as

$$a_\pm = (a_+^{\nu+} + a_-^{\nu-})^{\frac{1}{\nu}} \tag{5.7.17}$$

where

$$a_\pm = \gamma m_\pm \tag{5.7.18}$$

and $\gamma_\pm$ is the **mean ionic activity coefficient**, which is dependent on the substance.

Substituting the mean ionic activity of \Equation 5.7.18 into Equation 5.7.16,

$$\mu = (\nu_+\mu_+^\circ + \nu_-\mu_-^\circ) + \nu RT\ln a_\pm = (\nu_+\mu_+^\circ + \nu_-\mu_-^\circ) + RT\ln a_\pm^\nu = (\nu_+\mu_+^\circ + \nu_-\mu_-^\circ) + RT\ln a \tag{5.7.19}$$

when $a = a_\pm^\nu$. Equation 5.7.19 then represents the chemical potential of a nonideal electrolyte solutions. To calculate the mean ionic activity coefficient requires the use of the Debye-Hückel limiting law, part of the Debye-Hückel theory of electrolytes .

✓ Example 5.7.1

Let us now write out the chemical potential in terms of molality of the salt in our first example, $MgCl_2$. First from Equation 5.7.8, the stoichiometric coefficients of the ions are:

$$\nu_+ = 1, \nu_- = 2, \nu\ = 3$$

The mean ionic molality is

$$\begin{aligned} m_\pm &= (m_+^1 m_-^2)^{\frac{1}{3}} \\ &= (\nu_+ m \times \nu_- m)^{\frac{1}{3}} \\ &= m(1^1 2^2)^{\frac{1}{3}} \\ &= 1.6\, m \end{aligned}$$

The expression for the chemical potential of

$$MgCl_2 \tag{5.7.20}$$

is

$$\mu_{MgCl_2} = \mu^{\circ}_{MgCl_2} + 3RT \ln 1.6 \backslash \mathrm{m} m$$

References

1. Chang, Raymond. Physical Chemistry for the Biosciences. Sausalito, California: University Science Books, 2005.

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5.8: Ionic Activity

The properties of electrolyte solutions can significantly deviate from the laws used to derive chemical potential of solutions. In nonelectrolyte solutions, the intermolecular forces are mostly comprised of weak Van der Waals interactions, which have a r^{-7} dependence, and for practical purposes this can be considered ideal. In ionic solutions, however, there are significant electrostatic interactions between solute-solvent as well as solute-solute molecules. These electrostatic forces are governed by Coulomb's law, which has a r^{-2} dependence. Consequently, the behavior of an electrolyte solution deviates considerably from that an ideal solution. Indeed, this is why we utilize the activity of the individual components and not the concentration to calculate deviations from ideal behavior. In 1923, Peter Debye and Erich Hückel developed a theory that would allow us to calculate the mean ionic activity coefficient of the solution, $\gamma_{\pm}$, and could explain how the behavior of ions in solution contribute to this constant.

Assumptions of Debye-Hückel Theory

The Debye-Hückel theory is based on three assumptions of how ions act in solution:

1. Electrolytes completely dissociate into ions in solution.
2. Solutions of Electrolytes are very dilute, on the order of 0.01 M.
3. Each ion is surrounded by ions of the opposite charge, on average.

Debye and Hückel developed the following equation to calculate the mean ionic activity coefficient $\gamma_{\pm}$:

$$\log \gamma_{\pm} = -\frac{1.824 \times 10^6}{(\varepsilon T)^{3/2}} \mid z_+ z_- \mid \sqrt{I} \tag{5.8.1}$$

where

- ε is the dielectric constant,
- z_+ and z_- are the charges of the cation and anion, respectively, and
- I is the ionic strength of the solution.

The Equation 5.8.1 is known as the **Debye-Hückel Limiting Law**. The ionic strength is calculated by the following relation:

$$I = \frac{1}{2} \sum_i m_i z_i^2 \tag{5.8.2}$$

where m_i and z_i are the molality and the charge of the ith ion in the electrolyte. Since most of the electrolyte solutions we study are aqueous $(\varepsilon = 78.54)$ and have a temperature of 298 K, the Limiting Law in Equation 5.8.1 reduces to

$$\log \gamma_{\pm} = -0.509 \mid z_+ z_- \mid \sqrt{I} \tag{5.8.3}$$

Example 5.8.1

Calculate ionic strength, mean ionic activity coefficient $\gamma_{\pm}$, and the mean ionic molality $m_{\pm}$ for a 0.02 *molal* aqueous solution of zinc chloride, $ZnCl_2$.

Solution

Zinc chloride will dissolve as

$$ZnCl_2 \longrightarrow Zn^{2+}(aq) + 2\,Cl^-(aq)$$

The concentrations of the zinc and chloride ions will then be 0.02 and 0.04 molal, respectively. First calculate the mean ionic molality. The mean ionic molality is defined as the average molality of the two ions (see Electrolyte Solutions):

$$m_{\pm} = (m_+^{\nu+} m_-^{\nu-})^{\frac{1}{\nu}}$$

where ν is the stoichiometric coefficient of the ions, and the total of the coefficients in the exponent. In our case, the mean ionic molality is

$$\begin{aligned} m_{\pm} &= \left(m_{Zn}^{\nu(Zn)} m_{Cl}^{\nu(Cl)}\right)^{\frac{1}{\nu(Zn)+\nu(Cl)}} \\ &= \left[(0.02)^1 (0.04)^2\right]^{\frac{1}{3}} \\ &= \left[(0.02)(0.0016)\right]^{\frac{1}{3}} \\ &= 3.17 \times 10^{-2} \end{aligned}$$

To calculate the mean ionic activity coefficient, we first need the ionic strength of the solution from Equation 5.8.2:

$$\begin{aligned} I &= \frac{1}{2}\left[(0.02)(+2)^2 + (0.04)(-1)^2\right] \\ &= \frac{1}{2}(0.08 + 0.04) = 0.06 \end{aligned}$$

Now we can use Equation 5.8.3 to calculate the activity coefficient:

$$\begin{aligned} \log \gamma_{\pm} &= -0.509 \mid (+2)(-1) \mid \sqrt{0.06} \\ &= (-0.509)(2)(0.245) \\ &= -0.250 \\ \gamma_{\pm} &= 10^{-0.25} \\ &= 0.1627 \end{aligned}$$

Exercise 5.8.1

Determine the mean ionic activity coefficient and mean activity of a 0.004 molal of $\mathrm{Ba(HCO_3)_2}$?

Apr 11, 2020, 9:58 PM

https://socratic.org/questions/560b11bf581e2a331df2c7fd

Answer

$$\gamma_{\pm} = 10^{-0.10188} \approx 0.7909$$

$$a_{\pm} = 0.7909 \times 0.2785\, m = 0.2203\, m$$

Figure 5.8.1: Example activity coefficients. https://www.youtube.com/watch?v=MZCNooIEzQQ

The kinetic salt effect is the effect of salts preset in solution on the rate of a reaction.

Kinetic Salt Effect

In biological systems, salts influence how well proteins and DNA function. Salts are formed by ionic bonds, between a metal and an electromagnetic atom(s). Some examples of salts include NaCl, KCl, and Na_2SO_4. Salt molecules are able to disassociate, forming cations and anions. An increase in the charge (- or +) of a transition state or an activated complex results in an increase in solvation (creating more order in the system), and causes a decrease in the change of entropy (ΔS). In contrast, a decrease in the charge of the transition state causes an increase in ΔS.

$$I^- + C^+ \rightleftharpoons E^o \rightarrow Product \tag{5.8.4}$$

The kinetic salt effect describes the way salts stabilize reactants. For example, in the above reaction, each reactant has a charge. The negatively-charged reactant is stabilized by the positive charges from the salt, and the positively-charged reactant is stabilized by the negative charges from the salt. As a result, the rate at which the reactants come together decreases, thus decreasing the rate at which E forms. Because a charged intermediate is also stabilized in the solution, the half life of the intermediate at equilibrium increases, shifting the reaction toward product formation. Because the rate of the product formation is higher due to increased amounts of the intermediate present on the solution, first order kinetics is used to derive the rate constant equation:

$$\log K_{TS} = \log K_{TS^o} + 2 Z_A Z_B \sqrt{I} \tag{5.8.5}$$

where

- Z is the charge on the cation and ion from the salt. $Z_A Z_B$ is a product value.
- I is the ionic strength. I is also dependent on the solubility of the salt in the reaction mixture. Ionic strength is directly proportional to the solubility of the salt. Changing the ionic strength manipulates the solvation of the reactants and intermediates, thus changing ΔS, and affecting the reaction rate.
- $\log K_{TS^o}$ is the rate constant without the salt in the reaction mixture.
- A is also a constant for the solvent the solution is in. The A value for water is 0.509 at 298 K.

The relationship between $Z_A Z_B$, I, and the rate of the reaction is presented in tabular form below:

$Z_A Z_B$	Rate of Reaction
+	Increases (salt present in the reaction mixture)
-	Decreases (the ionic strength increases)

Note: I=0 at very dilute salt concentrations or if the salt is inert.

References

1. Atkins, P.W. Physical Chemistry. 5th Ed. New York: WH Freeman, 1994.
2. Chang, Raymond. Physical Chemistry for the Biosciences. Sausalito, California: University Science Books, 2005.

Contributors and Attributions

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5.9: Colligative Properties of Electrolyte Solutions

An electrolyte solution is a solution that generally contains ions, atoms or molecules that have lost or gained electrons, and is electrically conductive. For this reason they are often called ionic solutions, however there are some cases where the electrolytes are not ions. For this discussion we will only consider solutions of ions. A basic principle of electrostatics is that opposite charges attract and like charges repel. It also takes a great deal of force to overcome this electrostatic attraction.

Introduction

The general form of Coulomb's law describes the force of attraction between charges:

[Math Processing Error]

However, we must make some changes to this physics formula to be able to use it for a solution of oppositely charged ions. In Coulomb's Law, the constant *[Math Processing Error]*, where *[Math Processing Error]* is the permittivity of free space, such as in a vacuum. However, since we are looking at a solution, we must consider the effect that the medium (the solvent in this case) has on the electrostatic force, which is represented by the dielectric constant *[Math Processing Error]*:

[Math Processing Error]

Polar substances such as water have a relatively high dielectric constant.

Standard Definitions of Enthalpy, Entropy, and Gibbs Energy for Ions

Ions are not stable on their own, and thus no ions can ever be studied separately. Particularly in biology, all ions in a certain cell or tissue have a counterion that balances this charge. Therefore, we cannot measure the enthalpy or entropy of a single ion as we can atoms of a pure element. So we define a reference point. The *[Math Processing Error]* of a hydrogen ion *[Math Processing Error]* is equal to zero, as are the other thermodynamic quantities.

[Math Processing Error]

[Math Processing Error]

[Math Processing Error]

When studying the formation of ionic solutions, the most useful quantity to describe is chemical potential *[Math Processing Error]*, defined as the partial molar Gibbs energy of the ith component in a substance:

[Math Processing Error]

where *[Math Processing Error]* can be any unit of concentration of the component: mole fraction, molality, or for gases, the partial pressure divided by the pressure of pure component.

Ionic Solutions

To express the chemical potential of an electrolyte in solution in terms of molality, let us use the example of a dissolved salt such as magnesium chloride, *[Math Processing Error]*.

[Math Processing Error]

We can now write a more general equation for a dissociated salt:

[Math Processing Error]

where *[Math Processing Error]* represents the stoichiometric coefficient of the cation or anion and *[Math Processing Error]* represents the charge, and M and X are the metal and halide, respectively.

The total chemical potential for these anion-cation pair would be the sum of their individual potentials multiplied by their stoichiometric coefficients:

[Math Processing Error]

The chemical potentials of the individual ions are:

[Math Processing Error]

[Math Processing Error]

And the molalities of the individual ions are related to the original molality of the salt m by their stoichiometric coefficients

[Math Processing Error]

Substituting Equations [Math Processing Error] and [Math Processing Error] into Equation [Math Processing Error],

[Math Processing Error]

since the total number of moles [Math Processing Error], we can define the mean ionic molality as the geometric average of the molarity of the two ions:

[Math Processing Error]

then Equation [Math Processing Error] becomes

[Math Processing Error]

We have derived this equation for a ideal solution, but ions in solution exert electrostatic forces on one another to deviate from ideal behavior, so instead of molarities we must use the activity a to represent how the ion is behaving in solution. Therefore the mean ionic activity is defined as

[Math Processing Error]

where

[Math Processing Error]

and [Math Processing Error] is the **mean ionic activity coefficient**, which is dependent on the substance.

Substituting the mean ionic activity of \Equation [Math Processing Error] into Equation [Math Processing Error],

[Math Processing Error]

when [Math Processing Error]. Equation [Math Processing Error] then represents the chemical potential of a nonideal electrolyte solutions. To calculate the mean ionic activity coefficient requires the use of the Debye-Hückel limiting law, part of the Debye-Hückel theory of electrolytes .

✓ Example [Math Processing Error]

Let us now write out the chemical potential in terms of molality of the salt in our first example, [Math Processing Error]. First from Equation [Math Processing Error], the stoichiometric coefficients of the ions are:

[Math Processing Error]

The mean ionic molality is

[Math Processing Error]

The expression for the chemical potential of [Math Processing Error] is

[Math Processing Error]

References

1. Chang, Raymond. Physical Chemistry for the Biosciences. Sausalito, California: University Science Books, 2005.

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5.10: Biological Membranes

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5.E: Solutions (Exercises)

5.1: Concentration Units

5.5: Real Solutions

Q5.6

Calculate the molality for a 0.005M NH_4SO_4. What is the difference between the molarity and molality of the solution?

Q5.6

What is the difference between the molarity and the molality of a solution? Calculate the molality for a 0.05M ammonium sulfite [NH_4SO_3] solution.

S5.6

The molarity of a solution is the ratio between the number of moles of solute and the solution.

The molality of a solution is the ratio between the number of moles of solute and the mass of solvent:

$$\mathrm{Molality of solution} = \frac{0.05\mathrm{mol}}{1\mathrm{kg}} = 0.05m$$

Q5.7

After taking tylenol for stomach pains, a man has 0.300 mg of acetaminophen in his 5.0 L blood. After 4 hours, there is 0.010 mg left in his blood. Calculate the number of moles of acetaminophen per ml of blood and the total number of moles and grams before and after. (Molar Mass of Acetaminophen: 151.2 g/mol)

S5.7

Before:

[Math Processing Error]

[Math Processing Error]

After:

[Math Processing Error]

[Math Processing Error]

5.2: Partial Molar Quantities

Q5.16

If a diver swims to 50 ft below sea level, did the oxygen in his blood increase or decrease? What about a hiker who is 50 ft above sea level?

Q5.16

Charlie goes on a submarine ride with his family. On their submarine ride, they have dinner which Charlie washes down with a Coke. Charlie notes that upon the removal of the cap from the Coke bottle, it does not make much of a noise that he has grown accustomed to hearing when opening a soft drink bottle. Soon after their dinner, Charlie and his family make their way back up to the surface to disembark from their submarine journey. As they were ascending, Charlie started to burp. What has just occurred?

S5.16

When on a submarine, you submerge into the water and are below sea level. When below sea level, the total and partial pressures of CO_2 increases in comparison to when you are at or above sea level. Since Charlie's family has brought the Coke down from land (at sea level), the solubility of the CO_2 is increased and the concentration of the CO_2 in solution is raised. When Charlie returns to sea level, the conditions go back to normal which causes both the pressure and the solubility to decrease and the CO_2 inside of Charlie comes out and causes him to burp in order to release the CO_2 gas.

Q5.17

Calculate the Henry's Law constant for O_2 in blood at a partial pressure of 0.25. There's about 2.5 kg of blood in the individual and 15 g of *[Math Processing Error]* present.

S5.17

[Math Processing Error]

[Math Processing Error]

[Math Processing Error]

Q5.18

Imagine the ideal gas *[Math Processing Error]* (at 25°C) has a solubility of *[Math Processing Error]* at a partial pressure of 0.5 atm, and *[Math Processing Error]* at 5 atm. Use Henry's law to determine the number of moles of *[Math Processing Error]* at the given pressures.

5.6: Colligative Properties

Q5.19

Write the equation showing the relationship between the molality and the change of temperature. Show possible reasons that leading to the derivation of this equation.

S5.19

[Math Processing Error]

Molality is independent of temperature.

Q5.20

There are two liquids X and Y. The boiling point of liquid X is 125°C while the boiling point of liquid Y is 250°C. If liquids X and Y were mixed to form an ideal solution, would the boiling point of the solution be less than, greater than, or equal to that of (a) liquid X? (b) liquid Y?

S5.20

a. Boiling point of solution > Boiling point of liquid X
b. Boiling point of solution < Boiling point of liquid Y

Q5.25

Why don't you keep your honey in the fridge? Explain using the terms hypertonic, and hypotonic.

S5.25

Honey is a hypertonic solution and bacteria prefer a hypotonic environment.

Q5.27

The freezing point depression measurement of Compound X in Reagent A yields a molar mass of 144 g; the same measurement in Reagent Y gives a value of 72 g. What is the reason for this discrepancy? (Hint: Consider solvent-solute interactions).

Q5.28

What would be the volume of 20 moles of sugar (C12H22O11) dissolved in 0.5 g/cm^-3 of water at 10K? Given the freezing point depression constant for water is 1.86 K/mol kg, what would be the molality of the sugar?

Q5.28

You have a boiling pot with 4 L of water. You add 1000 grams of NaCl. Water boils at 100 ^{o} C and freezes at 0 ^{o} C. To what temperature is the boiling point of water elevated to with the addition of NaCl? To what temperature is the freezing point depressed to?

Q5.29a

Blood plasma, an enriched with platelets, contains several growth factors that help healing of tissues and bones. There are a lot of medical treatments which inject the comparable concentration of a certain solution into human blood. Explain why ?

S5.29a

The injected solution should be comparable to that of blood plasma. There is a certain amount of platelets which keep the state the blood plasma in equilibrium. If we inject too much, it significantly affects to human blood by changing the concentration of platelets.

Q5.29b

Immerse a human cell in hypertonic or hypotonic solution can cause harmful consequences. Explain what would happen in each situation and the case when we got injected with a high concentrated solutions in our vein?

Q5.30

The Davis water tower is 250 ft tall (about 76 meters). What is the osmotic pressure required to push water from the ground to the top of the tower?

S5.30

[Math Processing Error]

[Math Processing Error]

[Math Processing Error]

[Math Processing Error]

Q5.31

A solution of liquid A is mixed with liquid B and exerts ideal behavior. At *[Math Processing Error]* the total vapor pressure of a solution is 413mmHg containing 1.4 moles of A and 2.0 moles of B. After you add another mole of A to the solution, the vapor pressure increases to 486mmHg. At *[Math Processing Error]* calculate the vapor pressure of pure A and B.

S5.31

Step1: (Hint: Calculate the mole fraction of A and B)

[Math Processing Error]

[Math Processing Error]

Step 2: (Hint: Set up total pressure equation)

[Math Processing Error]

[Math Processing Error]

Step 3: (Hint: Calculate the mole fraction of A and B with the addition of 1 mole of A)

[Math Processing Error]

[Math Processing Error]

Step 4: (Hint: Set up the second total pressure equation)

[Math Processing Error]

Step 5: (Hint: Solve for *[Math Processing Error]* and *[Math Processing Error]* by substitution of the two total pressure equations)

[Math Processing Error]

[Math Processing Error]

Rearrange equation 1

[Math Processing Error]

Substitute into any equation and solve for *[Math Processing Error]*

[Math Processing Error]

[Math Processing Error]

Substitute *[Math Processing Error]* into any equation to get *[Math Processing Error]*

[Math Processing Error]

[Math Processing Error]

Q5.33

An ideal solution is composed of equal amount of component A with molar mass of 28.05g/mol and component B with molar mass of 80.91g/mol. At 35°C, component A has a vapor pressure of 0.2 atm and component B has a vapor pressure of 0.65 atm.

a. Calculate the mole fraction of each component in the solution
b. Calculate the partial pressure of each component at 35°C
c. If some of the vapor condenses back into a liquid, what will the mole fraction of each component in this liquid and the vapor pressure above this liquid be?

S5.33

(a) remember mole fraction = (mole of solute) / (total mole of solution) ; *[Math Processing Error]*

(b)*[Math Processing Error]*

(c)*[Math Processing Error]*

5.3: The Thermodynamics of Mixing

Q5.35a

Give a brief explanation for the lower vapor pressure of a solvent in presence of a solute from the entropy point of view. (Hint: Look at colligative property of lower vapor pressure).

S5.35a

The action of mixing a solvent and a solute leads is associated with an increase in entropy. The final solution therefore has a greater entropy than that of solvent, giving it less driving force for evaporation. This leads to the solvent's decrease in evaporation which results in a lower vapor pressure.

5.4: Binary Mixtures of Volatile Liquids

Q5.35b

Describe the process of vapor-pressure lowering from the colligative properties of solutions.

S5.35b

Suppose you have an ideal solution to which you can apply Raoult's law:

$$P_1 = x_1 P_1^*$$

(Note: This solution has both a solvent and a solute which is nonvolatile).

Next, since we know that $x_1 = 1 - x_2$, we can ultimately rearrange the equation to be:

$$P_1^* - P_1 = \Delta P = x_2 P_1^*$$

In the equation above, ΔP is directly proportional to the mole fraction of the solute.

Q5.35c

Sugar is added to water. Would there be more water molecules in the vapor above the sugar solution or in the vapor above the pure water?

S5.35c

We would expect more water molecules in the vapor above the pure water.

Q5.36

4.0 moles of a compound was added to 500 g of HCl. What was the freezing point of the pure solvent if the freezing point of the solution is 188.6 K. (K_f=*[Math Processing Error]*

S5.36

[Math Processing Error]

[Math Processing Error]

Q5.36a

After dissolving a substance weighing 0.246 grams in 100.0 g of water, the freezing point of the solution went down 1K below that of the pure solvent. What would be the molar mass of this substance?

S5.36a

The following information is needed.

[Math Processing Error]

Now solve for the molar mass of the solute.

[Math Processing Error]

Click here for more information on freezing point depression.

Q5.36b

5.525 grams of toluene is mixed with 20.0 grams of acetone. Calculate the freezing point of acetone. The freezing point of the solution is found to be -102.6° C. The K_f of acetone is 2.40 °C kg/mol, and the molar mass of toluene is 92.14 g/mol

S5.36b

We can relate the molality of the solution to the freezing point depression:

[Math Processing Error]

Rearranged:

[Math Processing Error]

[Math Processing Error]

[Math Processing Error]

[Math Processing Error]

[Math Processing Error]

Q5.37a

Two aqueous urea solutions have osmotic pressures of 1.4 atm and 3.0 atm, respectively, at a certain temperature. What is the osmotic pressure of a solution prepared by mixing equal volumes of these two solutions at the same temperature?

Q5.37b

A lab technician has 2 solutions of ammonia. Solution A exerts an osmotic pressure of 8 atm. When it is mixed with solution B in equal volume to produce solution C, it is determined that solution C exerts an osmotic pressure of 6.5 atm. What is the osmotic pressure of solution B?

Q5.38

A research scientist used 50 mL of sterilized water to conduct experiments and obtained odd results. She suspected that it had been contaminated with another compound and determined that the boiling point of the solution had increased to 105°C. How many moles of the compound (assume it dissolves as a molecule) had been added to the water?

Q5.39

Time-released pills are designed to have longer effect at a constant rate. The active ingredient is concealed by insoluble substances so that the active ingredient has to be dissolved by getting through the holes of insoluble layers covering outside. Explain how the insoluble layers regulate the absorption of the active ingredient.

Q5.41

Acetic Acid can make hydrogen bonds with water molecules and also with benzene. A solution of 4.0 g of acetic acid in 95g *[Math Processing Error]* has a freezing point of *[Math Processing Error]*. What is the molar mass of the solute?

S5.41

[Math Processing Error]

\(m=molality\)

[Math Processing Error]

[Math Processing Error]

[Math Processing Error]

[Math Processing Error]

[Math Processing Error]

[Math Processing Error]

Q5.43

Determine on whether each of the following statements is true or false and briefly explain your answers. (a) Colligative properties depends on both the number of solute molecules and the size of the solute molecules. (b) The addition of a nonvolatile solute to a solvent only changes the chemical potential of liquid *[Math Processing Error]*. (c) The mole fraction of a component is never the same as the activity of the same component.

S5.43

a. False; the definition of colligative properties are properties that ONLY depend on the number of solute molecules.
b. True; *[Math Processing Error]* and *[Math Processing Error]* are not affected because solute is nonvolatile and insoluble to the solid solvent. (c) False; in the case of ideal solutions, the activity coefficient *[Math Processing Error]* is 1 and *[Math Processing Error]*.

Q5.45

Provide an example of a nonideal solution explain why it is nonideal.(Hint: *Look over the concept of* *nonideal solutions)*

S5.45

An example of a non-ideal solution is a mixture of diethyl ether and water. Diethyl ether is a non-polar solvent used for dissolving organic molecules whereas water is polar. Intermolecular forces between these two components are weak; hence they will form two layers upon mixing; making the mixture a non-ideal solution.

Q5.46a

An unknown substance has a molal boiling-point elevation constant, K_b of 1.23 K/m. Find the molar mass of this substance. The enthalpy of vaporization for this substance is 38.56 kJ/mol at 78.37 ^oC.

S5.46a

For any substance:

[Math Processing Error]

Rearranging this equation, we get:

[Math Processing Error]

[Math Processing Error]

[Math Processing Error]

Q5.46b

Find K_b (the molal boiling-point elevation constant) for acetone solution at 56ºC, given that:

[Math Processing Error]

S5.46b

You need to use the following equation:

[Math Processing Error]

Plug in values and solve for the K_b.

[Math Processing Error]

Click here for more information on boiling point elevation.

Q5.47a

A home gardener and amateur scientist decides to prepare her olives by brining them. She begins the process by soaking the olives in fresh water. During this time she notices that the olives absorb moisture and swell. She then soaks the olives in a strong salt brine. During this time, she notices that the olives lose moisture and shrink. To what physical process can she attribute the shrinking and swelling? Why do the olives absorb the fresh water and lose moisture to the brine?

S5.47a

The movement of water in and out of the olives is due to diffusion. The high concentration of solutes in the brine relative to the concentration in the olives causes water to diffuse from olives into the brine, and the low concentration of solutes in the fresh water surrounding the olives causes the fresh water to diffuse into the olives, which have a comparatively high concentration of solutes.

Q5.47b

Describe the difference between a hypertonic, and hypotonic. Why does a cell shrink in a hypertonic solution, and expand in a hypotonic solution.

Q5.48

The following data give the pressures for water-methanol solution at 39.9ºC. Find the activity coefficients of both components based on:

a. Raoult's law
b. Henry's law

x_{water}	0	0.0490	0.3120	0.4750	0.6535	0.7904
P_{water}/torr	0	4.51	23.03	31.53	39.78	44.81
$P_{methanol}$/torr	255.6	253.39	188.27	152.87	116.22	80.89

Q5.49

A solution is made up of some amount of sucrose ($C_{12}H_{22}O_{11}$) and 1.03 kg water. Calculate the amount of sucrose (in grams) in solution if the solution freezes at -2°C and the activity coefficient of sucrose is 0.789.

S5.49

[Math Processing Error]

[Math Processing Error]

[Math Processing Error]

a is effective molar concentration so a = m in:

[Math Processing Error]

x is the actual amount of sucrose in solution, so

[Math Processing Error]

[Math Processing Error]

[Math Processing Error]

[Math Processing Error]

5.7: Electrolyte Solutions

5.8: Ionic Activity

Q5.54

You know that the mean activity coefficient is 0.42. From this information find what the ionic strength of the compound $LiNO_2$ is.

$$log\gamma = -.0509|z^+z^-|\sqrt{I}$$

$$log(0.42) = -0.509|1\cdot -1|\sqrt{I}$$

$$I = (\frac{log(0.42)}{0.509})^2$$

I=0.548

Q5.56

A 0.15 m $Ca(NO_3)_2$ solution has a mean ionic activity coefficient of 0.17 at 25°C. Calculate the mean molality, the mean ionic activity, and the activity of the compound.

Q5.58

In 0.03m aqueous $NaNO_3$ solution at temperature 300K., the size of the ionic atmosphere is 1/k, also known as Debye radius, is $27.8x10^{-10}$ m. Using the Debye radius formula to calculate the ionic strength I.

Q5.60

For a 0.0030m aqueous solution of *[Math Processing Error]* at 298K, calculate the ionic strength. (a) Calculate the activity coefficients of *[Math Processing Error]* and *[Math Processing Error]* ions in the solution and (b) calculate the mean ionic activity coefficients of these ions. (Hint: Use the Debye-Huckel limiting law)

S5.60

[Math Processing Error]

[Math Processing Error]

[Math Processing Error]

(a)

[Math Processing Error]

For *[Math Processing Error]*,

[Math Processing Error]

[Math Processing Error]

[Math Processing Error]

For *[Math Processing Error]*,

[Math Processing Error]

[Math Processing Error]

[Math Processing Error]

(b)

[Math Processing Error]

Q5.65

For an ideal mixture, what mole fraction of each gas maximizes the entropy of mixing:

[Math Processing Error]

Hint: Rewrite the above function in terms of only either x_1 or x_2, then derive.

S5.65

If we take the partial derivative of the entropy of mixing:

[Math Processing Error]

[Math Processing Error]

If we rewrite the function in terms of x_1

[Math Processing Error]

and derive using the chain rule:

[Math Processing Error]

[Math Processing Error]

[Math Processing Error]

[Math Processing Error]

To find the local maximum, we set this to 0 and solve for x_1

[Math Processing Error]

[Math Processing Error]

[Math Processing Error]

[Math Processing Error]

[Math Processing Error]

To check that this is a maximum and not a minimum, we plug in values to the left and right of the given x_1 value (ex. 0.4 and 0.6). We then find that at x_1<0.5 the derivative, or slope, is positive and at $x_{1>}$0.5m the slope is negative. This is further confirmed by the following diagram, where $T\Delta_{mix}S$ is maximized at mole fraction 0.5.

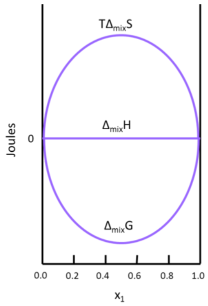

Figure 2. A graph of $T\Delta_{mix}S$, $\Delta_{mix}H$, and $\Delta_{mix}G$ as functions of x_1 for the mixing of two ideal gases.

Q5.64

The osmotic pressure arbitrary non-ideal diluted solution is measured at 2 different concentrations at 300K. At concentration of 5.20 g/L, osmotic pressure is 10.20 x 10^{-3} atm and at concentration of 8.90 g/L the osmotic pressure is 2.30 x 10^{-2} atm. Use this information to estimate the molar mass of the solute. (Hint: For dilute solutions, only the second virial coefficient is concerned. Look at equation for osmotic pressure and make a graph of π/c vs. c and look for the y-intercept of graph.)

S5.64

π (atm)	1.06×10^{-5}	2.30×10^{-5}
c (g/L)	5.20	8.90
π/c (atm•L/g)	2.038×10^{-6}	2.584×10^{-6}

slope of the graph of π/c vs. c is generated as:

[Math Processing Error]

[Math Processing Error]

[Math Processing Error]

Plug back into equation to solve for "y-intercept"

[Math Processing Error]

[Math Processing Error]

[Math Processing Error]

Q5.65

Assume that you have made an ideal solution of an unknown compound made of two components. Why does the mole fraction 0.5 achieve the maximum *[Math Processing Error]*?

S5.65

Use the equation.

[Math Processing Error]

Find the partial derivative since we want to find out the max value for this equation for x_1 . We find x_1 since it will show us x_2.

[Math Processing Error]

Now that we have the partial derivative, we set it to 0 and solve to attempt to find the maximum value.

[Math Processing Error]

Now we know that $x_1 = 0.5$ is either a min or max. If we plug in a number smaller then 0.5 and bigger than 0.5 into the partial derivative we found earlier, we can conclude that the slope of the equation is positive to the left of 0.5 and negative to the right of the equation. This is characteristic of maximum values. Thus $x_1 = 0.5$ and $x_2 = 0.5$ attain the maximum values of $\Delta_{mix}S$ since

$x_1 = 0.5$ is a max.

See here for more details about $\Delta_{mix}S$. See figure (▯ 11) on that page for more details about the max.

Q5.66

Producing a certain gas mixture involves mixing high-pressure nitrogen and low-pressure hydrogen together. In one such production, 3.22 moles of N_2 at 4.2 atm are mixed with 1.25 moles of H_2 at 0.8 atm. Determine the change in Gibbs' free energy.

5.9: Colligative Properties of Electrolyte Solutions

Q5.72

You are trying to produce a passive reverse osmosis system to obtain pure water from the ocean by using a semi-permeable membrane on one end of the intake pipe. At what depth would the bottom of the pipe need to be in order for pure water to begin to fill the pipe? Assume the ocean temperature is 17ºC, and the seawater is a 0.70 M NaCl solution. The density of seawater is 1.03 g/cm³.

5.10: Biological Membranes

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CHAPTER OVERVIEW

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6.5: Binding of Ligands and Metal Ions to Macromolecules

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6.6: Bioenergetics

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6.E: Chemical Equilibrium (Exercises)

Q6.1

Imagine a catalytic reaction that changes a reagent between two states, i.e.:

$$yY + cC \rightleftharpoons cC + zZ \tag{6.E.1}$$

The equilibrium constants K_c, K_χ, and K_p with respect to concentration, mole fraction, and pressure are given by

$$K_c = \frac{[Z]^z}{[Y]^y} \tag{6.E.2}$$

$$K_\chi = \frac{\chi_Z^z}{\chi_Y^y} \tag{6.E.3}$$

$$K_p = \frac{P_Z^z}{P_Y^y} \tag{6.E.4}$$

Given this information, express K_p in terms of K_c and K_χ.

Q6.2a

$$CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(s)} \tag{6.E.5}$$

a. The partial pressure of CO_2 is 0.1 atm, calculate K_p
b. If the reaction occurred in a 1L flask, what is the amount of CaO formed when 0.12 moles $CaCO_3$ was set to react?
c. What is the minimum about of CaO needed to cause the formation of $CaCO_3$?

Q6.2b

The decomposition of sodium chlorate is:

$$2NaClO_{3(s)} \rightleftharpoons 2NaCl_{(s)} + 3O_{2(g)} \tag{6.E.6}$$

Suppose 0.760 mole of sodium chlorate was to be decomposed in a 3.75 L container. At the temperature 336°C, the percent decomposition of $NaClO_3$ is 3.5%. Find the

a. pressure of O_2 gas in the container in atm and
b. equilibrium constant K_p of the reaction. Assume O_2 gas is an ideal gas.

Hint: Use partial pressure and look at chemical equilibrium of gaseous systems

S6.2b

a) number of moles of $NaClO_3$ decomposed is:

$$\frac{\#moles\,decomposed}{.760moles} = 0.035 \Rightarrow \#mole\,decomposed = 0.0266mole\,NaClO_3 \tag{6.E.7}$$

number of moles of O_2 formed is:

$$0.0266mol\,NaClO_3 \times \frac{3molO_3}{2mol\,NaClO_3} = 0.0399mol\,O_2 \tag{6.E.8}$$

$$P_{O_2}V = nRT \Rightarrow P_{O_2} = \frac{nRT}{V} \tag{6.E.9}$$

$$P_{O_2} = \frac{(0.0399mol)(0.08206\frac{L\cdot K}{K\cdot mol})(336+273)K}{3.75L} = 0.532atm \tag{6.E.10}$$

b)

$$K_p = \frac{P_{O_2}}{P^\circ} = \frac{0.532atm \times \frac{1.013bar}{1atm}}{1bar} = 0.539 \tag{6.E.11}$$

Q6.2c

Using the decomposition reaction of hydrogen peroxide (H_2O_2), assume that at 1048 °C and the pressure of the oxygen gas (O_2) is 1.5 bar.

$$2\,H_2O_2(aq) \rightleftharpoons 2\,H_2O(l) + O_2(g) \tag{6.E.12}$$

a. Determine the K_P for the reaction above.
b. If 0.92 mole of H_2O_2 is placed in a 3.0-L beaker at 1048°C, determine the fraction of H_2O_2 that will decompose.
c. Determine the same as (b) if 1.3 moles of H_2O_2 were placed inside the beaker instead.
d. What is the minimum amount of H_2O_2 (in moles) necessary in order to reach equilibrium?

S6.2c

a. $K_P = \frac{P_{O_2}}{P^\circ} = \frac{1.5\text{bar}}{1\text{bar}} = 1.5$

b. In order to calculate the number of moles of H_2O_2 that are decomposed, you first need to determine the moles of O_2 formed by the reaction. Treat O_2 as an ideal gas.

$$\text{NumberofmolesofO}_2\text{formed} = \frac{PV}{RT} = \frac{(1.5\text{bar})(\frac{1\text{atm}}{1.013\text{bar}})(3.0\text{L})}{(0.08206\text{LatmK}^{-1}\text{mol}^{-1})(1321\text{K})}$$

$$= 41.0 \times 10^{-3}\text{mol} \quad \text{NumberofmolesofH}_2\text{O}_2\text{decomposed} = (40.1 \times 10^{-3}\text{molO}_2)(\frac{2\text{molH}_2\text{O}_2}{1\text{molO}_2})$$

$$= 0.0802\text{mol}$$

$$\text{FractionofH}_2\text{O}_2\text{decomposed} = \frac{0.0802\text{mol}}{0.92\text{mol}} = 0.09$$

c. If 1.3 moles of H_2O_2 were used instead of 0.92 mole, the pressure of the O_2 would not be affected and would remain at 1.5 bar. The number of moles of H_2O_2 decomposed would still be 0.0802 mole, therefore, the fraction of H_2O_2 decomposed would be as follows:

$$\text{FractionofH}_2\text{O}_2\text{decomposed} = \frac{0.0802\text{mol}}{1.3\text{mol}} = 0.062$$

d. The pressure of O_2 must be greater than or equal to 1.5 bar in order for equilibrium to take place, therefore, the number of moles of H_2O_2 cannot be less than 0.0802 mol.

Q6.3

Find the value of K_p for cellular respiration if $P_{O_2} = 350torr$, with a 3:2 ratio to the pressure of CO_2

S6.3

$$C_6H_{12}O_6(s) + O_2(g) \rightleftharpoons CO_2(g) + H_2O(l) \tag{6.E.13}$$

$$P_{CO_2} = (350torr)\frac{2}{3} = 233.3torr \tag{6.E.14}$$

$$K_p = \frac{\frac{233.3torr}{750torr}}{\frac{350torr}{750torr}} = 0.666 \tag{6.E.15}$$

Q6.5

For the reaction of

$$N_2O_4 \rightarrow 2\,NO_2 \tag{6.E.16}$$

with K_p = 0.167 at 300 K. If 1.0 g of N_2O_4 is placed into a 250.0 mL container:

a. What would be its pressure if none dissociates?
b. What is its partial pressure at equilibrium (with dissociation)?
c. What is the total pressure in the container?

Q6.9a

Calculate $\Delta_{vap}H$ for the evaporation of methanol when the temperature is raised from 20 °C to 100 °C and if the K_2/K_1 ratio is 22.14?

$$CH_3OH_{(l)} \rightarrow CH_3OH_{(g)} \tag{6.E.17}$$

Q6.9b

Using the decomposition reaction of coppr (II) oxide below:

$$4CuO_{(s)} \rightleftharpoons 2Cu_2O_{(s)} + O_{2(g)} \tag{6.E.18}$$

determine the standard enthalpy of the reaction. (Note: The equilibrium vapor pressures of O_2 are 15.4 mmHg at 600°C and 927 mmHg at 850°C).

S6.9b

In this case, we must use the van't Hoff equation:

$$\ln \frac{K_2}{K_1} = \frac{\Delta_H^o}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{6.E.19}$$

in order to solve this particular problem. We can conclude that K_P is proportional to $P_{\mathrm{CO_2}}$ due to the defined relationship of:

$$K_P = \frac{P_{\mathrm{CO_2}}}{P^{\mathrm{o}}}.$$

Therefore,

$$\ln \frac{P_{\mathrm{CO_2},2}}{P_{\mathrm{CO_2},1}} = \frac{\Delta_{\mathrm{r}}H^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\ln \frac{927\mathrm{mmHg}}{15.4\mathrm{mmHg}} = \frac{\Delta_{\mathrm{r}}H^\circ}{8.314\mathrm{JK^{-1}mol^{-1}}}\left(\frac{1}{873.2\mathrm{K}} - \frac{1}{1123.2\mathrm{K}}\right)$$

$$\Delta_{\mathrm{r}}H^\circ = 1.34 \times 10^5 \mathrm{Jmol^{-1}}$$

Q6.10

A container of water at 20°C was placed in a freezer that was at a temperature of -5.0°C. The vapor pressure of water in the container went from 0.60 bar to 0.38 bar. Calculate the enthalpy of fusion for the reaction that took place.

S6.10

- $k_2 = 0.38\ bar$
- $k_1 = 0.60\ bar$
- $T_2 = 268\ K$
- $T_1 = 293\ K$

$$\ln \frac{k_2}{k_1} = \frac{\Delta_r H^\circ}{R} \frac{T_2 - T_1}{T_2 T_1} \tag{6.E.20}$$

$$\rightarrow \Delta_r H^\circ = \ln \frac{k_2}{k_1}(R)\frac{T_2 T_1}{T_2 - T_1} \tag{6.E.21}$$

$$\ln \frac{0.38bar}{0.60bar} 8.314 \frac{J}{mol \cdot K} \frac{(293\ K)(268\ K)}{268\ K - 293\ K}\left(\frac{1\ kJ}{1000\ J}\right) = 11.9 \frac{kJ}{mol} \tag{6.E.22}$$

Q6.11

The chemical responsible for the brown air throughout the Los Angeles area is $NO_2(g)$. To learn more about $NO_2(g)$, you decide to study this pollutant spectroscopically (by light absorption). You fill a gas cell with N_2O_4, equilibrate the temperature to 298.0 K and then open the stopcock on the cell to equilibrate the pressure to the barometric pressure (723.4 mm Hg) that day. You then reequilibrate the cell at 323.1 K, 348.0 K, and 372.9 K. The following data is obtained:

T/K	298.0	323.1	348.0	372.9
$[NO_2]$/M	0.01262	0.02140	0.02756	0.02920

Find K_P, $\Delta_{rxn} G$, $\Delta_{rxn} H$, and $\Delta_{rxn} S$ at each temperature for the reaction

$$N_2O_4(g) \rightleftharpoons 2\,NO_2(g). \tag{6.E.23}$$

Q6.14

What is the equilibrium constant and standard Gibbs energy change for:

$$CO_{(g)} \rightleftharpoons CO_{(g)} + ½O_{2(g)} \tag{6.E.24}$$

Assume that when $CO_{(g)}$ dissociates into $CO_{(g)}$ and $O_{2(g)}$ at 300 K and 1.5 atm, the overall dissociation is one two fifths complete.

Q6.15

The standard Gibbs energies of formation of proban-1-ol and proban-2-ol are -171.3 kJ mol^{-1} and -180.3 kJ mol^{-1}, respectively. Find the ratio of equilibrium vapor pressures of each isomer at 300 K.

S6.15

The ratio of equilibrium pressure is : 171.3/180.3 = 0.95

Q6.16

At what temperature does a particular reaction favor the formation of products at equilibrium if Δ_rH° = 215.7 kJ mol^{-1} and Δ_rS° = 348.8 J mol^{-1} K^{-1}?

S6.16

The reaction favors the formation of products at equilibrium when

$$\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ < 0 \tag{6.E.25}$$

$$\Delta_r H^\circ - T\Delta_r S^\circ = 215.7 * 10^3 J\, mol^{-1} - T(348.8 J\, mol^{-1}\ K^{-1}) < 0 \tag{6.E.26}$$

$$T > \frac{215.7 * 10^3 J\, mol^{-1}}{348.8 J\, mol^{-1}\ K^{-1}} \tag{6.E.27}$$

$$T > 616 K \tag{6.E.28}$$

Q6.17

Using a table of thermodynamic data, find Ksp at 298.15K for:

$$CO_{(g)} \rightarrow CO_{(g)} + ½O_{2(g)} \tag{6.E.29}$$

(Hint, this problem can be solved using the van’t Hoff equation in its integrated form)

Q6.18

Consider the the Haber process:

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \tag{6.E.30}$$

How does the equilibrium shift under the following changes

a. the volume of nitrogen gas is increased
b. the temperature is decreased
c. the pressure of the system is decreased

S6.18

a. The reaction shifts to the right : more products formed.
b. The reaction shifts to the right : favor exothermic reaction
c. The reaction shifts to the left : more pressure applied.

Q6.19

Given the general reaction A(*g*) ⇔2B(*g*), calculate the degree of dissociation of A at 25°C and 7.00 bar if $\Delta_r G^\circ$ = 6.76 kJ mol^{-1}. According to Le Chatelier's Principal, in what direction should this reaction proceed?

S6.19

$$\Delta_r G^\circ = -RTlnK_P \tag{6.E.31}$$

$$K_P = e^{\frac{\Delta_r G^\circ}{-RT}} = e^{\frac{6.76*10^3 J\, mol^{-1}}{-(8.314 J\, mol^{-1}\ K^{-1})298K}} \tag{6.E.32}$$

$$K_P = 0.0653 \tag{6.E.33}$$

$$K_P = \frac{4\alpha^2}{1-\alpha^2}P \tag{6.E.34}$$

$$\frac{4\alpha^2}{1-\alpha^2} = \frac{0.0653}{7} \tag{6.E.35}$$

$$\alpha = .048 \tag{6.E.36}$$

Degree of dissociation α = 0.048, the reaction proceeds 4.8%. Le Chatelier's Principal says that reactions will move towards the side with fewer moles of gas at high pressures.

Q6.19

How does Le Chatelier's Principle relate to the following equation?

$$\ln\frac{K_2}{K1} = \frac{\Delta_r H^\circ}{R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

S6.19

Le Chatelier's Principle basically states that a system will adjust itself in efforts to re-establish equilibrium when an outside stress is placed on it. Using the equation provided, we can conclude that raising the temperature causes the equilibrium to shift from left to right in an endothermic reaction. This suggests that it is favoring the formation of products. We can also conclude that the opposite is true. This conclusion reinforces Le Chatelier's Principle because the temperature acts as the external stress placed on the system in this case.

Q6.20

H_2 and H molecules are at equilibrium pressures of .35 bar and .30 bar, respectively. If the size of the container they are in is reduced by a factor of two, what will be the new partial pressures?

S6.20

$$H_2(g) \rightleftharpoons 2H(g) \tag{6.E.37}$$

$$K_p = \frac{P_H^2}{P_{H_2}} = \frac{.30^2}{.35} = .675 \tag{6.E.38}$$

At new volume:

$$P_H = .60 \tag{6.E.39}$$

$$P_{H_2} = .70 \tag{6.E.40}$$

Pressures will increase with decreased volume. Less molecules of gas will be favored.

P_H	P_{H_2}
0.60 bar - 2x	0.70 bar + x

$$.675 = \frac{.60 - (2x^2)}{.70 + x} \rightarrow 4x^2 + .675x + .113 \rightarrow x = .272 \tag{6.E.41}$$

$$P_{H_2} = .70bar + .272bar = .972bar \tag{6.E.42}$$

$$P_H = .60bar - (2).272bar = .056bar \tag{6.E.43}$$

Q6.21

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 + Heat$$

With Le Chatlier's principle in mind, does raising the temperature favor the forward reaction or the reverse?

S6.21

This reaction favors the reverse reaction.

Q6.23a

When a gas was heated at atmospheric pressure and 25°C, its color deepened. Heating above 150°C caused the color to fade, and at 550°C the color was barely detectable. At 550°C, however, the color was partially restored by increasing the pressure of the system. Which of the following scenarios best fits the above description? Justify your answer.

a. A mixture of Gas A and Gas B
b. Pure Gas B
c. A mixture of Gas X and Gas Y

(Hint: Gas B is bluish, and Gas Y is yellow. The other gases are colorless. Gas A and B are in their natural state, Gas AB has a Δ_fH° = -43.2 kJ / mol. The reaction of Gas X into Gas Y is endothermic.)

Q6.23b

Hydrogen gas and iodine react at equilibrium in a glass canister to form Hydrogen Iodide, a strong acid:

$$H_{2(g)} + I_{2(g)} \rightleftharpoons HI_{(g)} \tag{6.E.44}$$

Iodine gas is a deep purple color. Both Hydrogen Iodide and hydrogen gas are colorless. Assume that iodine sublimates readily at 37^o C, and that the reaction is endothermic in the direction written. What color is the gas mixture in the canister in the following scenarios? Provide an explanation for each.

a. The canister is heated to 40^o C
b. The canister is heated to 500^o C
c. Negative pressure is applied to the cannister at 500^o C

Hint: At room temperature, the gas is colorless. Solid iodine must be in gas phase to react.

S6.23b

a.) The color of the gas will be a deep purple. The iodine will have sublimated, but the temperature is not high enough to drive the reaction forward.

b.) The gas will be colorless, or almost completely so. This is because an increase in the temperature in an endothermic reaction drives the equilibrium constant higher. This can be justified using Le Chatelier's principle, which states that added stress to an equilibrium will be offset by the system.

$$H_{2(g)} + I_{2(g)} + heat \rightleftharpoons HI_{(g)} \tag{6.E.45}$$

Thus, when heat is added, the system will compensate by driving the reactants of the reaction forward into products. Another way to assess this is by the altered form of the van't Hoff equation:

$$lnK = -\frac{\Delta_r H^\circ}{RT} + \frac{\Delta_r S^\circ}{R} \tag{6.E.46}$$

Assuming that neither change in entropy nor enthalpy changes due to change in temperature, and that in an endothermic reaction the enthalpy is positive, as the temperature increases, so does K.

c.) The gas will become slightly purple. This is because a decrease in pressure will alter K and drive the reaction in the direction which produces more moles of gas. By this, Le Chatelier's principle once again holds.

Q6.24

$$Mg + Pb^{2+} \rightarrow Mg^{2+} + Pb \tag{6.E.47}$$

Write the two separate reactions happening here. Label which one is happening at the cathode end and which is happening at the anode end.

S6.24

Cathode:

$$Pb^{2+} + 2e^- \rightarrow Pb \tag{6.E.48}$$

Anode:

$$Mg \rightarrow Mg^{2+} + 2e^- \tag{6.E.49}$$

Q6.24

The reaction of N_2 (g) and H_2 (g) gas produces NH_3 (g). This reaction is exothermic explain what happens when you increase the temperature of the reaction. What happens when you increase the pressure?

S6.24

Since this reaction is exothermic heat is produced. Using Le Chatelier's principle we see that an increase in the temperature of the reaction will drive the reaction backward since heat is already in the product side. If we increase pressure we decrease the volume of the reaction therefore by Le Chatelier's principle an increase in the pressure should drive the reaction forward.

Q6.25

At places such as high mountain, the air pressure is lower than 1 atm, resulting lower partial pressure of Oxygen. What would you expect for the concentration of hemoglobin for the people living at such places?

Q6.26

Show the steps to get from

$$Y = \frac{[PL]}{[L] + [P]} \tag{6.E.50}$$

to

$$\frac{1}{Y} = 1 + \frac{K_d}{L} \tag{6.E.51}$$

Q6.27

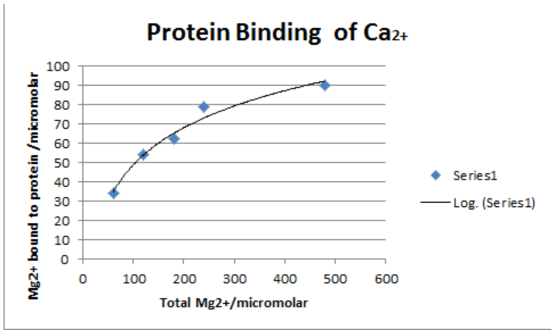
After an experiment of protein-binding you find the data respectively

Total $\frac{Mg^{2+}}{\mu M}$: 60 120 180 240 480

$\frac{Mg^{2+} bound to protein}{\mu M}$: 33.8 120 180 240 480

Determine the dissociation constant of Ca^{2+} graphically. The protein concentration was kept at 96 μM for each run.

Solution:



$$54.2 \mu M \, pH = pKa \tag{6.E.52}$$

$$54.2 \mu M (\frac{1 \times 10^6 M}{1 \mu M}) = 5.42 \times 10^{-5} \tag{6.E.53}$$

$$Ka = 10^{-5.42E-5} \tag{6.E.54}$$

$$Ka = .9998 \tag{6.E.55}$$

Q6.28

The dissociation constant for the following reaction is 3.2x10^{-4}. Dissolve 0.02M of $C_9H_8O_4$ in water, calculate the molarity of reactants at equilibrium.

$C_9H_8O_4 + H_2O$ <---> $H_3O^+ + C_9H_7O_4^-$

Q6.29

The reaction

$$Glyceraldehyde\ 3 - phosphate + NAD^+ + HPO_4^{2-} \rightarrow 1,3 - Biphosphoglycerate + NADH + H^+ \tag{6.E.56}$$

$$\triangle_r G^{\circ\prime} = 6.3\ kJ\ mol^{-1} \tag{6.E.57}$$

is catalyzed by GAPDH (Glyceraldehyde 3-phosphate Dehydrogenase). At 298 K, predict whether or not the reaction will be spontaneous with the following information:

[G3P] = 1.5x10^{-5} M; [BPG] = 3.0x10^{-3} M

[NAD$^+$] = 1.2x10^{-5} M; [NADH]=1.0x10^{-4} M

[HPO$_4^{2-}$]= 1.2x10^{-5} M; pH = 7.5

S6.29

Use the following equation.

$$\triangle_r G = \triangle_r G^{\circ\prime} + RTln \frac{([BPG]/1\ M)\left([H^+]/(1 \cdot 10^{-7})\right]^x ([NADH]/1\ M)}{([G3P]/1\ M])\,([NAD^+]/1\ M)\left([HPO_4^{2-}]/1\ M\right)}$$

Calculate [H$^+$]

cc by nc sa

$$[H^+] = 10^{-7.5} = 3.162X10^{-8} M \tag{6.E.58}$$
$$since\ pH = -log([H^+])$$

Plug values into equation and solve. Note: Since there is no coefficient in front of H^+ in the reaction, x=1.

$$\triangle_r G = 6.3\ kJmol^{-1} + (\frac{8.3145}{1000} kJ/mol^{-1}K^{-1})(298K)\ln \frac{(3\cdot 10^{-3}\ M)(3.162\cdot 10^{-8}\ M/(1\cdot 10^{-7}))]^1 \left(1.0\cdot 10^{-4}\ M\right)}{\left(1.5\cdot 10^{-5}\ M\right)\left(1.2\cdot 10^{-5}\ M\right)\left(1.2\cdot 10^{-5}\ M\right)} \tag{6.E.59}$$

$$\underline{\triangle_r G = 49.90\ kJ\ mol^{-1}} \tag{6.E.60}$$

Click here for some more information on bioenergetics and free energy.

Q6.29

The reaction:

$$Glucose + ATP \rightleftharpoons Glucose6 - phosphate + ADP \tag{6.E.61}$$

At 298K, the equilibrium constant for the reaction is 3.7×10^{-3}.Will the reaction occur spontaneously if the reaction is at the following concentrations:

[Glucose]=$3.2 \times 10^{-4} M$, [ATP]=$2.5 \times 10^{-3} M$, [G-6-P]=$1.2 \times 10^{-5} M$, [ADP]=$1.0 \times 10^{-5} M$.

S6.29

$$\begin{aligned}\Delta G^\circ &= -RTln(K_{eq}) = -(8.314 J/K*mol)(298K)ln(3.7\times 10^{-3})\\ &= 13872.97 J/mol = 13.87297 kJ/mol\end{aligned}$$

$$\begin{aligned}\Delta G &= \Delta G^\circ + RTln(\frac{[Product]}{[Reactant]})\\ &= 13.87297kJ/mol + (8.314\times 10^{-3} kJ/K*mol)(298K)ln(\frac{[1.2\times 10^{-5}][1.0\times 10^{-5}]}{[3.2\times 10^{-4}][2.5\times 10^{-3}]})\\ &= -7.942kJ/mol\end{aligned}$$

ΔG is negative, so the reaction is spontaneous at the given concentrations.

Q6.30

The established standard Gibbs energy for hydrolysis of ATP to ADP at 310K is $-30.5kjmol^{-1}$. At -4.6^oC, determine the $\Delta rG^{o'}$ in the process of the muscle of a hippo. (Hint: $\Delta rH^{o'} = -20.1kjmol^{-1}$

S6.30

Step 1:

$$\Delta rG^{o'} = \Delta rH^{o'} - T\Delta rS^{o'} \tag{6.E.62}$$

Step 2:

$$\Delta rS^{o'} = \frac{\Delta rH^{o'} - \Delta rG^{o'}}{T} \$\$\$\$ = \frac{(-20.1kjmol^{-1}) - (-3.0kjmol^{-1})}{310K} = 3.355 \times 10^{-2} kj\,K^{-1}\,mol^{-1} \tag{6.E.63}$$

Step 3:

$$\Delta rG^{o'} = \Delta rH^{o'} - T\Delta rS^{o'} \tag{6.E.64}$$

$$= (-20.1kjmol^{-1}) - (298.15K)(3.355\times 10^{-2} kj\,K^{-1}\,mol^{-1}) \tag{6.E.65}$$

$$=-29.1kj\,mol^{-1}$$

Q6.31a

Which step of glycolysis would not occur spontaneously at standard-state conditions and why?

Q6.31b

Consider a hydrolysis of PEP, a phosphate compound.

PEP + H_2O → pyruvate + P_i $\Delta_r G^{\circ\prime}$ = -61.9 kJ/mol

At the temperature of 288K, the following reaction took place and has a reaction Gibbs free energy of -49.5 kJ/mole. Find the concentration of PEP for the reaction if the other concentrations are: [Pi] = 3.54 x 10^{-1} M, [Pyruvate] = 1.85 x 10^{-2} M.

Hint: Use equation $\Delta_r G^\circ = -RT\ln K_p$

S6.31b

$$\Delta_r G = \Delta_r G^{\circ\prime} + RTln\frac{[pyruvate][P_i]}{[PEP]} \tag{6.E.66}$$

$$-49500\frac{J}{mol} = -61900\frac{J}{mol} + (8.314\frac{J}{K \cdot mol})(288K)ln\frac{(1.85\times10^{-2}M)(3.54\times10^{-1}M)}{[PEP]} \tag{6.E.67}$$

$$[PEP] = 3.69\times10^{-5}M \tag{6.E.68}$$

Q6.32

For the following reaction:

$$Fructose1,6-bisphosphate \rightleftharpoons dihydroxyacetonephosphate + glyceraldehyde3-phosphate \tag{6.E.69}$$

The $\Delta G^{\circ\prime} = 5.7kcal/mol$. Calculate the equilibrium constant and determine if the reaction is spontaneous or not at 310K.

S6.32

$\Delta G^{\circ\prime} = 5.7kcal/mol = 23.8488kJ/mol$

$\Delta G^{\circ\prime} = -RTln(k'_{eq})$

$k'_{eq} = e^{\frac{\Delta G^{\circ\prime}}{-RT}} = e^{\frac{23848.8J/mol}{(-8.314J/K*mol)(310K)}} = 9.58\times10^{-5}$

Small k'_{eq} suggest that this reaction is not a spontaneous process under the given conditions.

Q6.32a

Consider the following reaction:

Glucose + Fructose → Sucrose + H_2O

Find:

a. the value of the standard free energy at 300 K.
b. the ratio between $\Delta_r G^{o\prime}$ at 300 K and $\Delta_r G^{o\prime}$ at 333 K.

S6.32a

a) The standard free energy = (-1544.3)- (-908.9 + -875.9) = 240.2 kJ/mol

b)delta G^o at 300 K = delta G_1 + RTln Q = -34.6 kJ/mol

delta G^O at 333 K = delta G_2 + RTln Q = -26.8 kJ/mol

Q6.32b

Consider the formation of the dipeptide glycylclycine. Using the following information, calculate the $\Delta_r G^\circ$.

$$2\ Glycine \rightarrow Glycylglycine + H_2O \tag{6.E.70}$$

$$\triangle_r G^{\circ'} = 29.5\ kJ\ mol^{-1} \tag{6.E.71}$$

$$[Glycine] = 1.4M \tag{6.E.72}$$

$$[Glycylglycine] = 0.7M \tag{6.E.73}$$

$$[H_2O] = 1.0M \tag{6.E.74}$$

S6.32b

Use the following equation and plug in values.

$$\triangle_r G^{\circ} = \triangle_r G^{\circ'} + RT\ln(K) \tag{6.E.75}$$

$$\triangle_r G^{\circ} = \triangle_r G^{\circ'} + RT\ln\frac{[Glycylglycine]\cdot[H_2O]}{[Glycine]^2} \tag{6.E.76}$$

$$\triangle_r G^{\circ} = 29.5\ kJ\ mol^{-1} + (\frac{8.3145}{1000}\ kJ\ mol^{-1}\ K^{-1})(298K)\ln\frac{0.7M\cdot 1.0M}{1.4^2\ M} \tag{6.E.77}$$

$$\underline{\triangle_r G^{\circ} = 26.7\ kJ\ mol^{-1}} \tag{6.E.78}$$

Click here for some more information on bioenergetics and free energy.

Q6.32c

Consider the following reaction:

$$2NH_{3(g)} + H_2O_{(l)} \rightleftharpoons 2NH^+_{4(aq)} \tag{6.E.79}$$

$$\Delta_f \bar{G}^{\circ}(NH_{3(g)}) = -16.6\frac{KJ}{mol} \tag{6.E.80}$$

$$\Delta_f \bar{G}^{\circ}(H_2O_{(l)}) = -237.2\frac{KJ}{mol} \tag{6.E.81}$$

$$\Delta_f \bar{G}^{\circ}(NH^+_{4(aq)}) = -79.3\frac{KJ}{mol} \tag{6.E.82}$$

What is the equilibrium constant of this process? Is this process typically spontaneous process under standard conditions?

S6.32c

To calculate change in Gibbs free energy for the equation, we use the standard molar Gibbs energies of formation for the reactants and products:

$$\Delta_r G = 2\Delta_f \bar{G}^{\circ}(NH^+_{4(aq)}) - \Delta_f \bar{G}^{\circ}(H_2O_{(l)}) - 2\Delta_f \bar{G}^{\circ}(NH_{3(g)}) \tag{6.E.83}$$

$$= 2\left(-79.3\frac{kJ}{mol}\right) - \left(-267.2\frac{kJ}{mol}\right) - 2\left(-16.6\frac{kJ}{mol}\right) \tag{6.E.84}$$

$$= 141.8\frac{kJ}{mol} \tag{6.E.85}$$

To calculate the equilibrium constant:

$$\ln K = -\frac{\Delta_r G}{RT} = -\frac{141800\frac{J}{mol}}{(8.3145\frac{J}{K\cdot mol})(298K)} = -57.23 \tag{6.E.86}$$

$$K = e^{-57.23} = 1.40\times 10^{-25} \tag{6.E.87}$$

Because the K value is so low for this process, the reaction does not occur spontaneously at 25^{o} C

Q6.33a

Calculate the $\Delta_r G^\circ$ and equilibrium constant for the following reaction at 298K:

3-Phosphoglycerate → Phosphoenolpyruvate +H_2O

Given that:

2-Phosphoglycerate → 3-Phosphoglycerate $\Delta_r G^\circ$ = -4.2 kJ mol^{-1}

2-Phosphoglycerate → Phosphoenolpyruvate +H_2O $\Delta_r G^\circ$ = -16.4 kJ mol^{-1}

S6.33a

$\Delta_r G^\circ$ = 4.2 kJ mol^{-1} - 16.4 kJ mol^{-1} = 12.2 kJ mol^{-1}

$$\Delta_r G^\circ = -RT lnK \tag{6.E.88}$$

$$lnK = \frac{12.2 * 10^3 J\, mol^{-1}}{-(8.314 J\, mol^{-1}\ K^{-1})298K} \tag{6.E.89}$$

$$K = e^{.00492} \tag{6.E.90}$$

$$K = 1.00 \tag{6.E.91}$$

Q6.33b

Two acid dissociation reactions for carbonic and acetic acid and their corresponding pK_a values are displayed below.

$CH_3CO_2H \rightleftharpoons CH_3CO_2^- + H^+$; $pK_a = 4.75$

$H_2CO_3 \rightleftharpoons HCO_3^- + H^+$; $pK_a = 6.37$

Assuming the reactions take place at 298K, what is the equilibrium constant and change in gibbs' free energy associated with the following reaction?

$CH_3CO_2^- + H_2CO_3 \rightleftharpoons HCO_3^- + CH_3CO_2H$

Q6.34

Suppose the isomerization of DHAP to GAP in glycolysis has an enthalpy of -1.20 kJ/mol. At 25°C the Gibbs free energy of the reaction is 1.98 kJ/mol. Determine the equilibrium constant K of the isomerization at 25°C and at 35°C

Hint: Use van't Hoff equation

S6.34

For K at 25°C

$$\Delta_r G^\circ = -RT lnK_{25^\circ} \tag{6.E.92}$$

$$1980\frac{J}{mol} = -(8.314\frac{J}{K\cdot})(25+273)K(lnK_{25^\circ}) \Rightarrow K_{25^\circ} = 0.450 \tag{6.E.93}$$

For K at 35°C

$$ln\frac{K_2}{K_1} = \frac{\Delta_r H^\circ}{R}(\frac{1}{T_1} - \frac{1}{T_2}) \tag{6.E.94}$$

$$ln\frac{K_{35^\circ}}{0.45} = \frac{-1200 J/mol}{8.314\frac{J}{K\cdot mol}}(\frac{1}{(25+273)K} - \frac{1}{(35+273)K}) \tag{6.E.95}$$

$$K_{35^\circ} = 0.152 \tag{6.E.96}$$

Q6.35a

Steady state and equilibrium state have an important role in understanding enzyme kinetics. What are some significant differences between the two?

S6.35a

In a steady state, there is no net change over time in concentrations of reactants and products of a reaction since they are being produced and consumed at constant rates. In this sense a steady state is a dynamic equilibrium. A steady state can be going in either the forward reaction or the backward reaction.

A chemical equilibrium on the other hand is when a reaction goes in the forward and backward reaction at the same rate so there is no net change in the system.

This is important because cells maintain steady states so that they are able to use particular reactions continuously. If a cell were at chemical equilibrium it would be dead because it would be at the point where all reactions are not going anymore, among other reasons.

Also, it is important to note that in a steady state, reactions are reversible compared to chemical equilibrium where the reaction rate is zero.

Click here to see more information about steady states.

Q6.35b

Is the following an example of a steady state, equilibrium state, or neither:

a. Glycolysis, ingestion, and respiration
b. NaCl_{(s)}\rightleftharpoons Na^{+}_{(aq)}+Cl^{-}_{(aq)}
c. Sodium potassium ATPase
d. Citric Acid Cycle
e. oxidation of gold

S6.35b

a. steady state
b. equilibrium state
c. steady state
d. steady state
e. neither

Q6.36

Diatomic hydrogen gas and diatomic iodine gas are in equilibrium with hydrogen Iodide gas in a closed environment of unknown volume at an unknown temperature.

Find the pressure equilibrium constant if the partial pressures of the gases are as follows: P_{H2} = 812 mmhg P_{I2}= 587 mmhg P_{HI} = 980 mmhg

Find the activity equilibrium constant if the activity constants of the gases are as follows γ_{H2} = 1.45 γ_{I2}=0.844 γ_{HI} = 1.23

Use your results to find the thermodynamic equilibrium constant.

S6.36

The reaction in question is $H_2 + I_2 \rightleftharpoons 2HI$

The pressure equilibrium constant is given by $P_{HI}^2/(P_{H2}\ P_{I2})$, the activity equilibrium constant is given by $\gamma_{HI}^2/(\gamma_{H2}\ \gamma_{I2})$, and the thermodynamic equilibrium constant is given by the product of those two.

K_p = (980 mmhg)^2/(812 mmhg * 587 mmhg) = 2.01

$K_\gamma = 1.23^2/(1.45 * 0.844) = 1.24$

K_{thermo} = 1.24 * 2.01 = 2.49

Q6.38

$$SO_2 + Cl_2 \rightarrow SO_2Cl_2 \tag{6.E.97}$$

This reaction happens at 273K. You are given a Kp of 0.683. The pressure for SO_2 is 0.58 bar for Cl_2 is 0.93 bar, and SO_2Cl_2 is 0.776 bar. From this information, determine (delta)$_r$G.

$$\Delta_r G^\circ = -RTlnKp$$

=(-8.314Jmol^{-1}K^{-1})(273K)ln(0.683)

=865.4 J mol^{-1}

$$\Delta_r G = \Delta_r G^\circ + RTlnQ$$

$$= 865.4\frac{J}{mol} + (8.314\frac{J}{mol \cdot K})(273K)ln\frac{0.776}{0.58 \cdot 0.93}$$

=1.69 kj mol^{-1}

Q6.40

Assuming oxygen binding to hemoglobin can be represented by the following reaction:

$$Hb_{(aq)} + O_{2(g)} \rightarrow HbO_{2(aq)} \tag{6.E.98}$$

If the value of Δ_rG° for the reaction is -11.2 kJ mol^{-1} at 37°C, calculate the value of Δ_rG° for the reaction.

Q6.42

At T=300K, given the mole ratio between 2 isomers Cis-2-butene and Trans-2-butene in an equilibrium mixture is 1:4. Evaluate Δ_rG of the reversible reaction:

Cis-2-butene <------> Trans-2-butene

Q6.44

When discussing the reaction in biological cells, why would you use concentrations instead of activities?

S6.44

Concentrations are generally smaller and it's easier to compare the concentrations between two parts of a cell or between different molecules in a reaction whereas activity describes behavior.

Q6.46

The following data shows the oxygen binding concentration in snails. The protein concentration is 15mM. Find n and K_d by using the *Scatchard plot*

$[O_2]_{total}$	10 mM	14 mM	18 mM	22 mM	26 mM	30 mM	34 mM	38 mM	42 mM	46 mM
$[O_2]_{bound}$	9 mM	12 mM	16 mM	19 mM	22 mM	25 mM	28 mM	32 mM	35 mM	39 mM

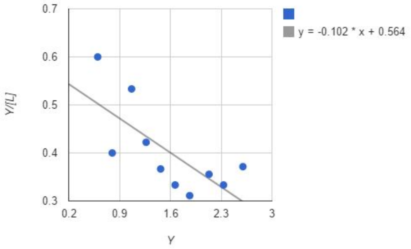
S6.46

$$y = mx + b$$

$$\frac{Y}{[L]} = (-\frac{1}{K_d})Y + \frac{n}{K_d}$$

$$Y = \frac{[O_2]_{bound}}{[P]}$$

. $[L] = [O_2]_{free}$



[O2]tot	10	14	18	22	26	30	34	38	42	46
[O2]bound	9	12	16	19	22	25	28	32	35	39
[O2]free	1	2	2	3	4	5	6	6	7	7
Y	0.6	0.8	1.067	1.267	1.467	1.667	1.867	2.133	2.333	2.6
Y/[L]	0.6	0.4	0.833	0.422	0.367	0.333	0.311	0.356	0.333	0.371

$$-\frac{1}{K_d} = -0.102$$

$$K_d = 9.804$$

$$\frac{n}{K_d} = 0.564$$

$$n = K_d * 0.564 = 5.529$$

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CHAPTER OVERVIEW

7: Electrochemistry

Electrochemistry is the study of chemical processes that cause electrons to move. This movement of electrons is called electricity, which can be generated by movements of electrons from one element to another in a reaction known as an oxidation-reduction ("redox") reaction.

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7.1: Electrochemical Cells

Electrochemistry is the study of chemical processes that cause electrons to move. This movement of electrons is called electricity, which can be generated by movements of electrons from one element to another in a reaction known as an oxidation-reduction ("redox") reaction. A redox reaction is a reaction that involves a change in oxidation state of one or more elements. When a substance loses an electron, its oxidation state increases; thus, it is oxidized. When a substance gains an electron, its oxidation state decreases, thus being reduced. For example, for the redox reaction

$$\mathrm{H_2 + F_2 \rightarrow 2\,HF}$$

can be rewritten as follows:

- Oxidation reaction

$$\mathrm{H_2 \rightarrow 2\,H^+ + 2\,e^-}$$

- Reduction reaction:

$$\mathrm{F_2 + 2\,e^- \rightarrow 2\,F^-}$$

- Overall Reaction

$$\mathrm{H_2 + F_2 \rightarrow 2\,H^+ + 2\,F^-}$$

Oxidation is the loss of electrons, whereas reduction refers to the acquisition of electrons, as illustrated in the respective reactions above. The species being oxidized is also known as the reducing agent or reductant, and the species being reduced is called the oxidizing agent or oxidant. In this case, H_2 is being oxidized (and is the reducing agent), while F_2 is being reduced (and is the oxidizing agent). The following acronym is useful in remembering this concept:

"OIL RIG"

"OIL RIG" is a useful mnemonic for remembering the definitions of oxidation nd reduction.

Oxidation **I**s **L**osing electrons; **R**eduction **I**s **G**aining electrons

Example 7.1.1: IRon-Vanadium Couple

Given the redox reaction

$$\mathrm{Fe^{3+} + V^{2+} \rightarrow Fe^{2+} + V^{3+}}$$

which species is oxidized? Which is reduced? Identify the reducing agent and the oxidizing agent.

Solution

$\mathrm{Fe^{3+}}$ is *reduced* into $\mathrm{Fe^{2+}}$ and $\mathrm{V^{2+}}$ is *oxidized* into $\mathrm{V^{3+}}$. This is because the oxidized species loses electrons, and the reduced species gains electrons.

Iron gains an electron

$$\mathrm{Fe^{3+} \rightarrow Fe^{2+}}$$

and vanadium loses an electron

$$\mathrm{V^{2+} \rightarrow V^{3+}}.$$

Thus, $\mathrm{Fe^{3+}}$ is the oxidizing agent and $\mathrm{V^{2+}}$ is the reducing agent.

Oxidation States

Rules for Assigning Oxidation States

1. Free elements have an oxidation state of 0. (e.g., He, $\mathrm{N_2}$, $\mathrm{O_2}$ has an oxidation state of 0)
2. The oxidation state of one ion must equal the net charge. (e.g., $\mathrm{F^-}$ oxidation state is -1, K^+ oxidation state is +1)
3. The sum of the oxidation state has to equal the total net charge for a compound. (e.g., $\mathrm{MnO_4^-}$ has a net charge of -1 with Mn(+7)O_4(-8)= -1)
4. The alkali metals (Group I elements) have an oxidation state of +1. (e.g., $\mathrm{Li_2O}$, Li= +1)
5. The alkaline earth metals (Group II elements) always have an oxidation state of +2. (e.g., CaO, Ca=+2)
6. Oxygen has an oxidation state of -2 in a compound
7. Fluorine has an oxidation state of -1 in a compound
8. Hydrogen has an oxidation state of +1 in a compound.
9. Transition metals and other metals may have more than one common ionic charge. (e.g., Chromium's common ionic charges are $\mathrm{Cr^{+2}}$ and $\mathrm{Cr^{+3}}$)

Exercise 7.1.1

What is the oxidation state of magnesium in $\mathrm{MgF_2}$?

Answer

Using rule 5 and 7.

$\mathrm{MgF_2}$ total charge=0 Total Charge=(+2)+(-1*2)=0

Exercise 7.1.2

What is the oxidation state of hydrogen in $\mathrm{H_2O}$?

Answer

Using rule 6 and 8

$\mathrm{H_2O}$ total charge=0 Total Charge=(+1*2)+(-2)=0

Balancing Redox Reactions

Method 1: Oxidation Number Method

- Step 1: Assign oxidation numbers to each atom.
- Step 2: Determine the net change in charge to determine the ratio of atoms
- Step 3: Use the ratio to eliminate the net charge change
- Step 4: Use the ratio as coefficients for the elements
- Step 5: Add H^+ (under acidic conditions), OH^- (under basic conditions), and H_2O to balance charges.

Method 2: Half-Reaction Method

- Step 1: Determine oxidation numbers for each atom
- Step 2: Use oxidation numbers to determine what is oxidized and what is reduced.
- Step 3: Write a half-reaction for reduction
- Step 4: Write a half-reaction for oxidation
- Step 5: Balance all elements except H and O
  - if have acid redox reaction: Balance the O using H_2O, balance the H using protons
  - if have base redox reaction: Balance O using OH^-
- Step 6: Add up the charge on each side
- Step 7: Balance the charges by adding electrons
- Step 8: Multiply the half-reactions by factors that cancel out electrons

- Step 9: Add the two half-reactions back together to eliminate out intermediates

Example 7.1.2: Manganese

Balance the following reaction in an acidic aqueous Solution

$$\mathrm{MnO_4^- + H_2C_2O_4 \rightarrow Mn^{2+} + CO_2}$$

Solution

- Reduction half-reaction:

$$2 \times \left(\mathrm{5\,e^- + 8\,H^+ + MnO_4^- \rightarrow Mn^{2+} + 4\,H_2O}\right)$$

- Oxidation half-reaction:

$$5 \times \left(\mathrm{H_2C_2O_4 \rightarrow 2\,CO_2 + 2\,H^+ + 2\,e^-}\right)$$

Combining and canceling gives the following:

$$\mathrm{10\,\cancel{e^-} + 16\,H^+ + 2\,MnO_4^{1-} + 5\,H_2C_2O_4 \rightarrow 2\,Mn^{2+} + 8\,H_2O + 10\,CO_2 + 10\,H^+ + \ 10\,\cancel{e^-}}$$

Answer

$$\mathrm{6\,H^+ + 2\,MnO_4^{1-} + 5\,H_2C_2O_4 \rightarrow 2\,Mn^{2+} + 8\,H_2O + 10\,CO_2}$$

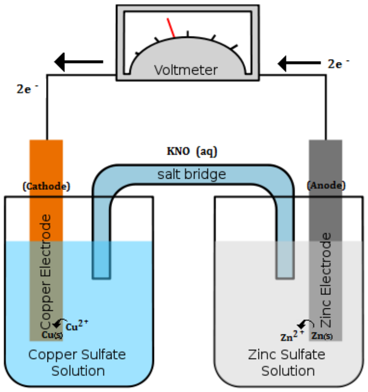
Voltaic (Galvanic) Cells

In 1793, Alessandro Volta discovered that electricity could be produced by placing different metals on the opposite sides of a wet paper or cloth. He made his first battery by placing Ag and Zn on the opposite sides of a moistened cloth with salt or weak acid Solution. Therefore, these batteries acquired the name voltaic cells. Voltaic (galvanic) cells are electrochemical cells that contain a **spontaneous reaction**, and always have a positive voltage. The electrical energy released during the reaction can be used to do work. A voltaic cell consists of two compartments called half-cells. The half-cell where oxidation occurs is called the anode. The other half-cell, where reduction occurs, is called the **cathode**. The electrons in voltaic cells flow from the negative electrode to the positive electrode—from anode to cathode (see figure below). (Note: the electrodes are the sites of the oxidation and reduction reactions). The following acronym is useful in keeping this information straight:

Red Cat and **An Ox**

Reduction **Cat**hode and **An**ode **Ox**idation

For an oxidation-reduction reaction to occur, the two substances in each respective half-cell are connected by a closed circuit such that electrons can flow from the reducing agent to the oxidizing agent. A salt bridge is also required to maintain electrical neutrality and allow the reaction to continue.



The figure above shows that $\mathrm{Zn(s)}$ is continuously oxidized, producing aqueous $\mathrm{Zn^{2+}}$:

$$\mathrm{Zn(s) \rightarrow Zn^{2+}(aq) + 2\,e^-}$$

Conversely, in the cathode, Cu^{2+} is reduced and continuously deposits onto the copper bar:

$$Cu^{2+}(aq) + 2\,e^{-} \rightarrow Cu(s)$$

As a result, the Solution containing $Zn(s)$ becomes more positively charged as the Solution containing $Cu(s)$ becomes more negatively charged. For the voltaic cell to work, the Solutions in the two half-cells must remain electrically neutral. Therefore, a salt bridge containing KNO_3 is added to keep the Solutions neutral by adding NO_3^-, an anion, into the anode Solution and K^+, a cation, into the cathode Solution. As oxidation and reduction proceed, ions from the salt bridge migrate to prevent charge buildup in the cell compartments.

The **cell diagram** (or **cell notation**) is a shorthand notation to represent the redox reactions of an electrical cell. For the cell described, the cell diagram is as follows:

$$Zn(s)|Zn^{2+}(aq)||Cu^{2+}(aq)|Cu(s)$$

- A double vertical line (||) is used to separate the anode half reaction from the cathode half reaction. This represents the salt bridge.
  - The anode (where oxidation occurs) is placed on the left side of the (||).
  - The cathode (where reduction occurs) is placed on the right side of the (||).
- A single vertical line (|) is used to separate different states of matter on the same side, and a comma is used to separate like states of matter on the same side. For example:

$$Fe^{2+}(aq), Fe^{3+}(aq)||Ag^{+}(aq)|Ag(s)$$

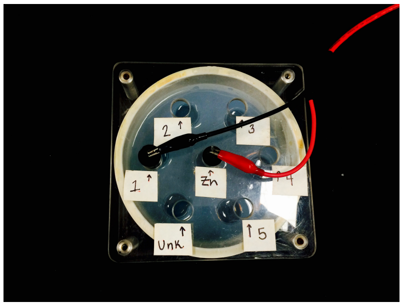


Figure* 7.1.2*: A voltaic cell works by the different reactivity of metal ions, and not require external battery source. Image taken at Hope College as part of their General Chemistry Lab curriculum.

The figure above shows a set of electrochemical half-cells that can be used to measure various voltages within galvanic cells. The cells shown are made of agar saturated with KCl Solution so as to act as a salt bridge. The zinc electrode in the middle can be used as a reference while the various concentrations of copper (labeled 1, 2, 3, 4 and 5) can be tested to form a calibration curve. The potential of the unknown can be used to determine the concentration of an unknown copper Solution. This application of the Nernst equation allows for rapid data collection without the need for a complicated salt bridge apparatus.

✓ Example 7.1.3: Copper-silver Reaction

Write the cell diagram for this reaction:

$$Cu(s) + 2\,Ag{+}(aq) \rightarrow Cu^{2+}(aq) + 2\,Ag(s)$$

Solution

$$Cu(s)|Cu^{2+}(aq)||Ag^{+}(aq)|Ag(s)$$

✓ Example 7.1.4: Aluminum-Tin Reaction

Write cell reactions for this cell diagram:

$$Al(s)|Al^{3+}(aq)||Sn^{2+}(aq)|Sn(s)$$

Answer

Oxidation: {$Al_{(s)}$ → $Al^{3+}_{(aq)}$ +$3e^-$} x 2

Reduction: {$Sn^{2+}_{(aq)}$ +$2e^-$ → $Sn_{(s)}$} x 3

Net: $2Al_{(s)}$ + $3Sn^{2+}_{(aq)}$ → $2Al^{3+}_{(aq)}$ + $3Sn_{(s)}$

Cell Potentials

The oxidation of Zn(s) into Zn^{2+} and the reduction of Cu^{2+} to Cu(s) occur spontaneously. In other words, the redox reaction between Zn and Cu^{2+} is spontaneous. This is due to the difference in potential energy between the two substances. The difference in potential energy between the anode and cathode dictates the direction of electronic movement. Electrons move from areas of higher potential energy to areas of lower potential energy. In this case, the anode has a higher potential energy; electrons therefore move from anode to cathode. The potential difference between the two electrodes is measured in units of volts. One volt (V) is the potential difference necessary to generate a charge of 1 coulomb (C) from 1 joule (J) of energy.

For a voltaic cell, this potential difference is called the **cell potential (or EMF for electromotive force, although it is not really a force)**, which is denoted **E_{cell}**. For a spontaneous reaction, E_{cell} is positive and ΔG (Gibbs free energy, used to determine if a reaction occurs spontaneously) is negative. Thus, when ΔG is negative the reaction is spontaneous. Merging electrochemistry with thermodynamics gives this formula:

$$\Delta G = -nFE_{cell}$$

Cell potential is different for each voltaic cell; its value depends upon the concentrations of specific reactants and products as well as temperature of the reaction. For **standard cell potential**, temperature of the reaction is assumed to be 25^o Celsius, the concentration of the reactants and products is 1 M, and reaction occurs at 1 atm pressure. The standard cell potential is denoted **E^o_{cell}**, and can be written as oxidation potential + reduction potential. For voltaic cells:

$$E^o_{cell} = E^o_{cathode} - E^o_{Anode} \tag{7.1.1}$$

Warning

To use Equation 7.1.1, the cell potentials must be in reduction form.

Since standard potentials are given in the form of standard reduction potential for each half-reaction, to calculate the standard cell potential E^o_{cell}, the substance is being oxidized must be identified; then the standard reduction potential of the oxidation reaction is subtracted from the standard reduction potential of the reducing reaction.

Example 7.1.5

What is the cell potential for the following reaction?

$$\mathrm{Zn(s)} + \mathrm{Cu^{2+}(aq)} \rightarrow \mathrm{Zn^{2+}(aq)} + \mathrm{Cu(s)}$$

Solution

$\mathrm{Zn(s)}$ is being oxidized, and $\mathrm{Cu(s)}$ is being reduced. The potentials for the two half reaction are given in the reduction form:

$$\mathrm{Zn(s)} \rightarrow \mathrm{Zn^{2+}(aq)} + 2\,e^-$$

$$\mathrm{Cu^{2+}(aq)} + 2\,e^- \rightarrow \mathrm{Cu(s)}$$

The cell potentials indicate which reaction takes place at the anode and which at the cathode. The cathode has a more positive potential energy, and thus:

- $\mathrm{Cu(s)}$ is the *cathode*
- $\mathrm{Zn(s)}$ is the *anode*.

To calculate E^o_{cell}, subtract the E^o of the oxidized half reaction from the E^o_{cell} of the reduction half reaction, we use Equation 7.1.1}:

$$E^o_{cell} = E^o_{cathode} - E^o_{anode}$$

Oxidation half reaction: E°= -0.763V

$$\mathrm{Zn(s) \rightarrow Zn^{2+}(aq) + 2\,e^-}$$

- Reduction half reaction: E°= +0.342V

$$\mathrm{Cu^{2+}(aq) + 2\,e^- \rightarrow Cu(s)}$$

Net reaction:

$$\mathrm{Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)}$$

Therefore:

$$E^o_{cell} = E^o_{cathode} - E^o_{anode} = 0.340\ V - (-0.763\ V) = +1.103\ V$$

Exercise 7.1.6

Calculate E^o_{cell} for the following redox reaction under standard conditions:

$$\mathrm{2\,Al(s) + 3\,Sn^{2+}(aq) \rightarrow 2\,Al^{3+}(aq) + 3\,Sn(s)}$$

Answer

Oxidation:

$$\{\mathrm{Al(s) \rightarrow Al^{3+}(aq) + 3\,e^-}\} \times 2 \quad -E^o = +1.676\,V$$

Reduction:

$$\{\mathrm{Sn^{2+}(aq) + 2\,e^- \rightarrow Sn(s)}\} \times 3 \quad E^o = -0.137\,V$$

Net reaction:

$$\mathrm{2\,Al(s) + 3\,Sn^{2+}(aq) \rightarrow 2\,Al^{3+}(aq) + 3\,Sn(s)}$$

Then using Equation 7.1.1

$$\begin{aligned} E^o_{cell} &= -0.137\,V - (-1.676V) \\ &= +1.539\,V. \end{aligned}$$

Voltage is an Intensive Property

Standard reduction potential is an intensive property, meaning that changing the stoichiometric coefficient in a half reaction does not affect the value of the standard potential. For example,

Oxidation:$\{Al_{(s)} \rightarrow Al^{3+}_{(aq)} + 3e^-\}$ x 2 is still E°= -1.676

Reduction:$\{Sn^{2+}_{(aq)} + 2e^- \rightarrow Sn_{(s)}\}$ x 3 is still E°= -0.137

If the stoichiometric coefficient is multiplied by 2, the standard potential does not change:

Example 7.1.7: Iron/Vanadium Chemistry

Calculate the cell potential in the following redox reaction under standard conditions:

$$\mathrm{Fe^{3+}(aq) + V^{2+}(aq) \rightarrow Fe^{2+}(aq) + V^{3+}(aq)}$$

Solution

Consult the table of standard reduction potentials (Table P1) for each half reaction:

$$Fe^{3+}_{(aq)} + e^- \rightarrow Fe^{2+}_{(aq)} \quad \text{with } E^o = 0.771\ V$$

$$V^{2+}_{(aq)} \rightarrow V^{3+}_{(aq)} + e^{-} \quad \text{with } E^{o} = -0.255\ V$$

The cell potential is

$$E^{o}_{cell} = E^{o}_{cathode} - E^{o}_{anode} = 0.771\ V - (-0.255\ V) = 1.026\ V$$

Glossary

- Anode: Electrode in an electrochemical cell on which the oxidation reaction occurs.
- Cathode: Electrode in an electrochemical cell on which the reduction reaction occurs
- Electrochemistry: A field of chemistry that focuses on the interchange between electrical and chemical energy
- Electricity: Flow of electrons over a wire that is affected by the presence and flow of electric charge.
- Electrolysis: The decomposition of a substance by means of electric current. This method pushes a redox reaction toward the non-spontaneous side.
- Electrolytic cell: Electrochemical cell that is being pushed toward the non-spontaneous direction by electrolysis.
- Electromotive force, EMF (or cell potential): Difference of potential energy of electrons between the two electrodes.
- Oxidation number: Charge on an atom if shared electrons where assigned to the more electronegative atom.
- Oxidation: Lose of electrons, can occur only in combination with reduction. [remember: Oxidation Is Loss, Reduction Is Gain = OIL RIG]
- Reduction: Gain of electrons, can occur only in combination with oxidation. [remember: OIL RIG]
- Redox reaction: Shorthand for reduction-oxidation reaction.
- Voltaic cell or galvanic cell: An electrochemical cell that uses redox reaction to produce electricity spontaneously.

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7.4: Types of Electrochemical Cells

Concentration Cells

A concentration cell is an electrolytic cell that is comprised of two half-cells with the same electrodes, but differing in concentrations. A concentration cell acts to dilute the more concentrated solution and concentrate the more dilute solution, creating a voltage as the cell reaches an equilibrium. This is achieved by transferring the electrons from the cell with the lower concentration to the cell with the higher concentration.

The standard electrode potential, commonly written as E^o_{cell}, of a concentration cell is equal to zero because the electrodes are identical. But, because the ion concentrations are different, there is a potential difference between the two half-cells. One can find this potential difference via the Nernst Equation,

$$E_{cell} = E^o_{cell} - \frac{0.0592}{n} logQ \tag{7.4.1}$$

at 25^{o}C. The E stands for the voltage that can be measured using a voltmeter (make sure if the voltmeter measures it in millivolts that you convert the number before using it in the equation). Note that the Nernst Equation indicates that cell potential is dependent on concentration, which results directly from the dependence of free energy on concentration. Remember that to find Q you use this equation:

$$aA + bB \rightleftharpoons cC + dD \tag{7.4.2}$$

$$Q = \frac{(C)^c * (D)^d}{(A)^a * (B)^b} \tag{7.4.3}$$

When Q=1, meaning that the concentrations for the products and reactants are the same, then taking the log of this equals zero. When this occurs, the E_{cell} is equal to the E^o_{cell}.

Another way to use the E^o_{cell} , or to find it, is using the equation below.

$$E^o_{cell} = E^o_{cathode} - E^o_{anode} \tag{7.4.4}$$

A voltage can also be generated by constructing an electrochemical cell in which each compartment contains the same redox active solution but at different concentrations. The voltage is produced as the concentrations equilibrate. Suppose, for example, we have a cell with 0.010 M $AgNO_3$ in one compartment and 1.0 M $AgNO_3$ in the other. The cell diagram and corresponding half-reactions are as follows:

$$Ag(s) \mid Ag^+(aq, 0.010\ M) \mid\mid Ag+(aq, 1.0\ M) \mid Ag(s) \tag{7.4.5}$$

cathode:

$$Ag^+(aq, 1.0\ M) + e^- \rightarrow Ag(s) \tag{7.4.6}$$

anode:

$$Ag(s) \rightarrow Ag^+(aq, 0.010\ M) + e^- \tag{7.4.7}$$

Overall

$$Ag^+(aq, 1.0\ M) \rightarrow Ag^+(aq, 0.010\ M) \tag{7.4.8}$$

As the reaction progresses, the concentration of Ag^+ will increase in the left (oxidation) compartment as the silver electrode dissolves, while the Ag^+ concentration in the right (reduction) compartment decreases as the electrode in that compartment gains mass. The total mass of $Ag(s)$ in the cell will remain constant, however. We can calculate the potential of the cell using the Nernst equation, inserting 0 for $E°_{cell}$ because $E°_{cathode} = −E°_{anode}$:

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \left(\frac{0.0591\text{ V}}{n}\right) \log Q = 0 - \left(\frac{0.0591\text{ V}}{1}\right) \log\left(\frac{0.010}{1.0}\right) = 0.12\text{ V} \tag{7.4.9}$$

An electrochemical cell of this type, in which the anode and cathode compartments are identical except for the concentration of a reactant, is called a **concentration cell**. As the reaction proceeds, the difference between the concentrations of Ag^+ in the two compartments will decrease, as will E_{cell}. Finally, when the concentration of Ag^+ is the same in both compartments, equilibrium will have been reached, and the measured potential difference between the two compartments will be zero (E_{cell} = 0).

✓ Example 7.4.2

Calculate the voltage in a galvanic cell that contains a manganese electrode immersed in a 2.0 M solution of $MnCl_2$ as the cathode, and a manganese electrode immersed in a 5.2 × 10^{-2} M solution of $MnSO_4$ as the anode (T = 25°C).

Given: galvanic cell, identities of the electrodes, and solution concentrations

Asked for: voltage

Strategy:

A. Write the overall reaction that occurs in the cell.
B. Determine the number of electrons transferred. Substitute this value into the Nernst equation to calculate the voltage.

Solution

A This is a concentration cell, in which the electrode compartments contain the same redox active substance but at different concentrations. The anions (Cl^- and SO_4^{2-}) do not participate in the reaction, so their identity is not important. The overall reaction is as follows:

$$Mn^{2+}_{(aq,2.0M)} \rightarrow Mn^{2+}_{(aq,5.2\times10^{-2}M)} \tag{7.4.10}$$

B For the reduction of Mn^{2+}(aq) to Mn(s), n = 2. We substitute this value and the given Mn^{2+} concentrations into Equation ???:

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \left(\frac{0.0591\text{ V}}{n}\right)\log Q = 0\text{ V} - \left(\frac{0.0591\text{ V}}{2}\right)\log\left(\frac{5.2\times10^{-2}}{2.0}\right) = 0.047\text{ V}$$

Thus manganese will dissolve from the electrode in the compartment that contains the more dilute solution and will be deposited on the electrode in the compartment that contains the more concentrated solution.

? Exercise 7.4.2

Suppose we construct a galvanic cell by placing two identical platinum electrodes in two beakers that are connected by a salt bridge. One beaker contains 1.0 M HCl, and the other a 0.010 M solution of Na_2SO_4 at pH 7.00. Both cells are in contact with the atmosphere, with P_{O_2} = 0.20 atm. If the relevant electrochemical reaction in both compartments is the four-electron reduction of oxygen to water:

$$O_{2(g)} + 4H^+_{(aq)} + 4e^- \rightarrow 2H_2O_{(l)} \tag{7.4.11}$$

What will be the potential when the circuit is closed?

Answer 0.41 V

Fuel Cells

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7.6: Biological Oxidation

Before the concept of biological oxidation can be understood and explored, the fundamental chemical process through which oxidation and reduction take place should be first established.

Foundation

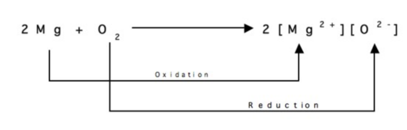
All reactions which involve electron flow are considered oxidation-reduction reactions. The basic definition can be defined as: One reactant is oxidized (loses electrons), while another is reduced (gains electrons). A couple of basic oxidation-reduction or "redox" example's are given here.

✓ Example 1

The reaction of magnesium metal with oxygen, involves the oxidation of magnesium

$$2Mg(s) + O_2(g) \rightarrow 2MgO(s) \tag{7.6.1}$$

Since the magnesium solid is oxidized, we expect to see a loss of electrons. Similarly, since oxygen must therefore be reduced, we should see a gain of electrons.



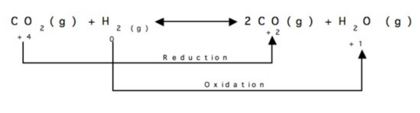
As the magnesium is oxidized there is a loss of 2 electrons while simultaneously, oxygen gains those two electrons. Another example of a redox reaction is with the two gasses CO_2 and H_2. This redox reaction also demonstrates the importance of implementing "oxidation numbers" in the methodology of redox reactions, allowing for the determination of which reactant is being reduced and which reactant is being oxidized.

✓ Example 2

The reaction of carbon dioxide gas with hydrogen gas, involving the oxidation of hydrogen

$$CO_2(g) + H_2(g) \rightarrow 2CO(g) + H_2O(g) \tag{7.6.2}$$

Since the hydrogen gas is being oxidized (reductant), we expect to see an overall loss of electrons for the resulting molecule. Similarly, we expect to see a gain in the overall number of electrons for the resulting molecule of the oxidant (CO_2).



Here it is possible to infer that the carbon of CO_2 is being reduced by review of its unique oxidation number. Such that, C (of CO_2) goes from an oxidation number of +4 to C (of CO) having an oxidation number of +2, representing a loss of two electrons. Similarly, H_2 is noted as going from an oxidation number of 0 to +1, or gaining one electron in a reduction process. For more information on oxidation numbers, review the following link: Oxidation-Reduction Reactions

A Basic Biological Model

The flow of electrons is a vital process that provides the necessary energy for the survival of all organisms. The primary source of energy that drives the electron flow in nearly all of these organisms is the radiant energy of the sun, in the form of electromagnetic radiation or Light. Through a series of nuclear reactions, the sun is able to generate thermal energy (which we can feel as warmth) from electromagnetic radiation (which we perceive as light). However, the particular wavelength of the electromagnetic spectrum we are able to detect with the human eye is only between 400 and 700 nm in wavelength. It should therefore be noted that the visible part of the electromagnetic spectrum is actually a small percentage of the whole; where a much greater percentage remains undetectable for the human eye.

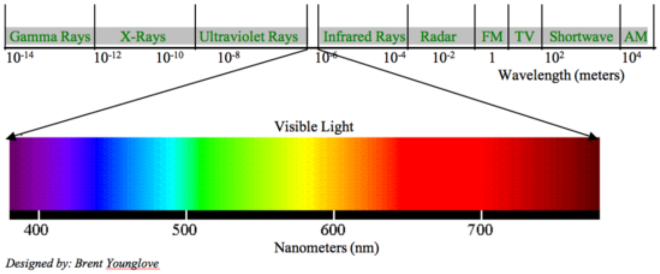


Figure 1: The electromagnetic spectrum with an emphasis on the visible light region

In physics, the use of the term "light" refers to electromagnetic radiation of any wavelength, independent of its detectability for the human eye. For plants, the upper and lower ends of the visible spectrum are the wavelengths that help drive the process of splitting water (H_2O) during photosynthesis, to release its electrons for the biological reduction of carbon dioxide (CO_2) and the release of diatomic oxygen (O_2) to the atmosphere. It is through the process of photosynthesis that plants are able to use the energy from light to convert carbon dioxide and water into the chemical energy storage form called glucose.

Plants represent one of the most basic examples of biological oxidation and reduction. The chemical conversion of carbon dioxide and water into sugar (glucose) and oxygen is a light-driven reduction process:

$$6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2 \tag{7.6.3}$$

The process by which non photosynthetic organisms and cells obtain energy, is through the consumption of the energy rich products of photosynthesis. By oxidizing these products, electrons are passed along to make the products carbon dioxide, and water, in an environmental recycling process. The process of oxidizing glucose and atmospheric oxygen allowed energy to be captured for use by the organism that consumes these products of the plant. The following reaction represents this process:

$$C_6H_{12}O_6 + O_2 \rightarrow 6CO_2 + 6H_2O + Energy \tag{7.6.4}$$

It is therefore through this process that heterotrophs (most generally "animals" which consume other organisms obtain energy) and autotrophs (plants which are able to produce their own energy) participate in an environmental cycle of exchanging carbon dioxide and water to produce energy containing glucose for organismal oxidation and energy production, and subsequently allowing the regeneration of the byproducts carbon dioxide and water, to begin the cycle again. Therefore, these two groups of organisms have been allowed to diverge interdependently through this natural life cycle.

Physical Chemistry's Understanding

Biological oxidation-reduction reactions, or simply *biological oxidations* utilize multiple stages or processes of oxidation to produce large amounts of Gibbs energy, which is used to synthesize the energy unit called adenosine triphosphate or ATP. To efficiently produce ATP, the process of glycolysis must be near an abundance of oxygen. Since glycolysis by nature is not an efficient process, if it lacks sufficient amounts of oxygen the end product pyruvate, is reduced to lactate with NADH as the reducing agent. However, in a more favorable aerobic process, the degradation of glucose through glycolysis proceeds with two additional processes known as the *citric acid cycle* and the terminal *respiratory chain;* yielding the end products carbon dioxide and water, which we exhale with each breath.

Figure 2: The three main processes for the breakdown of glucose into carbon dioxide and water

The products NADH and $FADH_2$ formed during glycolysis and the citric acid cycle are able to reduce molecular oxygen (O_2) thereby releasing large amounts of Gibbs energy used to make ATP. The process by which electrons are transferred from NADH or $FADH_2$ to O_2 by a series of electron transfer carriers, is known as *oxidative phosphorylation*. It is through this process that ATP is able to form as a result of the transfer of electrons.

Thee specific examples of redox reactions that are used in biological processes, involving the transfer of electrons and hydrogen ions as follows. During some biological oxidation reactions, there is a simultaneous transfer of hydrogen ions with electrons (1). In other instances, hydrogen ions may be lost by the substance being oxidized while transferring only its electrons to the substance being reduced (2). A third type of biological oxidation might involve only a transfer of electrons (3). It should be noted that biological oxidation rarely proceeds in a direct manner, and generally involves complex mechanisms of several enzymes. The outline below recaps the three processes of biological oxidation stated above, in descending order.

Table 1: Transfer of hydrogen ions and electrons for the general reaction scheme of A + B with intermediate stage shown

Reactants	**Intermediate Stage**	**Products**
$AH_2 + B$	$[A + 2H^+ + 2e^- + B]$	$A + BH_2$
$AH_2 + B$	$[A + 2H^+ + 2e^- + B]$	$A + B^{2-} + 2H^+$
$A^{2-} + B$	$[A + 2e^- + B]$	$A + B^{2-}$

In the last stage of the metabolic process (the terminal respiratory chain), the sequence by which electrons are carried is determined by relative redox potentials. The carrier molecules used to transfer electrons in this stage are called cytochromes, which are an electron-carrying protein containing a heme group. The iron atom of each cytochrome molecule can exist either in the oxidized (Fe^{3+}) or reduced (Fe^{2+}) form. Within the terminal respiratory chain, each carrier molecule alternates between the reduced state and the oxidized state, with molecular oxygen as the final electron acceptor at the end.

TRC.JPG

Figure 3. The terminal respitory chain showing electron transport and phosphorylation. Electrons from the citric acid cycle are transferred from one carrier to another, where each carrier alternates between the reduced and oxidized state. Molecular oxygen represents the final electron acceptor.

It is through the knowledge of redox potentials, that the knowledge of biological processes can be further expanded. The standard reduction potential is denoted as $E^{o'}$ and is often based on the hydrogen electrode scale of pH 7, rather than pH 0, a common reference point for listed values. Moreover, the superscript symbol (^{o}) denotes standard-state conditions, while the adjacent superscript symbol (') denotes the pH scale of 7 for biochemical processes.

It therefore becomes possible to trace the energy transfer in cells back to the fundamental flow of electrons from one particular molecule to another. Where this electron flow occurs via the physics principle of higher potential to lower potential; similar to a ball rolling down a hill, as opposed to the opposite direction. All of these reactions involving electron flow can be attributed to the basic definition of the oxidation-reduction pathway stated above.

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7.7: Membrane Potential

Membrane potential is what we use to describe the difference in voltage (or electrical potential) between the inside and outside of a cell.

Introduction

Without membrane potentials human life would not be possible. All living cells maintain a potential difference across their membrane. Simply stated, membrane potential is due to disparities in concentration and permeability of important ions across a membrane. Because of the unequal concentrations of ions across a membrane, the membrane has an electrical charge. Changes in membrane potential elicit action potentials and give cells the ability to send messages around the body. More specifically, the action potentials are electrical signals; these signals carry efferent messages to the central nervous system for processing and afferent messages away from the brain to elicit a specific reaction or movement. Numerous active transports embedded within the cellular membrane contribute to the creation of membrane potentials, as well as the universal cellular structure of the lipid bilayer. The chemistry involved in membrane potentials reaches to many scientific disciplines. Chemically it involves molarity, concentration, electrochemistry and the Nernst equation. From a physiological standpoint, membrane potential is responsible for sending messages to and from the central nervous system. It is also very important in cellular biology and shows how cell biology is fundamentally connected with electrochemistry and physiology. The bottom line is that membrane potentials are at work in your body right now and always will be as long as you live.

History

The subject of membrane potential stretches across multiple scientific disciplines; Membrane Potential plays a role in the studies of Chemistry, Physiology and Biology. The culmination of the study of membrane potential came in the 19th and early 20th centuries. Early in the 20th century, a man named professor Bernstein hypothesized that there were three contributing factors to membrane potential; the permeability of the membrane and the fact that [K+] was higher inside and lower on the outside of the cell. He was very close to being correct, but his proposal had some flaws. Walther H. Nernst, notable for the development of the Nernst equation and winner of 1920 Nobel Prize in chemistry, was a major contributor to the study of membrane potential. He developed the Nernst equation to solve for the equilibrium potential for a specific ion. Goldman, Hodgkin and Katz furthered the study of membrane potential by developing the Goldman-Hodgkin-Katz equation to account for any ion that might permeate the membrane and affect its potential. The study of membrane potential utilizes electrochemistry and physiology to formulate a conclusive idea of how charges are separated across a membrane.

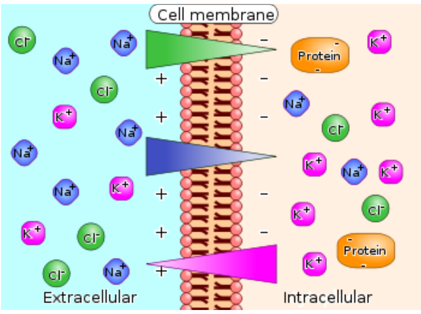

Figure 1. Differences in concentration of ions on opposite sides of a cellular membrane produce a voltage difference called the membrane potential. The largest contributions usually come from sodium (Na^+) and chloride (Cl^-) ions which have high concentrations in the extracellular region, and potassium (K^+) ions, which along with large protein anions have high concentrations in the intracellular region. Calcium ions, which sometimes play an important role, are not shown.

Membrane Potential and Cellular Biology

In discussing the concept of membrane potentials and how they function, the creation of a membrane potential is essential. The lipid bilayer structure of the cellular membrane, with its lipid-phosphorous head and fatty acid tail, provides a perfect building material that creates both a hydrophobic and hydrophilic side to the cellular membrane. The membrane is often referred to as a mosaic model because of its semi-permeability and its ability to keep certain substances from entering the cell. Molecules such as water can diffuse through the cell based on concentration gradients; however, larger molecules such as glucose or nucleotides require channels. The lipid bilayer also houses the Na^+/K^+ pump, ATPase pump, ion transporters, and voltage gated channels, and it is the site of vesicular transport. The structure regulates which ions enter and exit to determine the concentration of specific ions inside of the cell.

Why is membrane potential essential to the survival of all living creatures?

Animals and plants require the breakdown of organic substances through cellular respiration to generate energy. This process, which produces ATP, is dependent on the electron transport chain. Electrons travel down this path to be accepted by oxygen or other electron acceptors. The initial electrons are obtained from the breakdown of water molecules. The hydrogen build up in the extracellular fluid leaving a gradient. As per membrane potentials, when there a gradient, the molecules flow in the opposite direction. In this case, hydrogen flows back into the cell through a protein known as ATP synthase which creates ATP in the process. This action is essential to life because the number of ATP created from each glucose increases drastically. Chemical disequilibrium and membrane potentials allow bodily functions to take place.

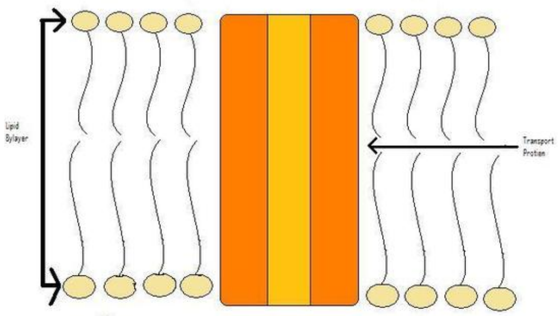

Figure 2

Transport proteins, more specifically the 'active' transport proteins, can pump ions and molecules against their concentration gradient. This is the main source of charge difference across the cellular membrane.

Physiology of Membrane Potential

Understanding Membrane Potential

The following points should help you to understand how membrane potential works

- The difference between the electrical and chemical gradient is important.
  - Electrical Gradient
    - Opposes the chemical gradient.
    - Represents the difference in electrical charge across the membrane
  - Chemical Gradient
    - Opposes the electrical gradient
    - Represents the difference in the concentration of a specific ion across the membrane.
  - A good example is K^+. The membrane is very permeable to K^+ and the $[K^+]$ inside the cell is great, therefore a positive charge is flowing out of the cell along with K^+. The $[K^+]$ inside the cell decreases causing the concentration gradient to flow towards the outside of the cell. This also causes the inside of the cell to become more electronegative increasing its electrical gradient.
- The Nernst equation can help us relate the numerical values of concentration to the electrical gradient.
- Leak Channels
  - Channels that are always open
  - Permit unregulated flow of ions down an electrochemical gradient.
- Na^+/K^+ ATPase Pump
  - Actively transports Na^+ out of the cell and K^+ into the cell.

- Helps to maintain the concentration gradient and to counteract the leak channels.

Membrane Potential and Physiology of Human Nerve Cells

Human nerve cells work mainly on the concept of membrane potentials. They transmit chemicals known as serotonin or dopamine through gradients. The brain receives these neurotransmitters and uses it to perform functions.

- Na^+ has a much higher concentration outside of the cell and the cell membrane is very impermeable to Na^+
- K^+ has a high concentration inside the cell due to the fact that the cell membrane is very permeable to K^+
- A^- is used to refer to large ions that are found completely inside of the cell and cannot penetrate the cell membrane.

Concentration (in Millimoles/ Liter) and permeability of Ions Responsible for Membrane Potential in a Resting Nerve Cell

ION	Extracellular	Intracellular	Relative Permeability
Na^+	150	15	1
K^+	5	150	25-30
A^-	0	65	0

Check out this YouTube video if you want to know more about how the Na^+/K^+ pump and how the membrane potential works. www.youtube.com/watch?v=iA-Gdkje6pg

How To Calculate A Membrane Potential

The calculation for the charge of an ion across a membrane, The Nernst Potential, is relatively easy to calculate. The equation is as follows: $(RT/zF) \log([X]_{out}/[X]_{in})$. RT/F is approximately 61, therefore the equation can be written as

$$(61/z) \ln([X]_{out}/[X]_{in})$$

- **R** is the universal gas constant ($8.314\ J.K^{-1}.mol^{-1}$).
- ***T*** is the temperature in Kelvin (°K = °C + 273.15).
- ***z*** is the ionic charge for an ion. For example, *z* is +1 for K^+, +2 for Mg^{2+}, -1 for F^-, -1 for Cl^-, etc. Remember, z does not have a unit.
- ***F*** is the Faraday's constant ($96485\ C.mol^{-1}$).
- $\mathbf{[X]_{out}}$ is the concentration of the ion outside of the species. For example the molarity outside of a neuron.
- $\mathbf{[X]_{in}}$ is the concentration of the ion inside of the species. For example, the molarity inside of a neuron.

The only difference in the Goldman-Hodgkin-Katz equation is that is adds together the concentrations of all permeable ions as follows

$$(RT/zF) \log([K^+]_o+[Na^+]_o+[Cl^-]_o /[K^+]_i+[Na^+]_i+[Cl^-]_i)$$

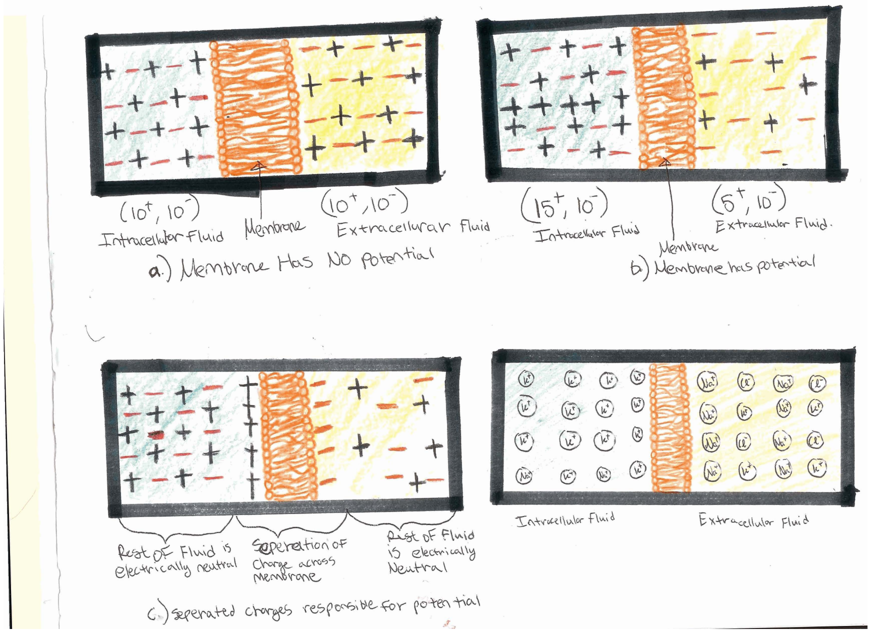

***Figure 3.** (Clockwise From Upper Left) 1)* The charges are equal on both sides; therefore the membrane has no potential. 2)There is an unbalance of charges, giving the membrane a potential. 3) The charges line up on opposite sides of the membrane to give the membrane its potential. 4) A hypothetical neuron in the human body; a large concentration of potassium on the inside and sodium on the outside.

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Problems

1. List the following in order from highest to lowest permeability. A^-, K^+, Na^+

2. Which of the following statement is NOT true?

a. The membrane potential usually requires a minimal difference of electrocharges across the membrane
b. Membrane impermeability plays a role in membrane potentials.
c. Membrane potential exists in all cellular structures, except for neurons.
d. The active transports play a vital role in membrane potentials.

3. What would be the equilibrium potential for the ion K^+ be if $[K^+]_{in}$= 5mM and $[K^+]_{in}$=150mM?

4. True or false: At resting membrane potential, the inside of the membrane is slightly negatively charged while the outside is slightly positively charged.

Answers:

1. **$K^+ > Na^+ > A^-$**

2. Answer **c.)**is **not** true; membrane potential exists in neurons and is responsible for action potential propagation in neurons.

3. $E_{K^+} = (61/z) \log([K^+]_{out}/[K^+]_{in}) = (61/1) \log([5mM]/[150mM]) =$ **-90mV**

$z=1$

4. **True.** The resting membrane potential is negative as a result of this disparity in concentration of charges.

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7.E: Electrochemistry (Exercises)

Q7.1

For an electrochemical cell driven by the reaction:

$$\mathrm{Cl_2 + 2\,Tl \rightarrow 2\,Cl^- + 2\,Tl^+} \tag{7.E.1}$$

Determine the electromotive force of the cell under standard conditions. Standard reduction potentials for the half cells are given below

$$\mathrm{Cl_2(g) + 2\,e^- \rightarrow 2\,Cl^-} \tag{7.E.2}$$

with Eo= +1.36 V

$$\mathrm{Tl^+ + e^- \rightarrow Tl} \tag{7.E.3}$$

with Eo= -0.336 V

S7.1

The change in gibbs free energy is an extrinsic quality that can be used to determine the EMF of the cell based on the SRPs of the half-cells. Because the number of electrons exchanged in each reaction are known, we can cancel out the Faraday constants in the equation to relate Gibbs' free energy directly to the EMF of the cell.

$\Delta G_{Tot} = \Delta G_1 + \Delta G_2 \rightarrow E^o_{tot} n_{tot} F = E^o_1 n_1 F + E^o_2 n_2 F \rightarrow E^o_{tot} = (E^o_1 n_1 + E^o_2 n_2)/n_{tot} = (1.36V*(2) - 0.336V(1))/2 = 2.38\ V$

Q7.8

For the following electrochemical cells, the value of K is given. Determine the change in Gibbs free energy for the reaction in the cell described, and determine the standard potential of the cell.

$Cu^{2+} + Sn \text{ -> } Sn^{2+} + Cu$; $K = e^{38.8}$

$2Li + Hg^{2+} \text{ -> } 2Li^+ + Hg$; $K = e^{381}$

$Au^{3+} + 3Zn \text{ -> } 3Zn^+ + Au$; $K = e^{264}$

Q7.9

Refer to the reaction below for the following question.

$$Zn + Sn^{4+} \rightleftharpoons Zn^{2+} + Sn^{2+} \tag{7.E.4}$$

Calculate the $E°$ for the specified reaction at 298 K.

S7.9

First, identify the anode and the cathode:

Anode: $\mathrm{Zn \rightarrow Zn^{2+} + 2e^-}$

Cathode: $\mathrm{Sn^{4+} + 2e^- \rightarrow Sn^{2+}}$

With this information established, you can then calculate the $E°$ using the half-reactions.

$E^\circ = 0.151\mathrm{V} - (-0.762\mathrm{V}) = 0.913\mathrm{V}$

Q7.9

$$Cu^{2+} + 2Tl \rightarrow Cu + 2Tl^{2+} \tag{7.E.5}$$

If the equilibrium constant is 8.66×10^{22}, what is the electric potential of the cell?

Q7.10a

In an experiment using standard conditions, you find the cell emf to be 0.0428 V for the following cell:

$$Ag_{(s)}|Ag^+||Ag^+|Ag_{(s)} \tag{7.E.6}$$

If the concentration of Ag^+ is 4.5 M at the cathode, calculate the concentration of Ag^+ at the anode.

S7.10a

Firstly, note the half reaction.

$$Ag^+ + e^- \rightarrow Ag \tag{7.E.7}$$

Then solve using the Nernst equation, noting that E° is 0 for concentration cells (same electrodes with different concentrations).

$$\begin{aligned} E &= E^o - \frac{RT}{vF}\ln\frac{[Anode]}{[Cathode]} \qquad (7.E.8)\\ 0.0428 &= 0 - \frac{(8.3145\, J\, mol^{-1})(298^{\circ} K)}{(1)(96,485 J)} \cdot \ln\frac{X}{4.5M} \qquad (7.E.9)\\ 0.0428 &= -0.0257 \cdot \ln\frac{X}{4.5M} \qquad (7.E.10)\\ -1.665 &= \ln(x) - \ln(4.5) \qquad (7.E.11)\\ \ln(4.5) + (-1.665) &= \ln(x) \qquad (7.E.12)\\ e^{-0.161} &= e^{\ln(x)} \qquad (7.E.13)\\ X &= 0.85M \rightarrow \underline{[Ag^+] = 0.85M} \qquad (7.E.14) \end{aligned}$$

Click here for more information on concentration cells.

Q7.10b

A *concentration* cell contains I and I_2. What is the pressure of I if the cell emf is -.05 V and the pressure of \(I_2\)is 3.75 bar?

S7.10b

$$2I_{(g)} \rightleftharpoons I_{2(g)} \tag{7.E.15}$$

$$E = \frac{-.0257V}{2} ln\frac{3.75bar}{x} \rightarrow x = 13.0bar \tag{7.E.16}$$

Q7.14

Cu(s)|Cu^{2+} (0.5M) || Cu^{2+}(aq)|Cu(s)

Calculate the electric potential difference for the above concentration cell

Q7.14

$\mathrm{Co}_{(s)} \mid \mathrm{Co}^{2+}(0.05M) \parallel \mathrm{Co}^{2+}_{(aq)}(0.1M) \mid \mathrm{Co}_{(s)}$

Using the above concentration cell, determine the emf. Assume the temperature is at 25°C.

S7.14

$\mathrm{Anode: Co} \rightarrow \mathrm{Co}^{2+}(0.05M) + 2\mathrm{e}^-$

$\mathrm{Cathode: Co}^{2+}(0.1M) + 2\mathrm{e}^- \rightarrow \mathrm{Co}$

The overall reaction is:

$\mathrm{Co}^{2+}(0.1M) \rightarrow \mathrm{Co}^{2+}(0.05M)$

The emf of the cell is dependent upon the concentrations of Co^{2+} at the anode and at the cathode.

$E = E^\circ - \frac{0.0257\mathrm{V}}{\nu}\ln\frac{0.05}{0.1} = 0\mathrm{V} - \frac{0.0257\mathrm{V}}{2}\ln\frac{0.05}{0.1} = 0.009\mathrm{V}$

Q7.16

Referring to the reaction:

$$\mathrm{FAD} + 2\mathrm{H}^+ + 2\mathrm{e}^- \rightarrow \mathrm{FADH}_2$$

and taking into account that at 298 K, the $E°'$ is -0.219 V. Use this information to determine the E' at pH = 3. Note: Both FAD and $FADH_2$ have equal moles of concentration.

S7.16

$$E' = E^{\circ\prime} = -0.219\text{V} - \frac{0.0257\text{V}}{\nu}\ln\frac{[\text{FADH}_2]}{[\text{FAD}]([\text{H}^+]/10^{-7})}$$

$$= -0.219\text{V} - \frac{0.0257\text{V}}{2}\ln\frac{3}{(3)(0.3/10^{-7})^2}$$

$$= 0.164\text{V}$$

Q7.15

Calculate E for the following reaction:

[(Zn(s)+Cu^{2+}(aq) \rightleftharpoons Cu(s) + Zn^{2+}(aq)\]

S7.15

$Zn(s) \rightarrow 2e^- + Zn^{2+}(aq)$ -Anode [Zn^{2+}]=.25M

$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ -Cathode [Cu^{2+}]=.35M

$$E^\circ = E_{cathode} - E_{anode} = .342V - (-.762V) = 1.104V \tag{7.E.17}$$

$$E = E^\circ - \frac{.0257V}{2} ln\frac{Cu^{2+}}{Zn^{2+}} = 1.10V - \frac{0.0257V}{2} ln\frac{.35M}{.25M} = 1.08V \tag{7.E.18}$$

Q7.14

Co(s)|Co^{2+} (0.05M) ||Co^{2+}(aq) (0.1M)|Co(s)

Calculate the emf for the above concentration cell.

Q7.21

To breakdown consumed alcohol, our body converted ethanol into an acetyldehyde by forming a redox reaction with NAD^+.

$$\text{ethanol} + NAD^+ \rightarrow \text{acetaldehyde} + NADH + H^+ \tag{7.E.19}$$

Determine $\Delta_r G^{\circ\prime}$ of reaction at 298 K and pH = 7 (Hint: Set up half reactions and find $E^{\circ\prime}$ of the whole reaction.)

S7.21

$$ethanol \rightarrow acetaldehyde + 2H^+ + 2e^- \qquad E^{\circ\prime} = +0.197V \tag{7.E.20}$$

$$NAD^+ + H^+ + 2e^- \rightarrow NADH \qquad E^{\circ\prime} = -0.320V \tag{7.E.21}$$

$$Overall: \ ethanol + NAD^+ \rightarrow acetaldehyde + NADH + H^+ \qquad E^{\circ\prime} = -0.123 \tag{7.E.22}$$

$$\Delta rG^{\circ\prime} = -vF\Delta E^{\circ\prime} = -(2)(96500\frac{C}{mol})(-0.123V) = 23739J = 23.7kJ/mol \tag{7.E.23}$$

Q7.21

The hydrolysis of ATP with the following concentrations:

ATP4- + H2O ▯▯ ADP3- + H+ + HPO4^2-
10mM 0.5mM pH 6 5mM

Calculate the change in biochemical standard Gibbs energy of reaction.

Q7.22

Calculate the equilibrium constant and $\Delta_r G^{o\prime}$ for hydrolysis of ATP at 25.0^{o}C:

$$\text{Glucose} + \text{ ATP} \rightarrow \text{ADP} + \text{ glucose-6-phosphate} \tag{7.E.24}$$

- [Glucose]$_{\text{initial}}$ = 0.05M
- [Glucose]$_{\text{equilibrium}}$ = 0.01M

S7.22

K_C = (0.04M/1M)/(0.01M/1M)=4.0

delta G^O = -8.3145J/Kmole *(25+273.15)K*ln 4.0=-3.44 *10^3kJ/mol

Q7.23

Calculate the $\Delta_rG^{o/}$ of a certain biochemical reaction that involves the exchange of 2 electrons and where $E^{o/}$ = 3.25 V

S7.23

$$\Delta_r G^{\circ\prime} = -vFE^{\circ\prime} \tag{7.E.25}$$

$$\Delta_r G^{\circ\prime} = -(2)(96500C\, mol^{-1})(3.25V) \tag{7.E.26}$$

$$\Delta_r G^{\circ\prime} = -627kJ\, mol^{-1} \tag{7.E.27}$$

Q7.25

In intestinal epithelial cells, transport of lactose across a membrane is coupled with the transport of 2 H^+ ions from a high to low concentration.

$$\Delta_r G^{\circ'} = 16.2kJ \qquad \psi = -0.15V \tag{7.E.28}$$

How much will the pH change across the membrane at 298 K and 1 atm be if one lactose molecule is transported?

Hint: What is the change in Gibbs Free Energy for the movement of $2H^+$ across this membrane? Write this as an expression as a function of change in pH.

S7.25

When we consider the chemical potential of a single H^+

$$\mu_{H^+} = \mu^\circ_{H^+} + RTln[H^+] + Fz\psi \tag{7.E.29}$$

- z = the ion charge
- F = Faraday constant
- \psi = electrical potential

$$pH = -log[H^+] \tag{7.E.30}$$

$$ln[H^+] = -2.3log[H^+] = -2.3pH \tag{7.E.31}$$

$$\mu_{H^+} = \mu^\circ_{H^+} - 2.3RTpH + F\psi \tag{7.E.32}$$

Change in Gibbs free energy is defined as the initial and final chemical potentials, or:

$$\Delta_r G = \mu_{H^+(low)} - \mu_{H^+(high)} \tag{7.E.33}$$

$$= -2.3RT\Delta pH + F\Delta\psi \tag{7.E.34}$$

As a function of change in pH, the equation can be written as

$$\Delta pH = \frac{\Delta_r G - F\Delta\psi}{-2.3RT} \tag{7.E.35}$$

Since this equation describes chemical potential across a membrane for a H^+ ions, the sign for change in Gibbs free energy should be opposite that of the transport lactose, or -16.2 KJ. Setting change in electric potential as -0.15 V and converting 12.7 KJ to J

$$\Delta pH = \frac{-16200J - (96500\frac{C}{mol})(-0.15V)}{(298K)(-2.3)(8.3145\frac{J}{K\cdot mol})} \tag{7.E.36}$$

$$= 0.30 \tag{7.E.37}$$

Q7.28

You are studying muscle cells. You notice inside the muscle there is 255 mM of Li+ and 16 mM of Rb+ and there is 58 Mm of Li+ and 249 mM of Rb+ outside the cell. From this information, decide if the membrane is more permeable to Li+ or Rb+.

S7.28

$\Delta E_{Rb^+} = 0.0257V ln \frac{[Rb^+]_{ex}}{[Rb^-]_{in}}$

$= 0.0275(1) ln \frac{16}{249}$

=-0.075

$\Delta E_{Li^+} = 0.0257V ln \frac{[Li^+]_{ex}}{[Li^-]_{in}}$

$= 0.0275(1) ln \frac{255}{58}$

=0.0407

So Rb^+ has a greater magnitude so the membrane is more permeable to it

Q7.29

Calculate the membrane potential of a cell that has [K+]out = 8 and [K+]in = 200. Assume standard temperature of 298 K.

Q7.30

Find E° for:
Cu^{2+} + e- -> Cu+
K+ + e- -> K
How can E° be used to find Ksp?

Q7.30a

Given the values of E° for the following reactions:

$Ag^+ + e^-$ → Ag E° = +0.851 V

AgCl + e^- → Ag + Cl^- E° = +0.222 V

Determine the solubility product (K_{sp}) of AgCl at 23.5°C.

Q7.30b

Given the half-reduction reaction:

$$Fe^{3+} + 3e^- \rightarrow Fe \tag{7.E.38}$$

$$FeCl_3 + e^- \rightarrow Fe + 3Cl^- \tag{7.E.39}$$

Calculate the K_{sp} of $FeCl_3$ at 298 K

Q7.31

Given the following reaction at pH 7.0:

$$CH_3COOH + CO_{2(g)} + 2H^+ + 2e^- \rightarrow CH_3COCOOH + H_2O \tag{7.E.40}$$

a. Write down the reaction that produces H^+ ion in term of E^o
b. Calculate the concentration of $CH_3COCOOH$ at 25^{o}C. Given the emf of the cell is -0.70 V.

Q7.31

A certain reaction in solution has provides H^+ ions and has an $E^°$ of .48V. If a calomel electrode is placed in solution (as part of a pH meter) and has an E_{ref} of .11 V. Find the pH of the solution.

S7.31

$$pH = \frac{E - E_{ref}}{0.0591V} \tag{7.E.41}$$

$$pH = \frac{.37V}{0.0591V} \tag{7.E.42}$$

$$pH = 6.26 \tag{7.E.43}$$

Q7.32a

If a since and iron block were to be exposed for an extended period of time, which would rust first?

S7.32a

Zinc is a more electropositive metal with a reduction potential of -0.762 V while iron has a reduction potential of -0.447 V. Since Zinc is more electropositive, it will be more likely to be oxidized so it will rust first.

Q7.32b

Aluminum is used widely to be a better protective metal than lead because it forms a corrosion resistance layer in most of environments. Explain this using Standard Reduction Potentials values?

Q7.34

The $\Delta r S^o$ of the Daniell cell is found to be $-26.8 JK^{-1} mol^{-1}$. Given this value at $95^o C$ calculate the emf of the cell and the temperature coefficient.

S7.34

Step 1: (Hint: $\Delta r S^o$ is directly related to temperature coefficient.)

$$\Delta r S^o = vF(\frac{\partial E^o}{\partial})_P \tag{7.E.44}$$

$$\Delta r S^o = vF(\frac{\partial E^o}{\partial T})_P = \frac{\Delta r S^o}{vF} = \frac{-26.8 JK^{-1}\, mol^{-1}}{2(96500 C\, mol^{-1})} = -1.38860 \times 10^{-4} vK^{-1} \tag{7.E.45}$$

Step 2:

$$\frac{\partial E^o}{\partial})_P = \frac{E^o_{369.15K} - E^o_{298.15K}}{368.15 - 298.15K} = \frac{E^o_{368.15K - 1.104V}}{70K} = 1.39 \times 10^{-4} VK^{-1} \tag{7.E.46}$$

$$E^o_{268.15K} = 1.094V \tag{7.E.47}$$

Q7.36

Calculate the equilibrium constant for the following reaction:

$$FeCl_2 \rightleftharpoons Fe^{2+} + 2Cl^- \tag{7.E.48}$$

(Hint: look up the reduction potential for the half reactions)

S7.36

Half reactions are

$$\begin{aligned} Fe &\rightarrow Fe^{2+} + 2e^- \\ &\varepsilon^\circ = 0.44V(this - is - oxidation) \\ Cl_2 + 2e^- &\rightarrow 2Cl^- \\ &\varepsilon^\circ = 1.36V(this - is - reduction) \end{aligned}$$

$$\varepsilon^\circ = \varepsilon^\circ_{cathode} - \varepsilon^\circ_{anode} = 1.36V - 0.44V = 0.92V$$

$$K = e^{\frac{vF\varepsilon^\circ}{RT}} = e^{\frac{(96500C/mol)(0.92V)}{(8.314J/K*mol)(298.15K)}} = 3.58 * 10^{15}$$

S7.36

$$\begin{aligned} Anode: 2K \rightarrow 2K^+ + 2e^- \\ \varepsilon^\circ = 5.84V \\ Cathode: 2H^+ 2e^- \rightarrow H_2 \\ \varepsilon^\circ = 0V \end{aligned}$$

$$\varepsilon^\circ = \varepsilon^\circ_{cathode} - \varepsilon^\circ_{anode} = -5.84V$$

$$\Delta_r \bar{G}^\circ = -vF\varepsilon^\circ = 2\Delta_f \bar{G}^\circ[K^+] + \Delta_f \bar{G}^\circ[H_2] - 2\Delta_f \bar{G}^\circ[K] - 2\Delta_f \bar{G}^\circ[H^+]$$

$$\begin{aligned} \Delta_f \bar{G}^\circ[K^+] &= -\frac{1}{2} vF\varepsilon^\circ - \frac{1}{2}\Delta_f \bar{G}^\circ[H_2] + \Delta_f \bar{G}^\circ[K] + \Delta_f \bar{G}^\circ[H^+] \\ &= -\frac{1}{2}(2)(96500C/mol)(-5.84V) - \frac{1}{2}(0kJ/mol) + (0kJ/mol) + (0kJ/mol) = 5.6 * 10^5 J/mol \end{aligned}$$

Q7.36

Do you expect a high Kw value at 276 K or 373 K? Explain.

S7.36

We expect a higher Kw value for 373 K.

Q7.38a

What is the the reaction for a solution with Au_3^++3e^- $^{\rightarrow}$Au and Ag^++e^- →Ag

S7.38a

The first thing we do is look at the standard reduction potentials table. We see that the reduction potential is higher for Au3+ so that will be the one that gets reduced. This means we reverse the reaction for Ag+.

$$Au^{3+} + 3e^- \rightarrow Au \tag{7.E.49}$$

3x(Ag→Ag^++e^-) we need the charges to add up to zero so we multiply it by 3 so there will be 3 electrons here as well

We end up with:

$$Au^{3+} + 3Ag \rightarrow Au + 3Ag^+ \tag{7.E.50}$$

Q7.38b

The magnitudes of the standard electrode potentials of two metals, A and B, are

A^{2+} + 2e^- → A |E°| = 0.63 V

B^{2+} + 2e^- →B |E°| = 1.24 V

Where the | | notation denotes that only the magnitude (but not the sign) of the E° value is shown. When the half-cells of A and B are connected, electrons flow from A to B. When A is connected to a SHE, electrons flow from A to SHE. (a) What are the signs for each of the E°? (b) What is the standard emf of a cell made up of A and B?

Q7.38c

The electrochemical properties of a pair of newly discovered metals, Q and G, are being studied in a lab. Their associated reduction reactions are shown below. A lab technician collecting the data makes a mistake, and does not record the sign of the standard potential for the half-cells in their notes. However, he remembers that when he connected the cell containing Q to the standard hydrogen electrode, the Q electrode was oxidized, and when he connected G to the standard hydrogen electrode, it was reduced. What are the signs of the standard potentials for the half-cells? When the two half-cells are connected, what is the electromotive force of the complete Q/G cell?

\[Q^+ + e^- -> Q= 0.38 V \]

\[G^+ + e^- -> G = 0.72 V \]

Q7.39

Consider a galvanic (voltaic) cell with silver wire suspended in 0.5M Ag^+ solution and a cobalt wire in 1.0M Co^{2+} solution. Write out the half cell reactions and overall reaction to find the cell's equilibrium constant and observed emf.

Hint: Look at examples of setting up half reactions

S7.39

Half cell reactions:

$$Cathode: \quad 2[Ag^{+}(aq)+e^{-}\rightarrow Ag(s)] \tag{7.E.51}$$

$$Anode: \quad Co(s)\rightarrow Co^{2+}(aq)+2e^{-} \tag{7.E.52}$$

$$Overall: \quad 2Ag^{+}(aq)+Co(s)\rightarrow 2Ag(s)+Co^{2+}(aq) \tag{7.E.53}$$

$$E^{\circ}=0.800\,V-(-.277\,V)=+1.077\,V \tag{7.E.54}$$

$$E^{\circ}=\frac{RT}{vF}lnK \tag{7.E.55}$$

$$+1.077\,V=\frac{8.314\frac{J}{K\cdot mol}(298K)}{(2)(26485)\frac{C}{mol}}lnK \tag{7.E.56}$$

$$K=2.51\times 10^{36} \tag{7.E.57}$$

$$E=E^{\circ}-\frac{RT}{v}ln\frac{[Co^{2+}]}{[Ag^{+}]}=+1.077V-\frac{0.0257V}{2}ln\frac{1.0M}{0.5M} \tag{7.E.58}$$

$$E=+1.068\,V \tag{7.E.59}$$

Q7.40a

Answer the following questions about aluminum:

a. Given that the standard electrical potential of Al^{3+} is -1.662, why does aluminum tarnish in air?
b. Would the the following reaction be spontaneous?

$$2Al+3Br_2\rightarrow Al_2Br_6 \tag{7.E.60}$$

c. Predict the reaction between aluminum and chloride gas.

Hint: look up values for E˚and appropriate half reactions.

S7.40a

(a) Silver tarnishes in air because the reduction potential for oxygen is high enough that it oxidizes aluminum.

$$E^{\circ}_{cell}=E^{\circ}_{cathode}-E^{\circ}_{anode} \tag{7.E.61}$$

$$E^{\circ}_{cell}=E^{\circ}_{oxygen}-E^{\circ}_{aluminum} \tag{7.E.62}$$

$$E^{\circ}_{cell}=1.23\ V\ -(-1.662\ V)>0 \tag{7.E.63}$$

Since E˚ > 0, then $\triangle_r G$ is less than zero (since $\triangle_r G$ = -vFE). Thus the reaction is spontaneous and aluminum will be oxidized (tarnish) in contact with air.

(b) Find the appropriate half reactions to fulfill the equation.

$$2Al+3Br_2\ \rightarrow Al_2Br_6\ (1) \tag{7.E.64}$$

$$Al^{3+}\ +3e^{-}\ \rightarrow Al,\ where\ E^{\circ}_{Al}=-1.662 \tag{7.E.65}$$

$$Br_2+2e^{-}\ \rightarrow 2Br^{-},\ where\ E^{\circ}_{Br}=+1.087 \tag{7.E.66}$$

Multiply both sides by the appropriate integer to fulfill equation (1).

$$-2\ times\ Al^{3+}\ +3e^{-}\ \rightarrow Al,\ where\ E^{\circ}_{Al}=-1.662 \tag{7.E.67}$$

$$3\ times\ Br_2+2e^{-}\ \rightarrow 2Br^{-},\ where\ E^{\circ}_{Br}=+1.087 \tag{7.E.68}$$

Switching around the half reactions you should achieve the following, which matches up to the equation (1).

$$2Al+3Br_2+6e^{-}\rightarrow 2Al^{3+}\ +6Br^{-}\ +6e^{-} \tag{7.E.69}$$

Use the equation to find the E˚. Keep in mind cathodes are reduced in the half reaction (you want the electrons to be on the left hand side of the half reaction after balancing) and anodes are oxidized in the half reaction (electrons on the right). Also note how standard reduction potential is an intrinsic property so there is no need to multiply by molar coefficients represented in the balanced equation.

$$\begin{aligned} E^\circ_{cell} &= E^\circ_{cathode} - E^\circ_{anode} \qquad (7.E.70) \\ E^\circ_{cell} &= E^\circ_{bromide} - E^\circ_{aluminum} \qquad (7.E.71) \\ E^\circ_{cell} &= (1.087\ V) - (-1.662\ V) > 0 \qquad (7.E.72) \\ E^\circ_{cell} &= 2.749\ V \qquad (7.E.73) \end{aligned}$$

Since $E^\circ > 0$, then $\triangle_r G$ is less than zero (since $\triangle_r G = -\nu FE$). Thus the reaction is spontaneous.

(c)$2Al + 3Cl_2 \rightarrow 2AlCl_3$ since Al^{3+} is aluminum's most stable form and Cl^-. Then it's a matter of balancing the equation.

Check here for additional information on Redox Chemistry.

Q7.40b

Using the electrochemical principle to explain how the reduction potential for oxygen is not adequate to oxidize the gold metal.

Q7.40c

Answer the following questions for the half-reaction below and E°[Pt|O_2,H_2O] = 1.229 V.

$Fe^{2+}(aq) + e^- \rightarrow Fe(s)$ E° = -0.447 V

(a) Predict whether or not iron will rust in air.

(b) Will the following half-reaction have a positive E°? (E°[Pt|Fe^{3+},Fe^{2+}] = 0.771 V)

$$Fe(s) \rightarrow Fe^{3+}(aq) + 3e^-$$

(c) Predict the reaction between iron and bromine gas (E°[Br_2] = 1.087 V)

Q7.40d

The standard reduction potential for Platinum, Pt, is as follows:

$$Pt^{2+} + 2e^- \rightarrow Pt_{(s)} \qquad E^\circ = +1.2V \tag{7.E.74}$$

a. Platinum is often used as a metal in fine jewelry because it does not tarnish noticeably. Why is this the case?
b. Based on the above standard reduction potential, will the following reaction be spontaneous,

$$Pt^{2+} + Cl^{2-} \rightarrow PtCl_4^{2-} \tag{7.E.75}$$

given that

$$PtCl_4^{2-} + 2e^- \rightarrow Pt_{(s)} + 4Cl^- \qquad E^\circ = +0.73V \tag{7.E.76}$$

c.) Gold is also used as a metal in fine jewelry. Based on your answer to part (a.) and the standard reduction potential for gold Au^{3+}, E°= 1.69, does gold tarnish?

S7.40d

a.) Platinum does not tarnish, or oxidize, very quickly in air since its reduction potential is only slightly lower than that of oxygen. Thus, any oxidation which does occur does so very slowly.

$$O_2 + 4H^+ + 4e^- \rightarrow H_2O \qquad E^\circ = +1.229V \tag{7.E.77}$$

b.) If the reaction has a positive standard reduction potential, then it is spontaneous. The reaction can be broken up into two half reactions whose values are provided.

$$Pt_{(s)} + 4Cl^- \rightarrow PtCl_4^{2-} + 2e^- \qquad E^\circ = -0.73V \tag{7.E.78}$$

$$Pt^{2+} + 2e^- \rightarrow Pt_{(s)} \qquad E^\circ = +1.2V \tag{7.E.79}$$

$$Pt^{2+} + Cl^{2-} \rightarrow PtCl_4^{2-} \tag{7.E.80}$$

so the standard reduction potential is:

$$E^o = -0.73V + 1.2V = +0.47V \tag{7.E.81}$$

Thus, the reaction is spontaneous.

c.) No. Since the standard reduction potential of gold is greater than that of oxygen, oxygen cannot spontaneously react with gold and oxidize it.

Q7.41

In figure 7.1 we observe a voltaic cell. Here the anode is oxidized (loss of electrons) and the cathode is reduced (gains electrons). The Zinc metal loses electron and Zn (s) becomes Zn $^{2+}$ ions. Explain how the Cu^{2+} ions become solid Copper.

Q7.42a

In the following reaction at 298K,

$$Ca_{(s)} + 2H^{+} \rightarrow\leftarrow Ca_{(aq)} + H_{2(g)} \tag{7.E.82}$$

Calculate the pressure of H_2 in bar to maintain equilibrium. The concentration of \([Ca^{2+}]=0.026M and the pH of the solution is buffered at 1.60 pH.

S7.42a

Step1:

$$Anode: Ca^{+2} \rightarrow Ca^{+2} + 2e^{-} \tag{7.E.83}$$

$$Cathode: 2H^{+} + 2e^{-} \rightarrow H_2 \tag{7.E.84}$$

$$E^{o} = 0V - (-0.34) = 0.34 \tag{7.E.85}$$

Step 2: EMF calculation

$$E = E^{o} - \frac{0.0257V}{v} ln \frac{[Ca^{+2}]P_{H_2}}{[H^{+}]^{2}} \tag{7.E.86}$$

$From\ the\ pH, [H^{+}] = 10^{-1.60} = 2.51 \times 10^{-2} M$

At E=0,

$$0 = 0.34 - \frac{0.0257V}{2} ln \frac{(0.026)P_{H2}}{(2.51 \times 10^{-2})^{2}} \tag{7.E.87}$$

$$P_{H_2} = 7.5 \times 10^{9} bar \tag{7.E.88}$$

Q7.42b

For the reaction at 300K:

$$Mg(s) + 2H^{+}(aq) \rightleftharpoons Mg^{2+}(aq) + H_2(g) \tag{7.E.89}$$

Given pressure following the reaction is 296.07 atm, and molarity of acid used is 0.025M. Compute the molarity of the $Mg^{2+.}$

Q7.44a

For the ion Sn^{2+}, use the electric potential table to determine the value of $\Delta f \bar{G}^{o}$.

S7.44a

$$Sn^{2+}_{(aq)} + 2e^{-} \rightarrow Sn_{(s)} \tag{7.E.90}$$

$$E^{o} = -0.137 \tag{7.E.91}$$

$Anode: Sn_{(s)} \rightarrow Sn^{2+} + 2e^{-}$

$Cathode: 2H^{+}_{(aq)} + 2e^{-} \rightarrow H_{2(g)}$

Overall Equation,

$$Sn_{(s)} + 2H^{+}_{(aq)} \rightarrow Sn^{2+}_{(aq)} + H_2 \quad E^{o} = 0.137V \tag{7.E.92}$$

$$\Delta rG^{o} = -vFE^{o} = \Delta_f \bar{G}^{o}[Sn^{2+}_{(aq)}] + \Delta_f \bar{G}^{o}[H_{2(g)}] - \Delta_f \bar{G}^{o}[Sn_{(s)}] - 2\Delta_f \bar{G}^{o}[H^{+}_{(aq)}] \tag{7.E.93}$$

$$-(2)(96500C\,mol^{-1})(0.137V) = \Delta_f\bar{G}^o[Sn^{2+}_{(aq)}] + 0kjmol^{-1} - 0kjmol^{-1} - 2(0kjmol^{-1}) \tag{7.E.94}$$

$$\Delta_f\bar{G}^o[Sn^{2+}_{(aq)}] = -2.6\times10^4\,J\,mol^{-1} \tag{7.E.95}$$

Q7.44b

Calculate the $\Delta_f\bar{G}^\circ$ for K^+ in the following reaction:

$$2K + 2H^+ \rightarrow 2K^+ + H_2 \tag{7.E.96}$$

Q7.46a

Determine the standard emf E^o for the following reaction (at 298 K and pH 0)

$I^-(aq) + H^+(aq) + Cr_2O_7^{2-}(aq) \rightarrow I_2(s) + Cr^{3+}(aq) + H_2O(l)$

Hint: Use standard change in free energy of formation and use the relationship between G^o and E^o

S7.46a

$$oxidation: 6I^-(aq) \rightarrow 3I_2 + 6e^- \tag{7.E.97}$$

$$reduction: 6e^- + 14H^+(aq) + Cr_2O7^{-2}(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l) \tag{7.E.98}$$

$$Overall: 6I^-(aq) + 14H^+(aq) + Cr_2O7^{-2}(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O + 3I_2(s) \tag{7.E.99}$$

$$\Delta_rG^\circ = 2\Delta_fG^\circ(Cr^{3+}) + 3\Delta_fG^\circ(I_2) + 7\Delta_fG^\circ(H_2O) - 6\Delta_fG^\circ(I^-) - 14\Delta_fG^\circ(H^+) - \Delta_fG^\circ(Cr_2O_7{}^{2-}) \tag{7.E.100}$$

$$\Delta_rG^\circ = [2(-214.2) + 3(0) + 7(-237.2) - 6(51.57) - 14(0) - (-1301.1)]\frac{kJ}{mol} = -1097.12\frac{kJ}{mol} \tag{7.E.101}$$

$$E^\circ = -\frac{\Delta_rG^\circ}{vF} = -\frac{-1097.12\frac{kJ}{mol}\times\frac{1000J}{1kJ}}{(6)(96500\frac{C}{mol})} = {\color{red}+1.89V} \tag{7.E.102}$$

Q7.46b

Calculate the ε° for the combustion of ethanol given that $\Delta_f\bar{G}^\circ_{ethanol} = -174.8kJ/mol.$

S7.46b

$$\begin{aligned} &Overall: C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O \\ &Anode: C_2H_5OH + 3H_2O \rightarrow 2CO_2 + 12H^+ + 12e^- \\ &Cathode: 3O_2 + 12H^+ + 12e^- \rightarrow 6H_2O \end{aligned}$$

$$\begin{aligned} \Delta_rG^\circ &= 2\Delta_f\bar{G}^\circ[CO_2] + 3\Delta_f\bar{G}^\circ[H_2O] - \Delta_f\bar{G}^\circ[C_2H_5OH] - 3\Delta_f\bar{G}^\circ[O_2] \\ &= 2(-394.4kJ/mol) + 3(-237.14kJ/mol) - (-174.8kJ/mol) - 3(0kJ/mol) \\ &= -1325.42kJ/mol \end{aligned}$$

$$\varepsilon^\circ = -\frac{\Delta_rG^\circ}{vF} = -\frac{-1325.42 * 10^3 J/mol}{(12)(96500C/mol)} = 1.145V$$

Q7.47a

Explain the biological significance of cytochromes by comparing the following half reaction in cytochrome c, a, or f vs. an electrode:

$$Fe^{3^+} + e^- \rightarrow Fe^{2^+} \tag{7.E.103}$$

S7.47a

For cytochrome c, E$^{\circ\,'}$ = +0.254

For Pt|Fe^{3+} , Fe^{2+}, E$^\circ$ = +0.771

Since cytochrome c has a smaller reduction potential, it makes it easier for for Iron to exist in both the oxidized form Fe^{3+} or the reduced form Fe^{2+}. This allows cytochromes to transfer electrons easily between other cytochromes in the electron transport chain. keep in mind that different cytochromes have slightly different reduction potentials.

See here more details about Electron Transfer Proteins.

Q7.47b

Practice

The standard reduction potential for the reduction of copper in aqueous solution is as follows:

$$Cu^{2+} + e^- \rightarrow Cu^+ \qquad E^\circ = +0.153V \tag{7.E.104}$$

In hemocyanin, the primary oxygen carrier in invertebrate blood, however, the standard reduction potential is:

$$Cu^{2+} + e^- \rightarrow Cu^+ \qquad E^{\circ'} = +0.540V \tag{7.E.105}$$

Why do these reduction potentials differ?

S7.47b

The standard reduction potential is used to measure the readiness with which an atom may be reduced at standard conditions (25 ^{o}C, 1 atm, reactants at 1M). In biological half-reactions, standard reduction potentials differ because the process cannot occur at standard concentrations. $E^{o'}$ occurs at pH 7, as opposed to pH 0, the reference point for electrode half reactions. To obtain a more intuitive understanding, we may use the Nernst equation:

$$E^{o'} = E^o - \frac{RT}{\gamma F} \ln \frac{[Cu^+]}{[Cu^{2+}]} \tag{7.E.106}$$

At a higher pH, more electrons are found in solution, due to the formation of Hydrogen ions. By le chatelier's principle, this pushes the above half reaction forward so that the concentration of Cu^{2+} is greater than that of Cu^+. This makes the value produced by the natural log negative. Thus. $E^{o'}$ is greater than E^o at higher pH.

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CHAPTER OVERVIEW

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CHAPTER OVERVIEW

9: Chemical Kinetics

Chemical kinetics is the study of the speed with which a *chemical* reaction occurs and the factors that affect this speed. This information is especially useful for determining how a reaction occurs.

Topic hierarchy

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9.1: Reaction Rates

In this Module, the quantitative determination of a reaction rate is demonstrated. Reaction rates can be determined over particular time intervals or at a given point in time. A rate law describes the relationship between reactant rates and reactant concentrations. Reaction rates are usually expressed as the concentration of reactant consumed or the concentration of product formed per unit time. The units are thus moles per liter per unit time, written as M/s, M/min, or M/h. To measure reaction rates, chemists initiate the reaction, measure the concentration of the reactant or product at different times as the reaction progresses, perhaps plot the concentration as a function of time on a graph, and then calculate the change in the concentration per unit time.

Figure $9.1.1$ The Progress of a Simple Reaction (A → B). The mixture initially contains only A molecules (purple). Over time, the number of A molecules decreases and more B molecules (green) are formed (top). The graph shows the change in the number of A and B molecules in the reaction as a function of time over a 1 min period (bottom).

The progress of a simple reaction (A → B) is shown in Figure $9.1.1$; the beakers are snapshots of the composition of the solution at 10 s intervals. The number of molecules of reactant (A) and product (B) are plotted as a function of time in the graph. Each point in the graph corresponds to one beaker in Figure $9.1.1$. The reaction rate is the change in the concentration of either the reactant or the product over a period of time. The concentration of A decreases with time, while the concentration of B increases with time.

$$\text{rate} = \frac{\Delta[\text{B}]}{\Delta t} = -\frac{\Delta[\text{A}]}{\Delta t} \tag{9.1.1}$$

Square brackets indicate molar concentrations, and the capital Greek delta (Δ) means "change in." Because chemists follow the convention of expressing all reaction rates as positive numbers, however, a negative sign is inserted in front of Δ[A]/Δt to convert that expression to a positive number. The reaction rate calculated for the reaction A → B using Equation $9.1.1$ is different for each interval (this is not true for every reaction, as shown below). A greater change occurs in [A] and [B] during the first 10 s interval, for example, than during the last, meaning that the reaction rate is greatest at first.

> *Reaction rates generally decrease with time as reactant concentrations decrease.*

Study 1: The Hydrolysis of Aspirin

We can use Equation $9.1.1$ to determine the reaction rate of hydrolysis of aspirin, probably the most commonly used drug in the world (more than 25,000,000 kg are produced annually worldwide). Aspirin (acetylsalicylic acid) reacts with water (such as water in body fluids) to give salicylic acid and acetic acid, as shown in Figure $9.1.2$.

Figure 9.1.2

Because salicylic acid is the actual substance that relieves pain and reduces fever and inflammation, a great deal of research has focused on understanding this reaction and the factors that affect its rate. Data for the hydrolysis of a sample of aspirin are in Table 9.1.1 and are shown in the graph in Figure 9.1.3. These data were obtained by removing samples of the reaction mixture at the indicated times and analyzing them for the concentrations of the reactant (aspirin) and one of the products (salicylic acid).

Table 9.1.1: Data for Aspirin Hydrolysis in Aqueous Solution at pH 7.0 and 37°C*

Time (h)	[Aspirin] (M)	[Salicylic Acid] (M)
0	5.55×10^{-3}	0
2.0	5.51×10^{-3}	0.040×10^{-3}
5.0	5.45×10^{-3}	0.10×10^{-3}
10	5.35×10^{-3}	0.20×10^{-3}
20	5.15×10^{-3}	0.40×10^{-3}
30	4.96×10^{-3}	0.59×10^{-3}
40	4.78×10^{-3}	0.77×10^{-3}
50	4.61×10^{-3}	0.94×10^{-3}
100	3.83×10^{-3}	1.72×10^{-3}
200	2.64×10^{-3}	2.91×10^{-3}
300	1.82×10^{-3}	3.73×10^{-3}

*The reaction at pH 7.0 is very slow. It is much faster under acidic conditions, such as those found in the stomach.

The **average reaction rate** for a given time interval can be calculated from the concentrations of either the reactant or one of the products at the beginning of the interval (time = t_0) and at the end of the interval (t_1). Using salicylic acid, the reaction rate for the interval between t = 0 h and t = 2.0 h (recall that change is always calculated as final minus initial) is calculated as follows:

$$\text{rate}_{(t=0-2.0\text{ h})} = \frac{[\text{salicylic acid}]_2 - [\text{salicylic acid}]_0}{2.0\text{ h} - 0\text{ h}} \tag{9.1.2}$$

$$= \frac{0.040 \times 10^{-3}\text{ M} - 0\text{ M}}{2.0\text{ h}} = 2.0 \times 10^{-5}\text{ M/h} \tag{9.1.3}$$

The reaction rate can also be calculated from the concentrations of aspirin at the beginning and the end of the same interval, remembering to insert a negative sign, because its concentration decreases:

$$\text{rate}_{(t=0-2.0\text{ h})} = -\frac{[\text{aspirin}]_2 - [\text{aspirin}]_0}{2.0\text{ h} - 0\text{ h}} \tag{9.1.4}$$

$$= -\frac{(5.51 \times 10^{-3}\text{ M}) - (5.55 \times 10^{-3}\text{ M})}{2.0\text{ h}} \tag{9.1.5}$$

$$= 2 \times 10^{-5}\text{ M/h} \tag{9.1.6}$$

If the reaction rate is calculated during the last interval given in Table 9.1.1(the interval between 200 h and 300 h after the start of the reaction), the reaction rate is significantly slower than it was during the first interval (t = 0–2.0 h):

$$\text{rate}_{(t=200-300\text{h})} = \frac{[\text{salicyclic acid}]_{300} - [\text{salicyclic acid}]_{200}}{300\,\text{h} - 200\,\text{h}} \tag{9.1.7}$$

$$= -\frac{(3.73 \times 10^{-3}\ \text{M}) - (2.91 \times 10^{-3}\ \text{M})}{100\ \text{h}} \tag{9.1.8}$$

$$= 8.2 \times 10^{-6}\ \text{M/h} \tag{9.1.9}$$

Study 2: The Fermentation of Sucrose

In the preceding example, the stoichiometric coefficients in the balanced chemical equation are the same for all reactants and products; that is, the reactants and products all have the coefficient 1. Consider a reaction in which the coefficients are not all the same, the fermentation of sucrose to ethanol and carbon dioxide:

$$\underset{\text{sucrose}}{C_{12}H_{22}O_{11}(aq)} + H_2O(l) \rightarrow 4C_2H_5OH(aq) + 4CO_2(g) \tag{9.1.10}$$

The coefficients indicate that the reaction produces four molecules of ethanol and four molecules of carbon dioxide for every one molecule of sucrose consumed. As before, the reaction rate can be found from the change in the concentration of any reactant or product. In this particular case, however, a chemist would probably use the concentration of either sucrose or ethanol because gases are usually measured as volumes and the volume of CO_2 gas formed depends on the total volume of the solution being studied and the solubility of the gas in the solution, not just the concentration of sucrose. The coefficients in the balanced chemical equation tell us that the reaction rate at which ethanol is formed is always four times faster than the reaction rate at which sucrose is consumed:

$$\frac{\Delta[C_2H_5OH]}{\Delta t} = -\frac{4\Delta[\text{sucrose}]}{\Delta t} \tag{9.1.11}$$

The concentration of the reactant—in this case sucrose—*decreases* with time, so the value of Δ[sucrose] is negative. Consequently, a minus sign is inserted in front of Δ[sucrose] in Equation 9.1.11 so the rate of change of the sucrose concentration is expressed as a positive value. Conversely, the ethanol concentration *increases* with time, so its rate of change is automatically expressed as a positive value.

Often the reaction rate is expressed in terms of the reactant or product with the smallest coefficient in the balanced chemical equation. The smallest coefficient in the sucrose fermentation reaction (Equation 9.1.10) corresponds to sucrose, so the reaction rate is generally defined as follows:

$$\text{rate} = -\frac{\Delta[\text{sucrose}]}{\Delta t} = \frac{1}{4}\left(\frac{\Delta[C_2H_5OH]}{\Delta t}\right) \tag{9.1.12}$$

✓ Example 9.1.1

Consider the thermal decomposition of gaseous N_2O_5 to NO_2 and O_2 via the following equation:

$$2N_2O_5(g) \xrightarrow{\Delta} 4NO_2(g) + O_2(g)$$

Write expressions for the reaction rate in terms of the rates of change in the concentrations of the reactant and each product with time.

Given: balanced chemical equation

Asked for: reaction rate expressions

Strategy:

A. Choose the species in the equation that has the smallest coefficient. Then write an expression for the rate of change of that species with time.
B. For the remaining species in the equation, use molar ratios to obtain equivalent expressions for the reaction rate.

Solution

A Because O_2 has the smallest coefficient in the balanced chemical equation for the reaction, define the reaction rate as the rate of change in the concentration of O_2 and write that expression.

B The balanced chemical equation shows that 2 mol of N_2O_5 must decompose for each 1 mol of O_2 produced and that 4 mol of NO_2 are produced for every 1 mol of O_2 produced. The molar ratios of O_2 to N_2O_5 and to NO_2 are thus 1:2 and 1:4, respectively. This means that the rate of change of $[N_2O_5]$ and $[NO_2]$ must be divided by its stoichiometric coefficient to obtain equivalent expressions for the reaction rate. For example, because NO_2 is produced at four times the rate of O_2, the rate of production of NO_2 is divided by 4. The reaction rate expressions are as follows:

$$\text{rate} = \frac{\Delta[\text{O}_2]}{\Delta t} = \frac{\Delta[\text{NO}_2]}{4\Delta t} = -\frac{\Delta[\text{N}_2\text{O}_5]}{2\Delta t}$$

Exercise 9.1.1

The key step in the industrial production of sulfuric acid is the reaction of SO_2 with O_2 to produce SO_3.

$$2SO_{2(g)} + O_{2(g)} \rightarrow 2SO_{3(g)} \tag{9.1.13}$$

Write expressions for the reaction rate in terms of the rate of change of the concentration of each species.

Answer

$$\text{rate} = -\frac{\Delta[\text{O}_2]}{\Delta t} = -\frac{\Delta[\text{SO}_2]}{2\Delta t} = \frac{\Delta[\text{SO}_3]}{2\Delta t}$$

Example 9.1.2

Using the reaction shown in Example 9.1.1, calculate the reaction rate from the following data taken at 56°C:

$$2N_2O_{5(g)} \rightarrow 4NO_{2(g)} + O_{2(g)} \tag{9.1.14}$$

Time (s)	$[N_2O_5]$ (M)	$[NO_2]$ (M)	$[O_2]$ (M)
240	0.0388	0.0314	0.00792
600	0.0197	0.0699	0.0175

Given: balanced chemical equation and concentrations at specific times

Asked for: reaction rate

Strategy:

A. Using the equations in Example 9.1.1, subtract the initial concentration of a species from its final concentration and substitute that value into the equation for that species.
B. Substitute the value for the time interval into the equation. Make sure your units are consistent.

Solution

A Calculate the reaction rate in the interval between t_1 = 240 s and t_2 = 600 s. From Example 9.1.1, the reaction rate can be evaluated using any of three expressions:

$$\text{rate} = \frac{\Delta[\text{O}_2]}{\Delta t} = \frac{\Delta[\text{NO}_2]}{4\Delta t} = -\frac{\Delta[\text{N}_2\text{O}_5]}{2\Delta t}$$

Subtracting the initial concentration from the final concentration of N_2O_5 and inserting the corresponding time interval into the rate expression for N_2O_5,

$$\text{rate} = -\frac{\Delta[\text{N}_2\text{O}_5]}{2\Delta t} = -\frac{[\text{N}_2\text{O}_5]_{600} - [\text{N}_2\text{O}_5]_{240}}{2(600\text{ s} - 240\text{ s})}$$

B Substituting actual values into the expression,

$$\text{rate} = -\frac{0.0197\text{ M} - 0.0388\text{ M}}{2(360\text{ s})} = 2.65 \times 10^{-5}\text{ M/s}$$

Similarly, NO_2 can be used to calculate the reaction rate:

$$\text{rate} = \frac{\Delta[\text{NO}_2]}{4\Delta t} = \frac{[\text{NO}_2]_{600} - [\text{NO}_2]_{240}}{4(600\text{ s} - 240\text{ s})} = \frac{0.0699\text{ M} - 0.0314\text{ M}}{4(360\text{ s})} = 2.67 \times 10^{-5}\text{ M/s} \tag{9.1.15}$$

Allowing for experimental error, this is the same rate obtained using the data for N_2O_5. The data for O_2 can also be used:

$$\text{rate} = \frac{\Delta[\text{O}_2]}{\Delta t} = \frac{[\text{O}_2]_{600} - [\text{O}_2]_{240}}{600\text{ s} - 240\text{ s}} = \frac{0.0175\text{ M} - 0.00792\text{ M}}{360\text{ s}} = 2.66 \times 10^{-5}\text{ M/s} \tag{9.1.16}$$

Again, this is the same value obtained from the N_2O_5 and NO_2 data. Thus, the reaction rate does not depend on which reactant or product is used to measure it.

? Exercise 9.1.2

Using the data in the following table, calculate the reaction rate of $SO_2(g)$ with $O_2(g)$ to give $SO_3(g)$.

$$2SO_{2(g)} + O_{2(g)} \rightarrow 2SO_{3(g)} \tag{9.1.17}$$

Time (s)	$[SO_2]$ (M)	$[O_2]$ (M)	$[SO_3]$ (M)
300	0.0270	0.0500	0.0072
720	0.0194	0.0462	0.0148

Answer 9.0×10^{-6} M/s

Instantaneous Rates of Reaction

The **instantaneous rate** of a reaction is the reaction rate at any given point in time. As the period of time used to calculate an average rate of a reaction becomes shorter and shorter, the average rate approaches the instantaneous rate. Comparing this to calculus, the instantaneous rate of a reaction at a given time corresponds to the slope of a line tangent to the concentration-versus-time curve at that point—that is, the derivative of concentration with respect to time.

$$rate = \lim_{\Delta t \to 0} \frac{-\Delta[R]}{\Delta t} = -\frac{d[R]}{dt} \tag{9.1.18}$$

The distinction between the instantaneous and average rates of a reaction is similar to the distinction between the actual speed of a car at any given time on a trip and the average speed of the car for the entire trip. Although the car may travel for an extended period at 65 mph on an interstate highway during a long trip, there may be times when it travels only 25 mph in construction zones or 0 mph if you stop for meals or gas. The average speed on the trip may be only only 50 mph, whereas the instantaneous speed on the interstate at a given moment may be 65 mph. Whether the car can be stopped in time to avoid an accident depends on its instantaneous speed, not its average speed. There are important differences between the speed of a car during a trip and the speed of a chemical reaction, however. The speed of a car may vary unpredictably over the length of a trip, and the initial part of a trip is often one of the slowest. In a chemical reaction, the initial interval typically has the fastest rate (though this is not always the case), and the reaction rate generally changes smoothly over time.

> *Chemical kinetics generally focuses on one particular instantaneous rate, which is the initial reaction rate, t = 0. Initial rates are determined by measuring the reaction rate at various times and then extrapolating a plot of rate versus time to t = 0.*

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9.2: Reaction Order

The kinetic theory of gases can be used to model the frequency of collisions between hard-sphere molecules, which is proportional to the reaction rate. Most systems undergoing a chemical reaction, however, are much more complex. The reaction rates may be dependent on specific interactions between reactant molecules, the phase(s) in which the reaction takes place, etc. The field of chemical kinetics is thus by-and-large based on empirical observations. From experimental observations, scientists have established that reaction rates almost always have a power-law dependence on the concentrations of one or more of the reactants. In the following sections, we will discuss different power laws that are commonly observed in chemical reactions.

0^{th} Order Reaction Kinetics

Consider a closed container initially filled with chemical species A. At $t=0$, a stimulus, such as a change in temperature, the addition of a catalyst, or irradiation, causes an irreversible chemical reaction to occur in which A transforms into product B:

$$a\mathrm{A} \longrightarrow b\mathrm{B} \tag{9.2.1}$$

The rate that the reaction proceeds, r, can be described as the change in the concentrations of the chemical species with respect to time:

$$r=-\frac{1}{a}\frac{d[\mathrm{A}]}{dt}=\frac{1}{b}\frac{d[\mathrm{B}]}{dt} \tag{9.2.2}$$

where $[\mathrm{X}]$ denotes the molar concentration of chemical species X with units of $\frac{\mathrm{mol}}{\mathrm{L}^3}$.

Let us first examine a reaction $\mathrm{A} \longrightarrow \mathrm{B}$ in which the reaction rate, r, is constant with time:

$$r=-\frac{d[\mathrm{A}]}{dt}=k \tag{9.2.3}$$

where k is a constant, also known as the rate constant with units of $\frac{\mathrm{mol}}{\mathrm{m}^3\mathrm{s}}$. Such reactions are called zeroth order reactions because the reaction rate depends on the concentrations of species A and B to the 0^{th} power. Integrating $[\mathrm{A}]$ with respect to T, we find that

$$[\mathrm{A}]=-kt+c_1 \tag{9.2.4}$$

At $t=0$, $[\mathrm{A}](0)=[\mathrm{A}]_0$. Plugging these values into the equation, we find that $c_1=[\mathrm{A}]_0$. The final form of the equation is:

$$[\mathrm{A}]=[\mathrm{A}]_0-kt \tag{9.2.5}$$

A plot of the concentration of species A with time for a 0^{th} order reaction is shown in Figure $9.2.1$, where the slope of the line is $-k$ and the y-intercept is $[\mathrm{A}]_0$. Such reactions in which the reaction rates are independent of the concentrations of products and reactants are rare in nature. An example of a system displaying 0^{th} order kinetics would be one in which a reaction is mediated by a catalyst present in small amounts.

1^{st} Order Reaction Kinetics

Experimentally, it is observed than when a chemical reaction is of the form

$$\sum_i \nu_i \mathrm{A}_i=0 \tag{9.2.6}$$

the reaction rate can be expressed as

$$r=k\prod_{\text{reactants}}[\mathrm{A}_i]^{\nu_i} \tag{9.2.7}$$

where it is assumed that the stoichiometric coefficients ν_i of the reactants are all positive. Thus, or a reaction $\mathrm{A} \longrightarrow \mathrm{B}$, the reaction rate depends on $[\mathrm{A}]$ raised to the first power:

$$r=\frac{d[\mathrm{A}]}{dt}=-k[\mathrm{A}] \tag{9.2.8}$$

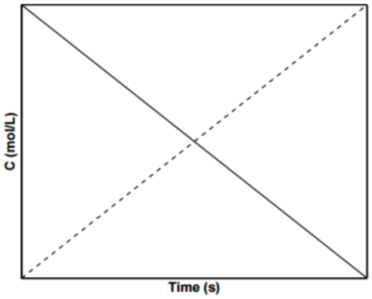

Figure 9.2.1: Plots of $[\mathrm{A}]$ (solid line) and $[\mathrm{B}]$ (dashed line) over time for a 0^{th} order reaction.

For first order reactions, k has the units of $\frac{1}{\mathrm{s}}$. Integrating and applying the condition that at $t = 0$ s, $[\mathrm{A}] = [\mathrm{A}]_0$, we arrive at the following equation:

$$[\mathrm{A}] = [\mathrm{A}]\, e^{-kt} \tag{9.2.9}$$

Figure $9.2.2$ displays the concentration profiles for species A and B for a first order reaction. To determine the value of k from experimental data, it is convenient to take the natural log of Equation 9.2.9:

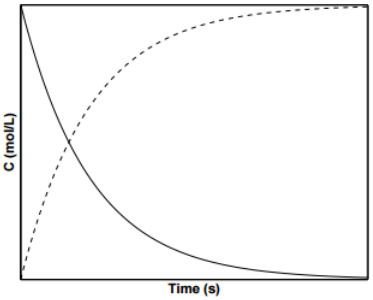

Figure 9.2.2: Plots of $[\mathrm{A}]$ (solid line) and $[\mathrm{B}]$ (dashed line) over time for a 1^{st} order reaction.

$$\ln([\mathrm{A}]) = \ln([\mathrm{A}]_0) - kt \tag{9.2.10}$$

For a first order irreversible reaction, a plot of $\ln([\mathrm{A}])$ vs. t is straight line with a slope of $-k$ and a y-intercept of $\ln([\mathrm{A}]_0)$.

2^{nd} Order Reaction Kinetics

Another type of reaction depends on the square of the concentration of species A - these are known as second order reactions. For a second order reaction in which $2\mathrm{A} \longrightarrow \mathrm{B}$, we can write the reaction rate to be

$$r = -\frac{1}{2}\frac{d[\mathrm{A}]}{dt} = k[\mathrm{A}]^2 \tag{9.2.11}$$

For second order reactions, k has the units of $\frac{\mathrm{m}^3}{\mathrm{mol} \cdot \mathrm{s}}$. Integrating and applying the condition that at $t = 0$ s, $[\mathrm{A}] = [\mathrm{A}]_0$, we arrive at the following equation for the concentration of A over time:

$$[\mathrm{A}] = \frac{1}{2kt + \frac{1}{[\mathrm{A}]_0}} \tag{9.2.12}$$

Figure $9.2.3$ shows concentration profiles of A and B for a second order reaction. To determine k from experimental data for

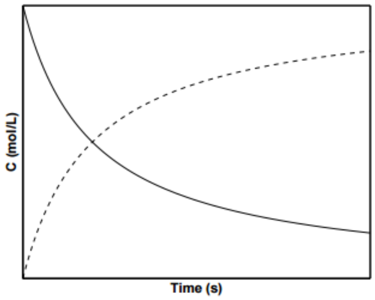

Figure 9.2.3: Plots of $[\mathrm{A}]$ (solid line) and $[\mathrm{B}]$ (dashed line) over time for a 2^{nd} order reaction.

second-order reactions, it is convenient to invert Equation 9.2.12:

$$\frac{1}{[\mathrm{A}]}=\frac{1}{[\mathrm{A}]_0}+2kt \tag{9.2.13}$$

A plot of $1/[\mathrm{A}]$ vs. t will give rise to a straight line with slope k and intercept $1/[\mathrm{A}]_0$.

Second order reaction rates can also apply to reactions in which two species react with each other to form a product:

$$\mathrm{A}+\mathrm{B}\xrightarrow{k}\mathrm{C} \tag{9.2.14}$$

In this scenario, the reaction rate will depend on the concentrations of both A and B to the first order:

$$r=-\frac{d[\mathrm{A}]}{dt}=-\frac{d[\mathrm{B}]}{dt}=k[\mathrm{A}][\mathrm{B}] \tag{9.2.15}$$

To integrate the above equation, we need to write it in terms of one variable. Since the concentrations of A and B are related to each other via the chemical reaction equation, we can write:

$$[\mathrm{B}]=[\mathrm{B}]_0-([\mathrm{A}]_0-[\mathrm{A}])=[\mathrm{A}]+[\mathrm{B}]_0-[\mathrm{A}]_0 \tag{9.2.16}$$

$$\frac{d[\mathrm{A}]}{dt}=-k[\mathrm{A}]([\mathrm{A}]+[\mathrm{B}]_0-[\mathrm{A}]_0) \tag{9.2.17}$$

We can then use partial fractions to integrate:

$$kdt=\frac{d[\mathrm{A}]}{[\mathrm{A}]([\mathrm{A}]+[\mathrm{B}]_0-[\mathrm{A}]_0)}=\frac{1}{[\mathrm{B}]_0-[\mathrm{A}]_0}\left(\frac{d[\mathrm{A}]}{[\mathrm{A}]}-\frac{d[\mathrm{A}]}{[\mathrm{B}]_0-[\mathrm{A}]_0+[\mathrm{A}]}\right) \tag{9.2.18}$$

$$kt=\frac{1}{[\mathrm{A}]_0-[\mathrm{B}]_0}\ln\frac{[\mathrm{A}][\mathrm{B}]_0}{[\mathrm{B}][\mathrm{A}]_0} \tag{9.2.19}$$

Figure 9.2.4 displays the concentration profiles of species A, B, and C for a second order reaction in which the initial concentrations of A and B are not equal.

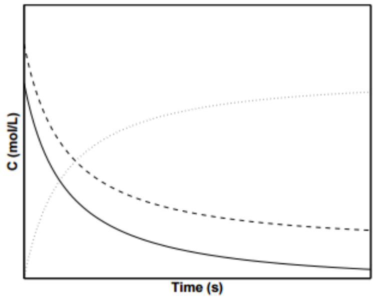

Figure 9.2.4: Plots of $[\mathrm{A}]$ (solid line), $[\mathrm{B}]$ (dashed line) and $[\mathrm{C}]$ (dotted line) over time for a 2^{nd} order reaction in which the initial concentrations of the reactants, $[\mathrm{A}]_0$ and $[\mathrm{B}]_0$, are not equal.

Contributors and Attributions

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9.3: Molecularity of a Reaction

In general, it is necessary to experimentally measure the concentrations of species over time in order to determine the apparent rate law governing the reaction. If the reactions are elementary reactions, (i.e. they cannot be expressed as a series of simpler reactions), then we can directly define the rate law based on the chemical equation. For example, an elementary reaction in which a single reactant transforms into a single product, is unimolecular reaction. These reactions follow 1^{st} order rate kinetics. An example of this type of reaction would be the isomerization of butane:

$$nC_4H_{10} \longrightarrow iC_4H_{10} \tag{9.3.1}$$

From the chemical reaction equation, we can directly write the rate law as

$$\frac{d\left[nC_4H_{10}\right]}{dt} = -k\left[nC_4H_{10}\right] \tag{9.3.2}$$

without the need to carry out experiments.

Elementary bimolecular reactions that involve two molecules interacting to form one or more products follow second order rate kinetics. An example would be the following reaction between a nitrate molecule and carbon monoxide to form nitrogen dioxide and carbon dioxide:

$$NO_3 + CO \longrightarrow NO_2 + CO_2 \tag{9.3.3}$$

For the above elementary reaction, we can directly write the rate law as:

$$\frac{d\left[NO_3\right]}{dt} = -k\left[NO_3\right]\left[CO\right] \tag{9.3.4}$$

Trimolecular elementary reactions involving three reactant molecules to form one or more products are rare due to the low probability of three molecules simultaneously colliding with one another.

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9.4: More Complex Reactions

A major goal in chemical kinetics is to determine the sequence of elementary reactions, or the reaction mechanism, that comprise complex reactions. For example, Sherwood Rowland and Mario Molina won the Nobel Prize in Chemistry in 1995 for proposing the elementary reactions involving chlorine radicals that contribute to the overall reaction of $O_3 \rightarrow O_2$ in the troposphere. In the following sections, we will derive rate laws for complex reaction mechanisms, including reversible, parallel and consecutive reactions.

Parallel Reactions

Consider the reaction in which chemical species A undergoes one of two irreversible first order reactions to form either species B or species C :

$$\text{A} \xrightarrow{k_1} \text{B} \tag{9.4.1}$$

$$\text{A} \xrightarrow{k_2} \text{C} \tag{9.4.2}$$

The overall reaction rate for the consumption of A can be written as:

$$\frac{d[\text{A}]}{dt} = -k_1[\text{A}] - k_2[\text{A}] = -(k_1+k_2)[\text{A}] \tag{9.4.3}$$

Integrating $[\text{A}]$ with respect to t, we obtain the following equation:

$$[\text{A}] = [\text{A}]_0 e^{-(k_1+k_2)t} \tag{9.4.4}$$

Plugging this expression into the equation for $\frac{d[\text{B}]}{dt}$, we obtain:

$$\frac{d[\text{B}]}{dt} = k_1[\text{A}] = k_1[\text{A}]_0 e^{-(k_1+k_2)t} \tag{9.4.5}$$

Integrating $[\text{B}]$ with respect to t, we obtain:

$$[\text{B}] = -\frac{k_1[\text{A}]_0}{k_1+k_2}\left(e^{-(k_1+k_2)t}\right) + c_1 \tag{9.4.6}$$

At $t = 0$, $[\text{B}] = 0$. Therefore,

$$c_1 = \frac{k_1[\text{A}]_0}{k_1+k_2} \tag{9.4.7}$$

$$[\text{B}] = \frac{k_1[\text{A}]_0}{k_1+k_2}\left(1 - e^{-(k_1+k_2)t}\right) \tag{9.4.8}$$

Likewise,

$$[\text{C}] = \frac{k_2[\text{A}]_0}{k_1+k_2}\left(1 - e^{-(k_1+k_2)t}\right) \tag{9.4.9}$$

The ratio of $[\text{B}]$ to $[\text{C}]$ is simply:

$$\frac{[\text{B}]}{[\text{C}]} = \frac{k_1}{k_2} \tag{9.4.10}$$

An important parallel reaction in industry occurs in the production of ethylene oxide, a reagent in many chemical processes and also a major component in explosives. Ethylene oxide is formed through the partial oxidation of ethylene:

$$2\ C_2H_4 + O_2 \xrightarrow{k_1} 2\ C_2H_4O \tag{9.4.11}$$

However, ethylene can also undergo a combustion reaction:

$$C_2H_4 + 3\ O_2 \xrightarrow{k_2} 2\ CO_2 + 2\ H_2O \tag{9.4.12}$$

To select for the first reaction, the oxidation of ethylene takes place in the presence of a silver catalyst, which significantly increases k_1 compared to k_2. Figure $9.4.1$ displays the concentration profiles for species A, B, and C in a parallel reaction in which $k_1 > k_2$.

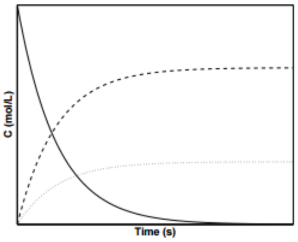

Figure $9.4.1$: Plots of $[\mathrm{A}]$ (solid line), $[\mathrm{B}]$ (dashed line) and $[\mathrm{C}]$ (dotted line) over time for a parallel reaction.

Consecutive Reactions

Consider the following series of first-order irreversible reactions, where species A reacts to form an intermediate species, I, which then reacts to form the product, P:

$$\mathrm{A} \xrightarrow{k_1} \mathrm{I} \xrightarrow{k_2} \mathrm{P} \tag{9.4.13}$$

We can write the reaction rates of species A, I and P as follows:

$$\frac{d\,[\mathrm{A}]}{dt} = -k_1\,[\mathrm{A}] \tag{9.4.14}$$

$$\frac{d\,[\mathrm{I}]}{dt} = k_1\,[\mathrm{A}] - k_2\,[\mathrm{I}] \tag{9.4.15}$$

$$\frac{d\,[\mathrm{P}]}{dt} = k_2\,[\mathrm{I}] \tag{9.4.16}$$

As before, integrating $[\mathrm{A}]$ with respect to t leads to:

$$[\mathrm{A}] = [\mathrm{A}]_0 e^{-k_1 t} \tag{9.4.17}$$

The concentration of species I can be written as

$$[\mathrm{I}] = \frac{k_1\,[\mathrm{A}]_0}{k_2 - k_1}\left(e^{-k_1 t} - e^{-k_2 t}\right) \tag{9.4.18}$$

Then, solving for $[\mathrm{P}]$, we find that:

$$[\mathrm{P}] = [\mathrm{A}]_0\left[1 + \frac{1}{k_1 - k_2}\left(k_2 e^{-k_1 t} - k_1 e^{-k_2 t}\right)\right] \tag{9.4.19}$$

Figure $9.4.2$ displays the concentration profiles for species A, I, and P in a consecutive reaction in which $k_1 = k_2$. As can be seen from the figure, the concentration of species I reaches a maximum at some time, t_{max}. Oftentimes, species I is the desired product. Returning to the oxidation of ethylene into ethylene oxide, it is important to note another reaction in which ethylene oxide can decompose into carbon dioxide and water through the following reaction

$$C_2H_4O + \frac{5}{2}\,O_2 \xrightarrow{k_3} 2\,CO_2 + 2\,H_2O \tag{9.4.20}$$

Thus, to maximize the concentration of ethylene oxide, the oxidation of ethylene is only allowed proceed to partial completion before the reaction is stopped.

Finally, in the limiting case when $k_2 \gg k_1$, we can write the concentration of P as

$$[\mathrm{P}] \approx [\mathrm{A}]_0\left\{1 + \frac{1}{-k_2} k_2 e^{-k_1 t}\right\} = [\mathrm{A}]_0\left(1 - e^{-k_1 t}\right) \tag{9.4.21}$$

Thus, when $k_2 \gg k_1$, the reaction can be approximated as $\mathrm{A} \rightarrow \mathrm{P}$ and the apparent rate law follows 1^{st} order kinetics.

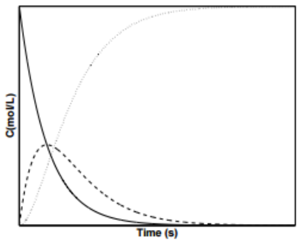

Figure 9.4.2: Plots of $[\mathrm{A}]$ (solid line), $[\mathrm{I}]$ (dashed line) and $[\mathrm{P}]$ (dotted line) over time for consecutive first order reactions.

Consecutive Reactions With an Equilibrium

Consider the reactions

$$\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{I} \xrightarrow{k_2} \mathrm{P} \tag{9.4.22}$$

We can write the reaction rates as:

$$\frac{d[\mathrm{A}]}{dt} = -k_1[\mathrm{A}] + k_{-1}[\mathrm{I}] \tag{9.4.23}$$

$$\frac{d[\mathrm{I}]}{dt} = k_1[\mathrm{A}] - k_{-1}[\mathrm{I}] - k_2[\mathrm{I}] \tag{9.4.24}$$

$$\frac{d[\mathrm{P}]}{dt} = k_2[\mathrm{I}] \tag{9.4.25}$$

The exact solutions of these is straightforward, in principle, but rather involved, so we will just state the exact solutions, which are

$$[\mathrm{A}](t) = \frac{[\mathrm{A}]_0}{2\lambda}\left[(\lambda - k_1 + K)\,e^{-(k_1+K-\lambda)t/2} + (\lambda + k_1 - K)\,e^{-(k_1+K+\lambda)t/2}\right] \tag{9.4.26}$$

$$[\mathrm{I}](t) = \frac{k_1[\mathrm{A}]_0}{\lambda}\left[e^{-(k_1+K-\lambda)t/2} - e^{-(k_1+K+\lambda)t/2}\right] \tag{9.4.27}$$

$$[\mathrm{P}](t) = 2k_1k_2[\mathrm{A}]_0\left[\frac{2}{(k_1+K)^2 - \lambda^2} - \frac{1}{\lambda}\left(\frac{e^{-(k_1+K-\lambda)t/2}}{k_1+K-\lambda} - \frac{e^{-(k_1+K+\lambda)t/2}}{k_1+K+\lambda}\right)\right] \tag{9.4.28}$$

where

$$K = k_2 + k_{-1} \tag{9.4.29}$$

$$\lambda = \sqrt{(k_1 - K)^2 - 4k_1k_{-1}} \tag{9.4.30}$$

Steady-State Approximations

Consider the following consecutive reaction in which the first step is reversible:

$$\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{I} \xrightarrow{k_2} \mathrm{P} \tag{9.4.31}$$

We can write the reaction rates as:

$$\frac{d[\mathrm{A}]}{dt} = -k_1[\mathrm{A}] + k_{-1}[\mathrm{I}] \tag{9.4.32}$$

$$\frac{d[\mathrm{I}]}{dt} = k_1[\mathrm{A}] - k_{-1}[\mathrm{I}] - k_2[\mathrm{I}] \tag{9.4.33}$$

$$\frac{d[\mathrm{P}]}{dt} = k_2[\mathrm{I}] \tag{9.4.34}$$

These equations can be solved explicitly in terms of $[\mathrm{A}]$, $[\mathrm{I}]$, and $[\mathrm{P}]$, but the math becomes very complicated quickly. If, however, $k_2 + k_{-1} \gg k_1$ (in other words, the rate of consumption of I is much faster than the rate of production of I), we can make the approximation that the concentration of the intermediate species, I, is small and constant with time:

$$\frac{d\,[\mathrm{I}]}{dt} \approx 0 \tag{9.4.35}$$

Equation 21.22 can now be written as

$$\frac{d\,[\mathrm{I}]}{dt} = k_1\,[\mathrm{A}] - k_{-1}\,[\mathrm{I}]_{ss} - k_2\,[\mathrm{I}]_{ss} \approx 0 \tag{9.4.36}$$

where $[\mathrm{I}]_{ss}$ is a constant represents the steady state concentration of intermediate species, $[\mathrm{I}]$. Solving for $[\mathrm{I}]_{ss}$,

$$[\mathrm{I}]_{ss} = \frac{k_1}{k_{-1} + k_2}[\mathrm{A}] \tag{9.4.37}$$

We can then write the rate equation for species A as

$$\frac{d\,[\mathrm{A}]}{dt} = -k_1\,[\mathrm{A}] + k_{-1}\,[\mathrm{I}]_{ss} = -k_1\,[\mathrm{A}] + k_{-1}\frac{k_1}{k_{-1} + k_2}[\mathrm{A}] = -\frac{k_1 k_2}{k_{-1} + k_2}[\mathrm{A}] \tag{9.4.38}$$

Integrating,

$$[\mathrm{A}] = [\mathrm{A}]_0 e^{-\frac{k_1 k_2}{k_{-1} + k_2}t} \tag{9.4.39}$$

Equation 21.28 is the same equation we would obtain for apparent 1^{st} order kinetics of the following reaction:

$$\mathrm{A} \xrightarrow{k'} \mathrm{P} \tag{9.4.40}$$

where

$$k' = \frac{k_1 k_2}{k_{-1} + k_2} \tag{9.4.41}$$

Figure $9.4.3$ displays the concentration profiles for species, A, I, and P with the condition that $k_2 + k_{-1} \gg k_1$. These types of reaction kinetics appear when the intermediate species, I, is highly reactive.

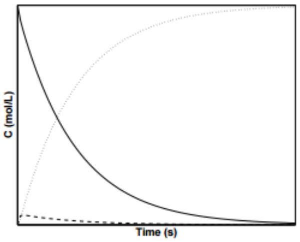

Figure $9.4.3$: Plots of $[\mathrm{A}]$ (solid line), $[\mathrm{I}]$ (dashed line) and $[\mathrm{P}]$ (dotted line) over time for $k_2 + k_{-1} \gg k_1$.

Lindemann Mechanism

Consider the isomerization of methylisonitrile gas, CH_3NC, to acetonitrile gas, CH_3CN:

$$CH_3NC \xrightarrow{k} CH_3CN \tag{9.4.42}$$

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:

$$\frac{d\,[CH_3NC]}{dt} = -k[CH_3NC]^2 \tag{9.4.43}$$

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

$$\mathrm{A}+\mathrm{M} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{A}^{*}+\mathrm{M} \tag{9.4.44}$$

$$\mathrm{A}^{*} \xrightarrow{k_2} \mathrm{B} \tag{9.4.45}$$

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:

$$\frac{d\left[\mathrm{A}^{*}\right]}{dt} = k_1[\mathrm{A}][\mathrm{M}] - k_{-1}\left[\mathrm{A}^{*}\right]_{ss}[\mathrm{M}] - k_2\left[\mathrm{A}^{*}\right]_{ss} \approx 0 \tag{9.4.46}$$

Solving for $[\mathrm{A}^{*}]$,

$$\left[\mathrm{A}^{*}\right] = \frac{k_1[\mathrm{M}][\mathrm{A}]}{k_2 + k_{-1}[\mathrm{M}]} \tag{9.4.47}$$

The reaction rates of species A and B can be written as

$$-\frac{d[\mathrm{A}]}{dt} = \frac{d[\mathrm{B}]}{dt} = k_2\left[\mathrm{A}^{*}\right] = \frac{k_1 k_2[\mathrm{M}][\mathrm{A}]}{k_2 + k_{-1}[\mathrm{M}]} = k_{\mathrm{obs}}[\mathrm{A}] \tag{9.4.48}$$

where

$$k_{\mathrm{obs}} = \frac{k_1 k_2[\mathrm{M}]}{k_2 + k_{-1}[\mathrm{M}]} \tag{9.4.49}$$

At high pressures, we can expect collisions to occur frequently, such that $k_{-1}[\mathrm{M}] \gg k_2$. Equation 21.33 then becomes

$$-\frac{d[\mathrm{A}]}{dt} = \frac{k_1 k_2}{k_{-1}}[\mathrm{A}] \tag{9.4.50}$$

which follows 1^{st} order rate kinetics.

At low pressures, we can expect collisions to occurs infrequently, such that $k_{-1}[\mathrm{M}] \ll k_2$. In this scenario, equation 21.33 becomes

$$-\frac{d[\mathrm{A}]}{dt} = k_1[\mathrm{A}][\mathrm{M}] \tag{9.4.51}$$

which follows second order rate kinetics, consistent with experimental observations.

Equilibrium Approximations

Consider again the following consecutive reaction in which the first step is reversible:

$$\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{I} \xrightarrow{k_2} \mathrm{P} \tag{9.4.52}$$

Now let us consider the situation in which $k_2 \ll k_1$ and k_{-1}. In other words, the conversion of I to P is slow and is the *rate-limiting step*. In this situation, we can assume that $[\mathrm{A}]$ and $[\mathrm{I}]$ are in equilibrium with each other. As we derived before for a reversible reaction in equilibrium,

$$K_{\mathrm{eq}} = \frac{k_1}{k_{-1}} \approx \frac{[\mathrm{I}]}{[\mathrm{A}]} \tag{9.4.53}$$

or, in terms of $[\mathrm{I}]$,

$$[\mathrm{I}] = K_{\mathrm{eq}}[\mathrm{A}] \tag{9.4.54}$$

These conditions also result from the exact solution when we set $k_2 \approx 0$. When this is done, we have the approximate expressions from the exact solution:

$$
\begin{aligned}
K &\approx k_{-1} && (9.4.55)\\
\lambda &\approx \sqrt{\left(k_1-k_{-1}\right)^2+4k_1k_{-1}} = \sqrt{k_1^2+2k_1k_{-1}+k_{-1}^2} = k_1+k_{-1} && (9.4.56)\\
\lambda-k_1+K &\approx k_1+k_{-1}+k_1-k_{-1} = 2k_1 && (9.4.57)\\
\lambda+k_1-K &\approx k_1+k_{-1}+k_1-k_{-1} = 2k_1 && (9.4.58)\\
k_1+K-\lambda &\approx k_1+k_{-1}-k_1-k_{-1} = 0 && (9.4.59)\\
k_1+K+\lambda &\approx k_1+k_{-1}+k_1+k_{-1} = 2\left(k_1+k_{-1}\right) && (9.4.60)
\end{aligned}
$$

and the approximate solutions become

$$
\begin{aligned}
[\mathrm{A}](t) &= \frac{[\mathrm{A}]_0}{2\left(k_1+k_{-1}\right)}\left[2k_{-1}+2k_1e^{-\left(k_1+k_{-1}\right)t}\right] && (9.4.61)\\
[\mathrm{I}](t) &= \frac{k_1[\mathrm{A}]_0}{\left(k_1+k_{-1}\right)}\left[1-e^{-\left(k_1+k_{-1}\right)t}\right] && (9.4.62)
\end{aligned}
$$

In the long-time limit, when equilibrium is reached and transient behavior has decayed away, we find

$$\frac{[\mathrm{I}]}{[\mathrm{A}]} \equiv K_{\mathrm{eq}} \rightarrow \frac{k_1}{k_{-1}} \tag{9.4.63}$$

Plugging the above equation into the expression for $d[\mathrm{P}]/dt$,

$$\frac{d[\mathrm{P}]}{dt} = k_2[\mathrm{I}] = k_2K_{\mathrm{eq}}[\mathrm{A}] = \frac{k_1k_2}{k_{-1}}[\mathrm{A}] \tag{9.4.64}$$

The reaction can thus be approximated as a 1^{st} order reaction

$$\mathrm{A} \xrightarrow{k'} \mathrm{P} \tag{9.4.65}$$

with

$$k' = \frac{k_1k_2}{k_{-1}} \tag{9.4.66}$$

Figure 9.4.4 displays the concentration profiles for species, A, I, and P with the condition that $k_2 \ll k_1 = k_{-1}$. When $k_1 = k_{-1}$, we expect $[\mathrm{A}] = [\mathrm{I}]$. As can be seen from the figure, after a short initial startup time, the concentrations of species A and I are approximately equal during the reaction.

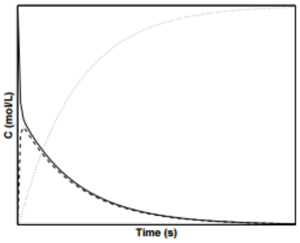

Figure 9.4.4: Plots of $[\mathrm{A}]$ (solid line), $[\mathrm{I}]$ (dashed line) and $[\mathrm{P}]$ (dotted line) over time for $k_2 \ll k_1 = k_{-1}$.

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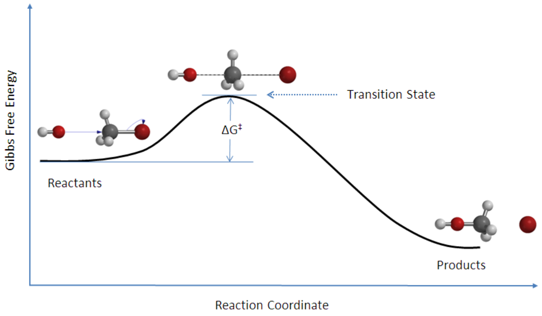
9.5: The Effect of Temperature on Reaction Rates

When molecules collide, the kinetic energy of the molecules can be used to stretch, bend, and ultimately break bonds, leading to chemical reactions. If molecules move too slowly with little kinetic energy, or collide with improper orientation, they do not react and simply bounce off each other. However, if the molecules are moving fast enough with a proper collision orientation, such that the kinetic energy upon collision is greater than the minimum energy barrier, then a reaction occurs. The minimum energy requirement that must be met for a chemical reaction to occur is called the activation energy, E_a.

Figure 9.5.1: In Greek mythology Sisyphus was punished by being forced roll an immense boulder up a hill, only to watch it roll back down, and to repeat this action forever. If this were a chemical reaction, then it would never be observed, since the reactants must overcome the energy barrier to get to the other side (products).

The reaction pathway is similar to what happens in Figure 9.5.1. To get to the other end of the road, an object must roll with enough speed to completely roll over the hill of a certain height. The faster the object moves, the more kinetic energy it has. If the object moves too slowly, it does not have enough kinetic energy necessary to overcome the barrier; as a result, it eventually rolls back down. In the same way, there is a minimum amount of energy needed in order for molecules to break existing bonds during a chemical reaction. If the kinetic energy of the molecules upon collision is greater than this minimum energy, then bond breaking and forming occur, forming a new product (provided that the molecules collide with the proper orientation).



Reaction: $HO^- + CH_3Br \rightarrow [HO{-}{-}{-}CH_3{-}{-}{-}Br]^\ddagger \rightarrow CH_3OH + Br^-$

Figure 9.5.2: Reaction coordinate diagram for the bimolecular nucleophilic substitution (S_N2) reaction between bromomethane and the hydroxide anion. from Wikipedia.

The activation energy (E_a), labeled $\Delta G^\ddagger$ in Figure 9.5.2, is the energy difference between the reactants and the activated complex, also known as transition state. In a chemical reaction, the transition state is defined as the highest-energy state of the system. If the molecules in the reactants collide with enough kinetic energy and this energy is higher than the transition state energy, then the reaction occurs and products form. In other words, the higher the activation energy, the harder it is for a reaction to occur and vice versa.

Overcoming the energy barrier from thermal energy involves addressing the fraction of the molecules that possess enough kinetic energy to react at a given temperature. According to kinetic molecular theory, a population of molecules at a given temperature is distributed over a variety of kinetic energies that is described by the Maxwell-Boltzman distribution law.

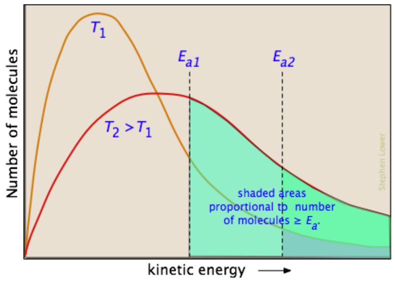
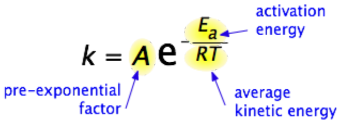


Figure 9.5.3 **:** Kinetic energy distributions (similar to Maxwell-Boltzman distributions for velocity) for a gas at two temperatures and critical energies for overcoming an activation barrier.

The two distribution plots shown here are for a lower temperature T_1 and a higher temperature T_2. The area under each curve represents the total number of molecules whose energies fall within particular range. The shaded regions indicate the number of molecules which are sufficiently energetic to meet the requirements dictated by the two values of E_a that are shown. It is clear from these plots that the fraction of molecules whose kinetic energy exceeds the activation energy increases quite rapidly as the temperature is raised. This the reason that virtually all chemical reactions (and all elementary reactions) proceed more rapidly at higher temperatures.

Arrhenius Equation

By 1890 it was common knowledge that higher temperatures speed up reactions, often doubling the rate for a 10-degree rise, but the reasons for this were not clear. Finally, in 1899, the Swedish chemist Svante Arrhenius (1859-1927) combined the concepts of activation energy and the Boltzmann distribution law into one of the most important relationships in physical chemistry:



$$k = A e^{-\frac{E_a}{RT}}$$

Take a moment to focus on the meaning of this equation, neglecting the *A* factor for the time being. First, note that this is another form of the exponential decay law discussed in the previous section of this series. What is "decaying" here is not the concentration of a reactant as a function of time, but the magnitude of the rate constant as a function of the exponent $–E_a/RT$. And what is the significance of this quantity? Recalling that *RT* is the *average kinetic energy*, it becomes apparent that the exponent is just the ratio of the activation energy E_a to the average kinetic energy. The larger this ratio, the smaller the rate (hence the negative sign). This means that high temperature and low activation energy favor larger rate constants, and thus speed up the reaction. Because these terms occur in an exponent, their effects on the rate are quite substantial.

Svante August Arrhenius

Svante August Arrhenius (19 February 1859 – 2 October 1927) was a Swedish scientist, originally a physicist, but often referred to as a chemist, and one of the founders of the science of physical chemistry. He received the Nobel Prize for Chemistry in 1903, becoming the first Swedish Nobel laureate, and in 1905 became director of the Nobel Institute where he remained until his death. The Arrhenius equation, Arrhenius definition of an acid, lunar crater Arrhenius, the mountain of Arrheniusfjellet and the Arrhenius Labs at Stockholm University are named after him. Today, Arrhenius is best known for his study published in 1896, on the greenhouse effect.

The two plots in Figure $9.5.4$ show the effects of the activation energy (denoted here by $E^{\ddagger}$) on the rate constant. Even a modest activation energy of 50 kJ/mol reduces the rate by a factor of 10^8.

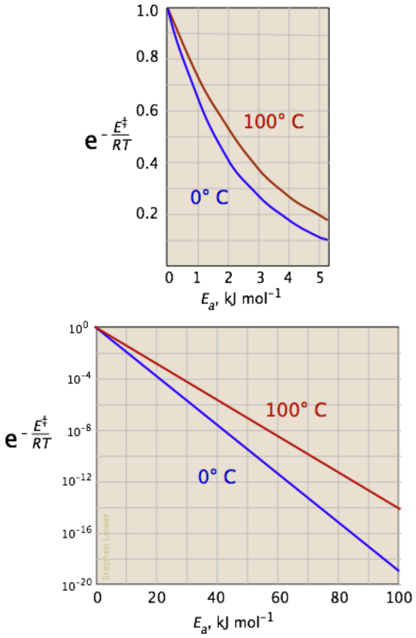


Figure $9.5.4$: Arrhenius plots. The logarithmic scale in the right-hand plot leads to nice straight lines.

Looking at the role of temperature, a similar effect is observed. (If the *x*-axis were in "kilodegrees" the slopes would be more comparable in magnitude with those of the kilojoule plot at the above right.)

Determining the activation energy

The Arrhenius equation

$$k = Ae^{-E_a/RT} \tag{9.5.1}$$

can be written in a non-exponential form that is often more convenient to use and to interpret graphically (Figure $9.5.4$). Taking the logarithms of both sides and separating the exponential and pre-exponential terms yields

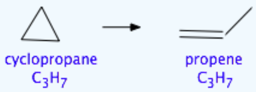
$$\ln k = \ln\left(Ae^{-E_a/RT}\right) = \ln A + \ln\left(e^{-E_a/RT}\right) \tag{9.5.2}$$

$$\ln k = \ln A + \frac{-E_a}{RT} = \left(\frac{-E_a}{R}\right)\left(\frac{1}{T}\right) + \ln A \tag{9.5.3}$$

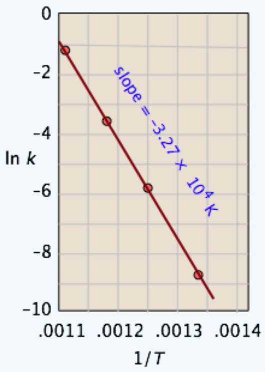
which is the equation of a straight line whose slope is $-E_a\ /R$. This affords a simple way of determining the activation energy from values of k observed at different temperatures, by plotting $\ln k$ as a function of $1/T$.

✓ Example $9.5.1$: Isomerization of Cyclopropane

For the isomerization of cyclopropane to propene,



the following data were obtained (calculated values shaded in pink):



T, °C	477	523	577	623
1/*T*, $K^{-1} \times 10^3$	1.33	1.25	1.18	1.11
k, s^{-1}	0.00018	0.0027	0.030	0.26
ln *k*	–8.62	–5.92	–3.51	–1.35

From the calculated slope, we have

$-(E_a/R) = -3.27 \times 10^4$ K

$E_a = -(8.314\ \text{J mol}^{-1}\ \text{K}^{-1})(-3.27 \times 10^4\ \text{K}) = 273\ \text{kJ mol}^{-1}$

This activation energy is high, which is not surprising because a carbon-carbon bond must be broken in order to open the cyclopropane ring. (C–C bond energies are typically around 350 kJ/mol.) This is why the reaction must be carried out at high temperature.

Calculating E_a without a plot

Because the ln *k* vs.-1/*T* plot yields a straight line, it is often convenient to estimate the activation energy from experiments at only two temperatures. The ln *A* term is eliminated by subtracting the expressions for the two ln-*k* terms via the following steps:

$$\ln k_1 = \ln A - \frac{E_a}{k_B T_1} \tag{9.5.4}$$

at T_1 and

$$\ln k_2 = \ln A - \frac{E_a}{k_B T_2} \tag{9.5.5}$$

at T_2. By rewriting the second equation:

$$\ln A = \ln k_2 + \frac{E_a}{k_B T_2} \tag{9.5.6}$$

and substitute for $\ln A$ into the first equation:

$$\ln k_1 = \ln k_2 + \frac{E_a}{k_B T_2} - \frac{E_a}{k_B T_1} \tag{9.5.7}$$

This simplifies to:

$$\ln k_1 - \ln k_2 = -\frac{E_a}{k_B T_1} + \frac{E_a}{k_B T_2} \tag{9.5.8}$$

$$\ln \frac{k_1}{k_2} = -\frac{E_a}{k_B}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{9.5.9}$$

Example 9.5.2

A widely used rule-of-thumb for the temperature dependence of a reaction rate is that a **ten degree** rise in the temperature approximately doubles the rate. This is not generally true, especially when a strong covalent bond must be broken. For a reaction that does show this behavior, what would the activation energy be?

Solution

Center the ten degree interval at 300 K. Substituting into the above expression yields

$$E_a = \frac{(8.314)(\ln 2/1)}{\frac{1}{295} - \frac{1}{305}} = \frac{(8.314)(0.693)}{0.00339 K^{-1} - 0.00328\ K^{-1}} \tag{9.5.10}$$

= (5.76 J mol^{-1} K^{-1}) / (0.00011 K^{-1}) = 52400 J mol^{-1} = **52.4 kJ mol^{-1}**

Example 9.5.3

It takes about 3.0 minutes to cook a hard-boiled egg in Los Angeles, but at the higher altitude of Denver, where water boils at 92°C, the cooking time is 4.5 minutes. Use this information to estimate the activation energy for the coagulation of egg albumin protein.

Solution

The ratio of the rate constants at the elevations of Los Angeles and Denver is 4.5/3.0 = 1.5, and the respective temperatures are 373 K and 365 K. With the subscripts 2 and 1 referring to Los Angeles and Denver respectively:

$$E_a = \frac{(8.314)(\ln 1.5)}{\frac{1}{365\text{ K}} - \frac{1}{373\text{ K}}} = \frac{(8.314)(0.405)}{0.00274\text{ K}^{-1} - 0.00268\text{ K}^{-1}} \tag{9.5.11}$$

$$= \frac{(3.37\text{ J mol}^{-1}\text{K}^{-1})}{5.87 \times 10^{-5}\text{ K}^{-1}} = 5740\text{ J mol}^{-1} = 5.73\text{ kJ mol}^{-1} \tag{9.5.12}$$

Comment: This low value seems reasonable because thermal denaturation of proteins primarily involves the disruption of relatively weak hydrogen bonds; no covalent bonds are broken (although disulfide bonds can interfere with this interpretation).

The pre-exponential factor

Up to this point, the pre-exponential term, *A* in the Arrhenius equation, has been ignored because it is not directly involved in relating temperature and activation energy, which is the main practical use of the equation.

$$k = Ae^{-E_a/RT}$$

However, because *A* multiplies the exponential term, its value clearly contributes to the value of the rate constant and thus of the rate. Recall that the exponential part of the Arrhenius equation expresses the fraction of reactant molecules that possess enough kinetic energy to react, as governed by the Maxwell-Boltzmann law. This fraction can run from zero to nearly unity, depending on the magnitudes of E_a and of the temperature.

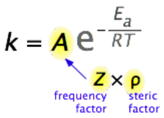
If this fraction were 0, the Arrhenius law would reduce to

$$k = A \tag{9.5.13}$$

In other words, A is the fraction of molecules that would react if either the activation energy were zero, or if the kinetic energy of all molecules exceeded E_a — admittedly, an uncommon scenario (although barrierless reactions have been characterized).

The Role of Collisions

What would limit the rate constant if there were no activation energy requirements? The most obvious factor would be the rate at which reactant molecules come into contact. This can be calculated from kinetic molecular theory and is known as the *frequency-* or *collision factor*, Z.



In some reactions, the relative orientation of the molecules at the point of collision is important, so a geometrical or *steric factor* (commonly denoted by ρ (Greek lower case *rho*) can be defined. In general, we can express A as the product of these two factors:

$$A = Z\rho \tag{9.5.14}$$

Values of ρ are generally very difficult to assess; they are sometime estimated by comparing the observed rate constant with the one in which A is assumed to be the same as Z. Usually, the more complex the reactant molecules, the lower the steric factors. The deviation from unity can have different causes: the molecules are not spherical, so different geometries are possible; not all the kinetic energy is delivered into the right spot; the presence of a solvent (when applied to solutions) and other factors (Figure 9.5.4).

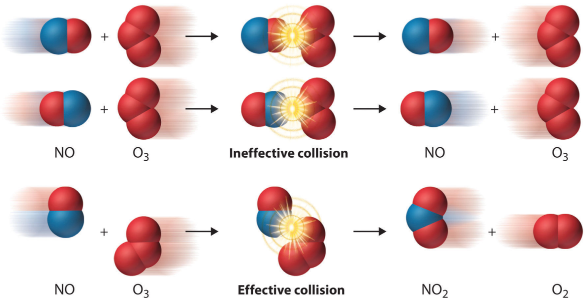


Figure 9.5.5: The Effect of Molecular Orientation on the Reaction of NO and O_3. Most collisions of NO and O_3 molecules occur with an incorrect orientation for a reaction to occur. Only those collisions in which the N atom of NO collides with one of the terminal O atoms of O_3 are likely to produce NO_2 and O_2, even if the molecules collide with $E > E_a$.

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9.6: Potential Energy Surfaces

A potential energy surface (PES) describes the potential energy of a system, especially a collection of atoms, in terms of certain parameters, normally the positions of the atoms. The surface might define the energy as a function of one or more coordinates; if there is only one coordinate, the surface is called a potential energy curve or energy profile. It is helpful to use the analogy of a landscape: for a system with two degrees of freedom (e.g. two bond lengths), the value of the energy (analogy: the height of the land) is a function of two bond lengths (analogy: the coordinates of the position on the ground). The Potential Energy Surface represents the concepts that each geometry (both external and internal) of the atoms of the molecules in a chemical reaction is associated with it a unique potential energy. This creates a smooth energy “landscape” and chemistry can be viewed from a topology perspective (of particles evolving over "valleys""and passes").

Potential Energy Curves (1-D Potential Energy Surfaces)

The PES is the energy of a molecule as a function of the positions of its nuclei r. This energy of a system of two atoms depends on the distance between them. At large distances the energy is zero, meaning “no interaction”. At distances of several atomic diameters attractive forces dominate, whereas at very close approaches the force is repulsive, causing the energy to rise. The attractive and repulsive effects are balanced at the minimum point in the curve. Plots that illustrate this relationship are quite useful in defining certain properties of a chemical bond.

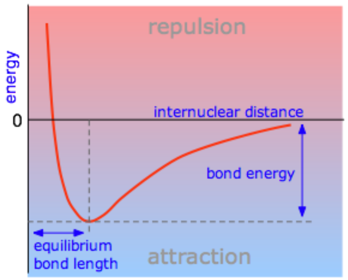

Figure 9.6.1: A potential Energy Curve for a covalent bond.

The internuclear distance at which the potential energy minimum occurs defines the **bond length**. This is more correctly known as the *equilibrium* bond length, because thermal motion causes the two atoms to vibrate about this distance. In general, the stronger the bond, the smaller will be the bond length.

Attractive forces operate between all atoms, but unless the potential energy minimum is at least of the order of *RT*, the two atoms will not be able to withstand the disruptive influence of thermal energy long enough to result in an identifiable molecule. Thus we can say that a chemical bond exists between the two atoms in H_2. The weak attraction between argon atoms does not allow Ar_2 to exist as a molecule, but it does give rise to the *van Der Waals force* that holds argon atoms together in its liquid and solid forms.

Potential, Kinetic, and Total Energy for a System

Potential energy and kinetic energy Quantum theory tells us that an electron in an atom possesses kinetic energy K as well as potential energy V, so the total energy E is always the sum of the two: $E = V + K$. The relation between them is surprisingly simple: $K = -0.5V$. This means that when a chemical bond forms (an exothermic process with $\Delta E < 0$), the decrease in potential energy is accompanied by an increase in the kinetic energy (embodied in the momentum of the bonding electrons), but the magnitude of the latter change is only half as much, so the change in potential energy always dominates. The bond energy $-\Delta E$ has half the magnitude of the fall in potential energy.

Mathematical definition and computation

The geometry of a set of atoms can be described by a vector, r, whose elements represent the atom positions. The vector r could be the set of the Cartesian coordinates of the atoms, or could also be a set of inter-atomic distances and angles. Given r, the energy as a function of the positions, $V(r)$, is the value of $V(r)$ for all values of r of interest. Using the landscape analogy from the introduction, $V(r)$ gives the height on the "energy landscape" so that the concept of a potential energy surface arises. An example is the PES for water molecule (Figure $9.6.1$) that show the energy minimum corresponding to optimized molecular structure for water- O-H bond length of 0.0958 nm and H-O-H bond angle of 104.5°

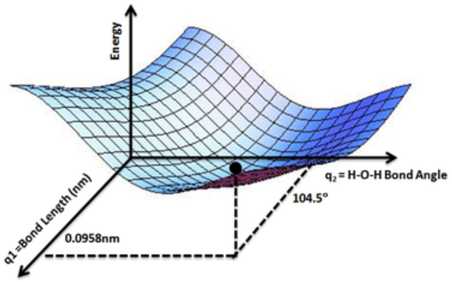

Figure 9.6.2: PES for water molecule: Shows the energy minimum corresponding to optimized molecular structure for water- O-H bond length of 0.0958nm and H-O-H bond angle of 104.5°. of Wikipedia (Credit: Aimnature).

The Dimensionality of a Potential Energy Surface

To define an atom's location in 3-dimensional space requires three coordinates (e.g., x, y,and z or r, θ and phi in Cartesian and Spherical coordinates) or *degrees of freedom*. However, a reaction and hence the corresponding PESs do not depend of the absolute position of the reaction, only the relative positions (internal degrees). Hence both translation and rotation of the entire system can be removed (each with 3 degree of freedom, assuming non-linear geometries). So the dimensionality of a PES is

$$3N-6 \tag{9.6.1}$$

where N is the number of atoms involves in the reaction, i.e., the number of atoms in each reactants). The PES is a hypersurface with many degrees of freedom and typically only a few are plotted at any one time for understanding. See Calculate Number of Vibrational Modes to get a more details picture of how this applies to calculating the number of vibrations in a molecule

To study a chemical reaction using the PES as a function of atomic positions, it is necessary to calculate the energy for **every atomic** arrangement of interest. Methods of calculating the energy of a particular atomic arrangement of atoms are well described in the computational chemistry article, and the emphasis here will be on finding approximations of $(V(r)$ to yield fine-grained energy-position information.

For very simple chemical systems or when simplifying approximations are made about inter-atomic interactions, it is sometimes possible to use an analytically derived expression for the energy as a function of the atomic positions. An example is

$$H + H_2 \rightarrow H_2 + H \tag{9.6.2}$$

system as a function of the **three** H-H distances. For more complicated systems, calculation of the energy of a particular arrangement of atoms is often too computationally expensive for large scale representations of the surface to be feasible.

Application of Potential Energy Surfaces

A PES is a conceptual tool for aiding the analysis of molecular geometry and chemical reaction dynamics. Once the necessary points are evaluated on a PES, the points can be classified according to the first and second derivatives of the energy with respect to position, which respectively are the gradient and the curvature. Stationary points (or points with a zero gradient) have physical meaning: energy minima correspond to physically stable chemical species and saddle points correspond to transition states, the highest energy point on the reaction coordinate (which is the lowest energy pathway connecting a chemical reactant to a chemical product). Three

- PES do not show kinetic energy, only potential energy.
- At T = 0 K (no KE), species will want to be at the lowest possible potential energy, (i.e., at a minimum on the PES).
- Between any two minima (valley bottoms) the lowest energy path will pass through a maximum at a **saddle point**, which we call that saddle point a transition-state structure.

The PES concept finds application in fields such as chemistry and physics, especially in the theoretical sub-branches of these subjects. It can be used to theoretically explore properties of structures composed of atoms, for example, finding the minimum energy shape of a molecule or computing the rates of a chemical reaction.

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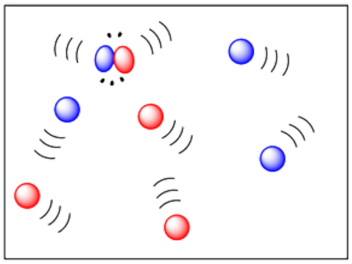
9.7: Theories of Reaction Rates

The macroscopic discussion of kinetics discussed in previous sections can be now expanded into a more microscopic picture in terms of molecular level properties (e..g, mass and velocities) involving two important theories: (1) collision theory and (2) transition-state theory.

Collision Theory

If two molecules need to collide in order for a reaction to take place, then factors that influence the ease of collisions will be important. The more energy there is available to the molecules, the faster they will move around, and the more likely they are to bump into each other. Higher temperatures ought to lead to more collisions and a greater frequency of reactions between molecules. In the drawing below, the cold, sluggish molecules on the left are not likely to collide, but the energetic molecules on the right are due to collide at any time.



The rate at which molecules collide which is the frequency of collisions is called the collision frequency, Z, which has units of collisions per unit of time. Given a container of molecules A and B, the collision frequency between A and B is defined by:

$$Z = N_A N_B \sigma_{AB} \sqrt{\frac{8 k_B T}{\pi \mu_{AB}}} \tag{9.7.1}$$

where:

- N_A and N_B are the numbers of molecules A and B, and is directly related to the concentrations of A and B.
- The mean speed of molecules obtained from the Maxwell-Boltzmann distribution for thermalized gases

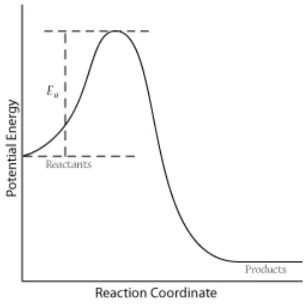
$$\sqrt{\frac{8 k_B T}{\pi \mu_{AB}}} \tag{9.7.2}$$

- σ_{AB} is the averaged sum of the collision cross-sections of molecules A and B. The collision cross section represents the collision region presented by one molecule to another.
- μ is the reduced mass and is given by

$$\mu = \frac{m_\mathrm{A} m_\mathrm{B}}{m_\mathrm{A} + m_\mathrm{B}} \tag{9.7.3}$$

The concepts of collision frequency can be applied in the laboratory: (1) The temperature of the environment affects the average speed of molecules. Thus, reactions are heated to increase the reaction rate. (2) The initial concentration of reactants is directly proportional to the collision frequency; increasing the initial concentration will speed up the reaction.

For a successful collision to occur, the reactant molecules must collide with enough kinetic energy to break original bonds and form new bonds to become the product molecules. This energy is called the activation energy for the reaction; it is also often referred to as the energy barrier.



The fraction of collisions with enough energy to overcome the activation barrier is given by:

$$f = e^{\frac{-E_a}{RT}} \tag{9.7.4}$$

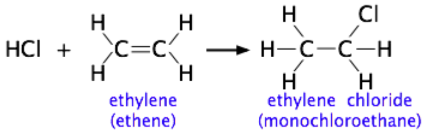
where:

- f is the fraction of collisions with enough energy to react
- E_a is the activation energy

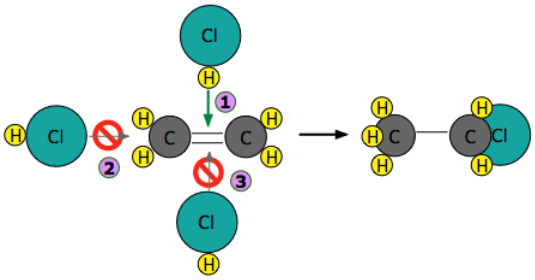
The fraction of successful collisions is directly proportional to the temperature and inversely proportional to the activation energy.

> The fraction of successful collisions is directly proportional to the temperature and inversely proportional to the activation energy.

The more complicated the structures of the reactants, the more likely that the value of the rate constant will depend on the trajectories at which the reactants approach each other. This kind of *electrophilic addition reaction* is well-known to all students of organic chemistry. Consider the addition of a hydrogen halide such as HCl to the double bond of an alkene, converting it to a chloroalkane.



Experiments have shown that the reaction only takes place when the HCl molecule approaches the alkene with its hydrogen-end, and in a direction that is approximately perpendicular to the double bond, as shown at ① below.



The reason for this becomes apparent when we recall that HCl is highly polar owing to the high electronegativity of chlorine, so that the hydrogen end of the molecule is slightly positive. The steric factor, ρ is then introduced to represent is the probability of the reactant molecules colliding with the right orientation and positioning to achieve a product with the desirable geometry and stereospecificity. Values of ρ are generally very difficult to assess and range from 0 to 1, but are sometime estimated by comparing the observed rate constant with the one in which the preexponential constant A is assumed to be the same as Z.

The lesson you should take from this example is that once you start combining a variety of chemical principles, you gradually develop what might be called "chemical intuition" which you can apply to a wide variety of problems. This is far more important than memorizing specific examples.

All Three Factors Combined

The rate constant of the gas-phase reaction is proportional to the product of the *collision frequency* and the *fraction of successful reactions*. As stated above, sufficient kinetic energy is required for a successful reaction; however, they must also collide properly. Compare the following equation to the Arrhenius equation:

$$k = Z\rho e^{\frac{-E_a}{RT}} \tag{9.7.5}$$

where

- k is the rate constant for the reaction
- ρ is the steric factor.
- Zρ is the pre-exponential factor, A, of the Arrhenius equation. It is the frequency of total collisions that collide with the right orientation. In practice, it is the pre-exponential factor that is directly determined by experiment and then used to calculate the steric factor.
- E_a is activation energy
- T is absolute temperature
- R is gas constant.

Although the collision theory deals with gas-phase reactions, its concepts can also be applied to reactions that take place in solvents; however, the properties of the solvents (for example: solvent cage) will affect the rate of reactions. Ultimately, collision theory illustrates how reactions occur; it can be used to approximate the rate constants of reactions, and its concepts can be directly applied in the laboratory. Read this for a more detailed discussion of Collision Theory.

Transition-State Theory

Transition state theory (TST) provides a more accurate alternative to the previously used Arrhenius equation and the collision theory. The transition state theory attempts to provide a greater understanding of activation energy, E_a, and the thermodynamic properties involving the transition state. Collision theory of reaction rate, although intuitive, lacks an accurate method to predict the probability factor for the reaction. The theory assumes that reactants are hard spheres rather than molecules with specific structures. In 1935, Henry Eyring helped develop a new theory called the transition state theory to provide a more accurate alternative to the previously used Arrhenius equation and the collision theory. The Eyring equation involves the statistical frequency factory, v, which is fundamental to the theory.

According to TST, between the state where molecules are reactants and the state where molecules are products, there is a state known as the transition state. In the transition state, the reactants are combined in a species called the activated complex. The theory suggests that there are three major factors that determine whether a reaction will occur:

1. The concentration of the activated complex
2. The rate at which the activated complex breaks apart
3. The way in which the activated complex breaks apart: whether it breaks apart to reform the reactants or whether it breaks apart to form a new complex, the products.

Collision theory proposes that not all reactants that combine undergo a reaction. However, assuming the stipulations of the collision theory are met and a successful collision occurs between the molecules, transition state theory allows one of two outcomes: a return to the reactants, or a rearranging of bonds to form the products.

Consider a bimolecular reaction:

$$A + B \rightarrow C \tag{9.7.6}$$

$$K = \frac{[C]}{[A][B]} \tag{9.7.7}$$

where K is the equilibrium constant. In the transition state model, the activated complex AB is formed:

$$A + B \rightleftharpoons AB^{\ddagger} \rightarrow C \tag{9.7.8}$$

$$K^{\ddagger} = \frac{[AB]^{\ddagger}}{[A][B]} \tag{9.7.9}$$

There is an energy barrier, called activation energy, in the reaction pathway. A certain amount of energy is required for the reaction to occur. The transition state, $AB^{\ddagger}$, is formed at maximum energy. This high-energy complex represents an unstable intermediate. Once the energy barrier is overcome, the reaction is able to proceed and product formation occurs.

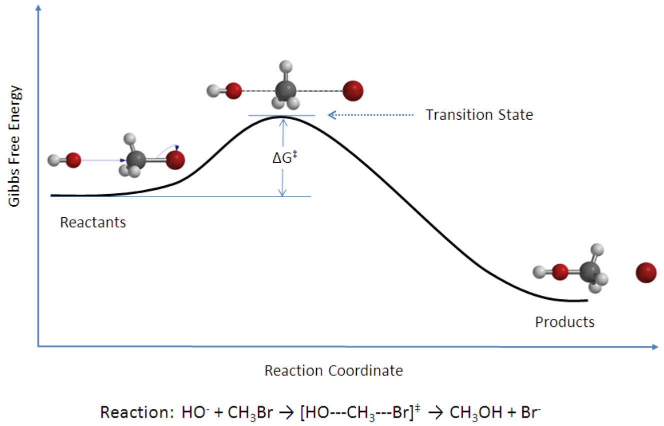


Figure 9.7.1: Reaction coordinate diagram for the bimolecular nucleophilic substitution (S_N2) reaction between bromomethane and the hydroxide anion. form Wikipedia.

The rate of a reaction is equal to the number of activated complexes decomposing to form products. Hence, it is the concentration of the high-energy complex multiplied by the frequency of it surmounting the barrier.

$$rate = v[AB^{\ddagger}] \tag{9.7.10}$$

$$= v[A][B]K^{\ddagger} \tag{9.7.11}$$

The rate can be rewritten:

$$rate = k[A][B] \tag{9.7.12}$$

Combining Equations 9.7.12 and 9.7.11 gives:

$$k[A][B] = v[A][B]K^{\ddagger} \tag{9.7.13}$$

$$k = vK^{\ddagger} \tag{9.7.14}$$

where

- v is the frequency of vibration,
- k is the rate constant and
- $K^{\ddagger}$ is the thermodynamic equilibrium constant.

Statistical mechanics (not shown) provides that the frequency, v, is equivalent to the thermal energy, k_BT, divided by Planck's constant, h.

$$v = \frac{k_BT}{h} \tag{9.7.15}$$

where

- k_B is the Boltzmann's constant (1.381×10^{-23} J/K),
- T is the absolute temperature in Kelvin (K) and
- h is Planck's constant (6.626×10^{-34} Js).

Substituting Equation 9.7.15 into Equation 9.7.14:

$$k = \frac{k_BT}{h}K^{\ddagger} \tag{9.7.16}$$

Equation ref is often tagged with another term (M^{1-m}) that makes the units equal with M is the molarity and m is the molecularly of the reaction.

$$k = \frac{k_BT}{h}K^{\ddagger}(M^{1-m}) \tag{9.7.17}$$

It is important to note here that the equilibrium constant $K^\ddagger$ can be calculated by absolute, fundamental properties such as bond length, atomic mass, and vibration frequency. This gives the transition rate theory the alternative name absolute rate theory, because the rate constant, k, can be calculated from fundamental properties.

Thermodynamics of Transition State Theory

To reveal the thermodynamics of the theory, $K^\ddagger$ must be expressed in terms of $\Delta G^\ddagger$. $\Delta G^\ddagger$ is simply,

$$\Delta G^{o\ddagger} = G^o(transitionstate) - G^o(reactants) \tag{9.7.18}$$

By definition, at equilibrium, $\Delta G^\ddagger$ can be expressed as:

$$\Delta G^\ddagger = -RT\ln K^\ddagger \tag{9.7.19}$$

Rearrangement gives:

$$[K]^\ddagger = e^{-\frac{\Delta G^\ddagger}{RT}} \tag{9.7.20}$$

From Equation 9.7.17

$$k = ve^{-\frac{\Delta G^\ddagger}{RT}}(M^{1-m}) \tag{9.7.21}$$

It is also possible to obtain terms for the change in enthalpy and entropy for the transition state. Because

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \tag{9.7.22}$$

it follows that the derived equation becomes,

$$k = \frac{k_B T}{h} e^{\Delta S^\ddagger/R} e^{-\Delta H^\ddagger/RT} M^{1-m} \tag{9.7.23}$$

Equation 9.7.23 is known as the Eyring Equation and was developed by Henry Eyring in 1935, is based on transition state theory and is used to describe the relationship between reaction rate and temperature. It is similar to the Arrhenius Equation, which also describes the temperature dependence of reaction rates.

The linear form of the Eyring Equation is given below:

$$\ln\frac{k}{T} = \frac{-\Delta H^\dagger}{R}\frac{1}{T} + \ln\frac{k_B}{h} + \frac{\Delta S^\ddagger}{R} \tag{9.7.24}$$

The values for $\Delta H^\ddagger$ and $\Delta S^\ddagger$ can be determined from kinetic data obtained from a $\ln\frac{k}{T}$ vs. $\frac{1}{T}$ plot. The Equation is a straight line with negative slope, $\frac{-\Delta H^\ddagger}{R}$, and a y-intercept, $\frac{\Delta S^\ddagger}{R} + \ln\frac{k_B}{h}$.

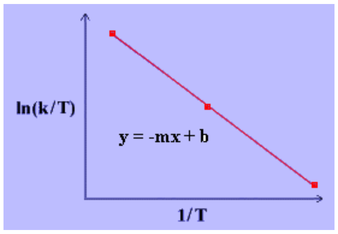


Figure 9.7.2: Linearized TST theory

Conclusion

In this article, the complete thermodynamic formulation of the transition state theory was derived. This equation is more reliable than either the Arrhenius equation and the equation for the Collision Theory. However, it has its limitations, especially when considering the concepts of quantum mechanics. Quantum mechanics implies that tunneling can occur, such that particles can bypass the energy barrier created by the transition state. This can especially occur with low activation energies, because the probability of tunneling increases when the barrier height is lowered.

In addition, transition state theory assumes that an equilibrium exists between the reactants and the transition state phase. However, in solution non-equilibrium situations can arise, upsetting the theory. Several more complex theories have been presented to correct for these and other discrepancies. This theory still remains largely useful in calculating the thermodynamic properties of the transition state from the overall reaction rate. This presents immense usefulness in medicinal chemistry, in which the study of transition state analogs is widely implemented.

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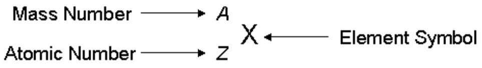
9.8: Isotope Effects in Chemical Reactions

The **kinetic isotope effect** (KIE) is a phenomenon associated with isotopically substituted molecules exhibiting different reaction rates. Isotope effects such as KIEs are invaluable tools in both physical and biological sciences and are used to aid in the understanding of reaction kinetics, mechanisms, and solvent effects.

Introduction

Research was first introduced on this topic over 50 years ago and has grown into an enormous field. The scientists behind much of the understanding and development of kinetic isotope effects were Jacob Bigeleisen and Maria Goeppert Mayer who published the first paper on isotope effects [J. Chem. Phys., 15, 261 (1947)]. Kinetic isotope effects specifically explore the change in rate of a reaction due to isotopic substitution.

An element is identified by its symbol, mass number, and atomic number. The atomic number is the number of protons in the nucleus while the mass number is the total number of protons and neutrons in the nucleus. Isotopes are two atoms of the same element that have the same number of protons but different numbers of neutrons. Isotopes are specified by the mass number.



As an example consider the two isotopes of chlorine, you can see that their mass numbers vary, with ^{35}Cl being the most abundant isotope, while their atomic numbers remain the same at 17.

$$^{35}Cl \text{ and } ^{37}Cl \tag{9.8.1}$$

The most common isotope used in light atom isotope effects is hydrogen (^{1}H) commonly replaced by its isotope deuterium (^{2}H). Note: Hydrogen also has a third isotope, tritium (^{2}H). Isotopes commonly used in heavy atom isotope effects include carbon (^{12}C, ^{13}C, nitrogen (^{14}N, ^{15}N), oxygen, sulfur, and bromine. Not all elements exhibit reasonably stable isotopes (i.e. Fluorine, ^{19}F), but those that due serve as powerful tools in isotope effects.

Potential Energy Surfaces

Understanding potential energy surfaces is important in order to be able to understand why and how isotope effects occur as they do. The harmonic oscillator approximation is used to explain the vibrations of a diatomic molecule. The energies resulting from the quantum mechanic solution for the harmonic oscillator help to define the internuclear potential energy of a diatomic molecule and are

$$E_n = \left(n + \frac{1}{2}\right) h\nu \tag{9.8.2}$$

where

- n is a positive integer (n=1,2,3...),
- h is Planck's constant and
- ν is the frequency of vibration.

The Morse potential is an analytic expression that is used as an approximation to the intermolecular potential energy curves:

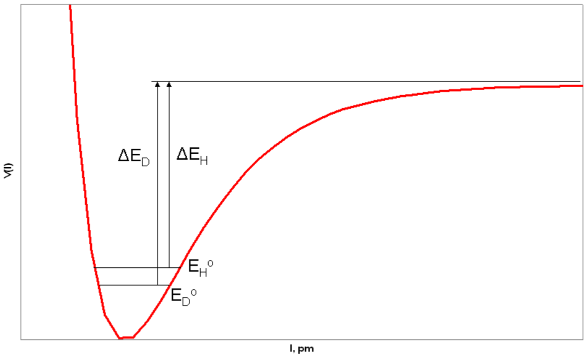
$$V(l) = D_e \left(1 - e^{-\beta(l-l_o)}\right)^2 \tag{9.8.3}$$

where

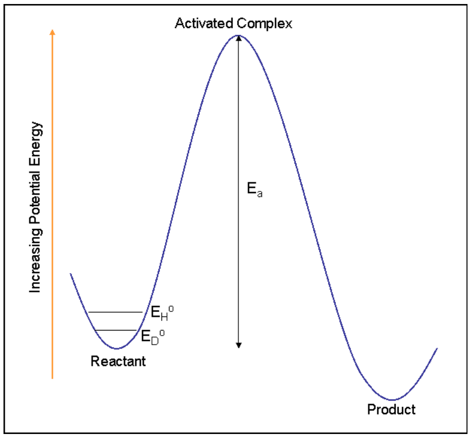
- $V(l)$ is the potential energy,
- D_e is the dissociation energy of the molecule,
- β is the measure of the curvature of the potential at its minimum,
- l is displacement, and
- l_o is the equilibrium bond length.

The D_e, β, and l_o variables can be looked up in a textbook or CRC handbook.

Below is an example of a Morse potential curve with the zero point vibrational energies of two isotopic molecules (for example R-H and R-D where R is a group/atom that is much heavier than H or D). The y-axis is potential energy and the x axis is internuclear distance. In this figure E_D^o and E_H^o correspond to the zero point energies of deuterium and hydrogen. The zero point energy is the lowest possible energy of a system and equates to the ground state energy. Zero point energy is dependent upon the reduced mass of the molecule as will be shown in the next section. The heavier the molecule or atom, the lower the frequency of vibration and the smaller the zero point energy. Lighter molecules or atoms have a greater frequency of vibration and a higher zero point energy. We see this is the figure below where deuterium is heavier than hydrogen and therefore has the lower zero point energy.



This results in different bond dissociation energies for R-D and R-H. The bond dissociation energy for R-D (E_D) is greater than the bond dissociation energy of R-H (E_H). This difference in energy due to isotopic replacement results in differing rates of reaction, the effect that is measured in kinetic isotope effects. The reaction rate for the conversion of R-D is slower than the reaction rate for the conversion of R-H.



It is important to note that isotope replacement does not change the electronic structure of the molecule or the potential energy surfaces of the reactions the molecule may undergo. Only the rate of the reaction is affected.

Activation Energies

The energy of the vibrational levels of a vibration (i.e., a bond) in a molecule is given by

$$E_n = \left(n + \frac{1}{2}\right) h\nu \tag{9.8.4}$$

where we assume that the molecule is in its ground state and we can compare zero-point vibrational energies,

$$E_o = \left(\frac{1}{2}\right) hv \tag{9.8.5}$$

Using the harmonic oscillator approximation the fundamental vibrational frequency is

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \tag{9.8.6}$$

where

- k is the force constant of the bond and
- μ is the reduced mass

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \tag{9.8.7}$$

The Arrhenius equation is used to determine reaction rates and activation energies and since we are interested in the change in rate of reactions with different isotopes, this equation is very important,

$$k = Ae^{-\frac{E_a}{kT}} \tag{9.8.8}$$

where

- k is the reaction rate,
- E_a is the activation energy, and
- A is the Arrhenius constant.

The Arrhenius equation can be used to compare the rates of a reaction with R-H and R-D,

$$k_H = A_H e^{-\frac{E_a^H}{kT}} \tag{9.8.9}$$

$$k_D = A_D e^{-\frac{E_a^D}{kT}} \tag{9.8.10}$$

where k_H and k_D are the rates of reaction associated with R-H and the isotope substituted R-D. We will then assume the Arrhenius constants are equal ($A_H = A_D$). The ratio of the rates of reaction gives an approximation for the isotope effect resulting in:

$$\frac{k_H}{k_D} = e^{-\frac{E_a^H - E_a^D}{kT}} \tag{9.8.11}$$

By using the relationship that for both R-H and R-D

$$E_o = \left(\frac{1}{2}\right) h\nu \tag{9.8.12}$$

a substitution can be made resulting in

$$\frac{k_H}{k_D} = e^{\frac{h(\nu_H - \nu_D)}{2kT}} \tag{9.8.13}$$

The vibrational frequency (Equation 5) can then be substituted for R-H and R-D and the value of the expected isotope effect can be calculated.

$$\frac{k_H}{k_D} = e^{\frac{h\left(\frac{k_{RH}}{\mu_{RH}} - \frac{k_{RD}}{\mu_{RD}}\right)}{4\pi kT}} \tag{9.8.14}$$

The same general procedure can be followed for any isotope substitution.

In summary, the greater the mass the more energy is needed to break bonds. A heavier isotope forms a stronger bond. The resulting molecule has less of a tendency to dissociate. The increase in energy needed to break the bond results in a slower reaction rate and the observed isotope effect.

Kinetic Isotope Effects

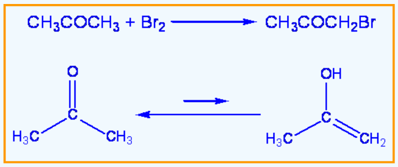
Kinetic Isotope Effects (KIEs) are used to determine reaction mechanisms by determining rate limiting steps and transition states and are commonly measured using NMR to detect isotope location or GC/MS to detect mass changes. In a KIE experiment an atom is replaced by its isotope and the change in rate of the reaction is observed. A very common isotope substitution is when hydrogen is replaced by deuterium. This is known as a deuterium effect and is expressed by the ratio k_H/k_D (as explained above). Normal KIEs for the deuterium effect are around 1 to 7 or 8. Large effects are seen because the percentage mass change between hydrogen and deuterium is great. Heavy atom isotope effects involve the substitution of carbon, oxygen, nitrogen, sulfur, and bromine, with effects that are much smaller and are usually between 1.02 and 1.10. The difference in KIE magnitude is directly related to the percentage change in mass. Large effects are seen when hydrogen is replaced with deuterium because the percentage mass change is very large (mass is being doubled) while smaller percent mass changes are present when an atom like sulfur is replaced with its isotope (increased by two mass units).

Primary KIEs

Primary kinetic isotope effects are rate changes due to isotopic substitution at a site of bond breaking in the rate determining step of a reaction.

✓ Example

Consider the bromination of acetone: kinetic studies have been performed that show the rate of this reaction is independent of the concentration of bromine. To determine the rate determining step and mechanism of this reaction the substitution of a deuterium for a hydrogen can be made.



When hydrogen was replaced with deuterium in this reaction a $\frac{k_H}{k_D}$ of 7 was found. Therefore the rate determining step is the tautomerization of acetone and involves the breaking of a C-H bond. Since the breaking of a C-H bond is involved, a substantial isotope effect is expected.

Heavy Atom Isotope Effects

A rule of thumb for heavy atom isotope effects is that the maximum isotopic rate ratio is proportional to the square root of the inverse ratio of isotopic masses.

$$\mathrm{PhCH_2{-}CH_2S^+Me_2} \qquad \overset{\text{Base}}{} \qquad \mathrm{PhCH{=}CH_2 + SMe_2 + BH^+}$$

- Expected:

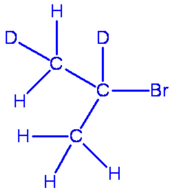
$$\frac{k_{32}}{k_{34}} = \sqrt{\frac{34}{32}} = 1.031 \tag{9.8.15}$$

- Experimental:

$$\frac{k_{32}}{k_{34}} = 1.072 \tag{9.8.16}$$

Secondary KIEs

Secondary kinetic isotope effects are rate changes due to isotopic substitutions at a site other than the bond breaking site in the rate determining step of the reaction. These come in three forms: α, β, and γ effects.



β secondary isotope effects occur when the isotope is substituted at a position next to the bond being broken.

$$(\mathrm{CH_3})_2\mathrm{CHBr} + \mathrm{H_2O} \xrightarrow{k_H} (\mathrm{CH_3})_2\mathrm{CHOH} \tag{9.8.17}$$

$$(\mathrm{CD_3})_2\mathrm{CHBr} + \mathrm{H_2O} \xrightarrow{k_D} (\mathrm{CD_3})_2\mathrm{CHOH} \tag{9.8.18}$$

This is thought to be due to hyperconjugation in the transition state. Hyperconjugation involves a transfer of electron density from a sigma bond to an empty p orbital (for more on hyperconjugation see outside links).

Solvent Effects in Reactions

Reactions may be affected by the type of solvent used (for example H_2O to D_2O or ROH to ROD). There are three main ways solvents effect reactions:

1. The solvent can act as a reactant resulting in a primary isotope effect.
2. Rapid hydrogen exchange can occur between substrate molecules labeled with deuterium and hydrogen atoms in the solvent. Deuterium may change positions in the molecule resulting in a new molecule that is then reacted in the rate determining step of the reaction.
3. The nature of solvent and solute interactions may also change with differing solvents. This could change the energy of the transition state and result in a secondary isotope effects.

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Problems

1. Describe the difference between primary and secondary kinetic isotope effects.
2. Estimate the $k_{N\text{-}H}/k_{N\text{-}D}$ for a deuterium substitution on nitrogen given that v_H=9.3x1013 Hz and the activation energy is equal to 5.31 kJ/mol.
3. Using the 'rule of thumb' for heavy isotope effects, calculate the expected effect for a bromine isotope substitution, ^{79}Br and ^{81}Br.
4. Explain some of the main ways kinetic isotope effects are used.
5. As discussed, the rate-limiting step in the bromination of acetone is the breaking of a carbon-hydrogen bond. Estimate kC-H/KC-D for this reaction at 285 K. (Given: vtilde$_{C\text{-}H}$=3000 cm^{-1} and vtilde$_{C\text{-}D}$=2100 cm^{-1})

Solutions

1. Primary isotope effects involve isotopic substitution at the bond being broken in a reaction, while secondary isotope effects involve isotopic Substitution on bonds adjacent to the bond being broken.
2. 8.5
3. 1.0126
4. To determine reaction mechanisms, to determine rate limiting steps in reactions, to determine transition states in reactions.
5. 9.685

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9.9: Reactions in Solution

Learning Objectives

Make sure you thoroughly understand the following essential ideas:

- Describe some of the major differences between the kinetics of reactions in the gas phase, compared with those in liquid solutions.
- What role do solvent cages play in solution kinetics?
- Explain the distinction between diffusion-control and activation-control of reaction rates in solutions.
- How can the polarity of a solvent affect the energetics of a reaction mechanism?

The kinetics fundamentals we covered in the earlier sections of this lesson group relate to processes that take place in the gas phase. But chemists and biochemists are generally much more concerned with solutions. This lesson will take you through some of the extensions of basic kinetics that you need in order to understand the major changes that occur when reactions take place in liquid solutions.

What's different about kinetics in liquid solutions?

Most of the added complications of kinetics and rate processes in liquid solutions arise from the *much higher density* of the liquid phase. In a typical gas at atmospheric pressure, the molecules occupy only about 0.2 per cent of the volume; the other 99.8 percent is empty space. In a liquid, molecules may take up more than half the volume, and the "empty" spaces are irregular and ever-changing as the solvent molecules undergo thermal motions of their own.

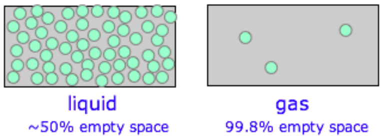


Figure 9.9.1: Liquid vs. Gases.

In a typical liquid solution, the solvent molecules massively outnumber the reactant solute molecules, which tend to find themselves momentarily (~10^{-11} sec) confined to a "hole" within the liquid. This trapping becomes especially important when the solvent is strongly hydrogen-bonded as is the case with water or alcohol.

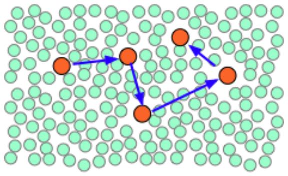
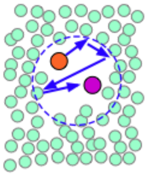
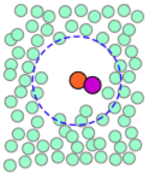
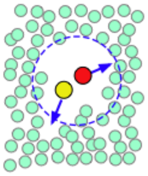
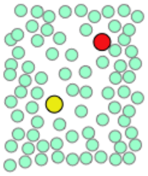


Figure 9.9.2: Brownian motion of a particle in solution

When thermal motions occasionally release a solute molecule from this trap, it will jump to a new location. The jumps are very fast (10^{-12} - 10^{-13} sec) and short (usually a few solvent-molecule diameters), and follow an entirely random pattern, very much as in **Brownian motion**. Consider a simple bimolecular process A + B → products. The reactant molecules will generally be jumping from hole to hole in the solvent matrix, only occasionally finding themselves in the same *solvent cage* where thermal motions are likely to bring them into contact.

Table 9.9.1: Solvent cages and encounter pairs

A pair of reactants end up in the same solvent cage, where they bounce around randomly and exchange kinetic energy with the solvent molecules.	Eventually the two reactants form an *encounter pair*. If they fail to react the first time, they have many more opportunities during the lifetime of the cage.	The products form and begin to move away from each other.	Finally, after about 10^{-11} sec, the solvent cage breaks up and the products diffuse away.

The process can be represented as

$$A+B \rightarrow \{AB\} \rightarrow \text{products} \tag{9.9.1}$$

in which the $\{AB\}$ term represents the caged reactants including the *encounter pair* and the activated complex.

Contrast this scenario with a similar reaction taking place in the gas phase; the molecules involved in the reaction will often be the only ones present, so a significant proportion of the collisions will be A-B encounters. However, if the collision should fail to be energetically or geometrically viable, the reactant molecules fly apart and are unlikely to meet again anytime soon. In a liquid, however, the solute molecules are effectively in a constant state of collision — if not with other reactants, then with solvent molecules which can exchange kinetic energy with the reactants. So once an A-B encounter pair forms, the two reactants get multiple whacks at each other, greatly increasing the probability that they will obtain the kinetic energy needed to kick them over the activation hump before the encounter pair disintegrates.

Limiting Cases: Diffusion-Controlled and Activation-Controlled Reactions

The encounter pair model introduces some new rate parameters:

$$\mathrm{A+B} \underset{k_{-1}}{\overset{k1}{\rightleftharpoons}} \mathrm{AB} \longrightarrow \text{products} \tag{9.9.2}$$

The first step is an equilibrium between the reactants outside and inside the solvent cage. The rate constants k_1 and k_2 reflect those relating to diffusion of molecules through the solvent; their values are strongly dependent on the viscosity (and thus the temperature) of the solvent. (Note that k_1 is a second-order rate constant, while k_2 is first-order.)

Diffusion is the transport of a substance through a concentration gradient; that is, from a region of higher concentration to one of lower concentration. Think of the way the color of tea spreads out when a tea bag is immersed in hot water. Diffusion occurs because random thermal motions are statistically more likely to move molecules out of a region of higher concentration than in the reverse direction, simply because in the latter case fewer molecules are available to make the reverse trip. Eventually the concentrations become uniform and equilibrium is attained.

As molecules diffuse through a liquid, they must nudge neighboring molecules out of the way. The work required to do this amounts to an activation energy, so diffusion can be thought of as a kinetic process with its own rate constant k_d and activation energy. These parameters depend on the sizes of the solute and solvent molecules and on how strongly the latter interact with each other. This suggests two important *limiting cases* for reactions in solution.

For water at room temperature, k_1 is typically 10^9-10^{10} dm^{-3} mol^{-1} s^{-1} and k_2 is around 10^{-9}-10^{-10} dm^{-3} mol^{-1} s^{-1}. Given these values, $k_3 > 10^{12}$ s^{-1} implies diffusion control, while values $< 10^9$ s^{-1} are indicative of activation control.

- **Diffusion Controlled** ($k_3 \gg k_2$): If the activation energy of the A+B reaction is very small or if escape of molecules from the $\{\mathrm{AB}\}$ cage is difficult, the kinetics will be dominated by k_1, and thus by the activation energy of diffusion. Such a process is said to be *diffusion controlled*. Reactions in aqueous solution in which $E_a > 20$ kJ/mol are likely to fall into this category.
- **Activation Controlled** ($k_3 \ll k_2$): Alternatively, if the activation energy of the A+B reaction dominates the kinetics, and the reaction is *activation-controlled*.

Several general kinds of reactions are consistently very "fast" and thus are commonly found to be diffusion-controlled in most solvents:

Gas-phase rate constants are normally expressed in units of mol s^{-1}, but rate constants of reactions in solution are conventionally given in mol/L units, or dm^3 mol^{-1} s^{-1}. Conversion between them depends on a number of assumptions and is non-trivial.

- **Recombination of atoms and radicals**

For example the formation of I_2 from I atoms in hexane at 298 K has $k_3 = 1.3\times10^{12}$ $dm^3\ mol^{-1}\ s^{-1}$.

- **Acid-base reactions** which involve the transport of H^+ and OH^- ions tend to be very fast.

  The most famous of these is one of the fastest reactions known:

  $$H^+ + OH^- \rightarrow H_2O$$

  for which $k_3 = 1.4\times10^{11}$ $dm^3\ mol^{-1}\ s^{-1}$ at 298 K.

Polar solvents such as water and alcohols interact with ions and polar molecules through attractive dipole-dipole and ion-dipole interactions, leading to lower-energy solvated forms which stabilize these species. In this way, a polar solvent can alter both the thermodynamics and kinetics (rate) of a reaction.

Solvent Thermodynamic Effect

If the products of the reaction are markedly more or less polar than the reactants, solvent polarity can change the overal thermodynamics (equilibrium constant) of the reaction. Nowhere is this more apparent than when an ionic solid such as salt dissolves in water. The Na^+ and Cl^- ions are bound together in the solid through strong coulombic forces; pulling the solid apart in a vacuum or in a nonpolar solvent is a highly endothermic process. In contrast, dissolution of NaCl in water is slightly exothermic and proceeds spontaneously.

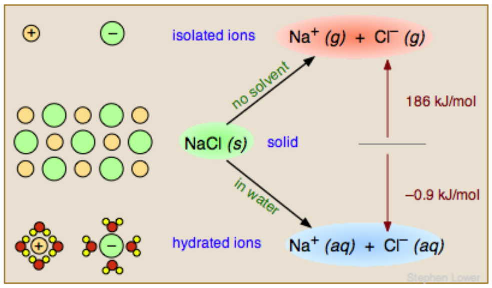
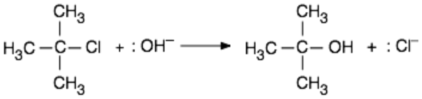


Figure 9.9.3: The solvent thermodynamics effect for table salt in water.

The water facilitates this process in two important ways. First, its high dielectric constant of 80 reduces the force between the separated ions to 1/80 of its normal value. Secondly, the water molecules form a *solvation shell* around the ions (lower left), rendering them energetically (thermodynamically) more stable than they were in the NaCl solid.

Solvent Kinetic Effect

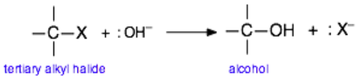
In the same way, a reaction whose mechanism involves the formation of an intermediate or activated complex having a polar or ionic character will have its activation energy, and thus its rate, subject to change as the solvent polarity is altered. As an example we will consider an important class of reactions that you will hear much about if you take a course in organic chemistry. When an aqueous solution of a strong base such as KOH is added to a solution of *tertiary*-butyl chloride in ethanol, the chlorine is replaced by a hydroxyl group, leaving *t*-butyl alcohol as a product:



$$(CH_3)_3C{-}Cl + :OH^- \longrightarrow (CH_3)_3C{-}OH + :Cl^-$$

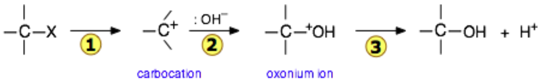
This reaction is one of a large and important class known as *S_N1 nucleophilic substitution processes* that are discussed in most organic chemistry courses. In these reactions, a species that possesses a pair of non-bonding electrons (also called a *nucleophile* or *Lewis base*) uses them to form a new bond with an *electrophile* — a compound in which a carbon atom has a partial positive charge owing to its bonds to electron-withdrawing groups. In the example here, other nucleophiles such as NH_3 or even H_2O would serve as well.

In order to reflect the generality of this process and to focus on the major changes that take place, we will represent this reaction as



$$-\overset{|}{\underset{|}{C}}-X + :OH^- \longrightarrow -\overset{|}{\underset{|}{C}}-OH + :X^-$$

Extensive studies of this class of reactions in the 1930's revealed that it proceeds in two activation energy-controlled steps, followed by a simple dissociation into the products:



In step ①, which is rate-determining, the chlorine leaves the alkyl chloride which becomes an intermediate known as a *carbocation* ("cat-ion"). These ions, in which the central carbon atom lacks a complete octet, are highly reactive, and in step ② the carbocation is attacked by the hydroxide ion which supplies the missing electron. The immediate product is another cation in which the positive charge is on the oxygen atom. This *oxonium ion* is unstable and rapidly dissociates (③)into the alcohol and a hydrogen ion.

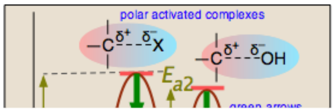


Figure 9.9.4: reaction Coordinate

The reaction coordinate diagram helps us understand the effect of solvent polarity on this reaction. Polar solvent molecules interact most strongly with species in which the electric charge is concentrated in one spot. Thus the carbocation is stabilized to a greater degree than are the activated complexes in which the charge is spread out between the positive and negative ends. As the heavy green arrows indicate, a more polar solvent will stabilize the carbocation more than it will either of the activated complexes; the effect is to materially reduce the activation energy of the rate-determining step, and thus speed up the reaction. Because neither the alkyl chloride nor the alcohol is charged, the change in solvent polarity has no effect on the equilibrium constant of the reaction. This is dramatically illustrated by observing the rate of the reaction in solvents composed of ethanol and water in varying amounts:

Table 9.9.2: Data

% water	10	20	30	40	50	60
$k_1 \times 10^6$	1.7	9.1	40.3	126	367	1294

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9.10: Fast Reactions in Solution

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?

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.

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.

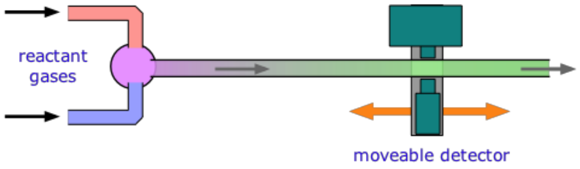


Figure 9.10.1: A continuous flow fast kinetic system.

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.

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.

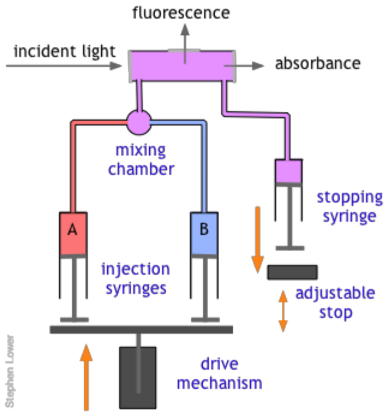


Figure 9.10.2: A stop flow fast kinetic system.

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.

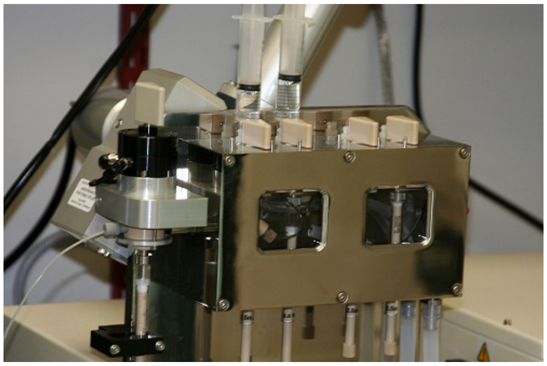


Figure 9.10.3: Stop-flow equipment at a biochemistry research laboratory for measuring rapid reactions and properties such as enzyme kinetics. from Wladimir Labeikovsky.

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.

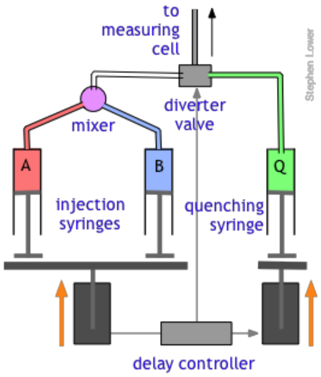


Figure 9.10.4: A quench flow fast kinetic system.

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.

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.

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.

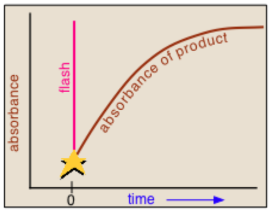


Figure 9.10.5: Basic principle of a flash-photolysis relaxation experiment where an excitation pulse purturbed a system at equilibrium and the subsequent dynamics are resolved in time.

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.

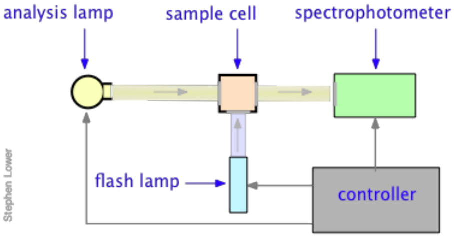


Figure 9.10.6: A flash-photolysis relaxation experiment

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

$$2H_2O \rightarrow H_3O^+ + OH^- \tag{9.10.1}$$

and the formation of the triiodide ion in aqueous solution

$$I^- + I_2 \rightarrow I_3^- \tag{9.10.2}$$

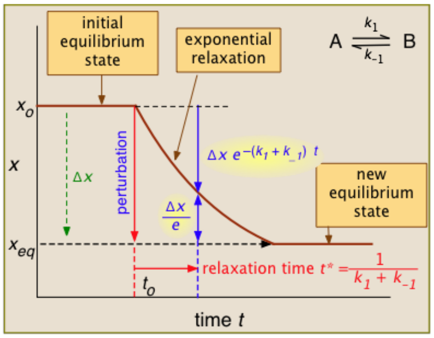
Reactions of these kinds could not be studied until the mid-1950s when techniques were developed to shift the equilibrium by imposing an abrupt physical change on the system.

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

$$\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{B} \tag{9.10.3}$$

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

$$x_t = x_o e^{-kt} \tag{9.10.4}$$

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 \(Δ*x*/e = Δ*x*/2.718\). 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 9.10.3 can be written as

$$\frac{d[\mathrm{B}]}{dt} = k_1[\mathrm{A}] - k_{-1}[\mathrm{B}] \tag{9.10.5}$$

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

$$[\mathrm{A}] = [\mathrm{B}]_{\mathrm{eq},1} - [\mathrm{B}] \tag{9.10.6}$$

The rate of change of species B can then be written as

$$\frac{d[\mathrm{B}]}{dt} = k_1\left([\mathrm{B}]_{\mathrm{eq},1} - [\mathrm{B}]\right) - k_{-1}[\mathrm{B}] = k_1[\mathrm{B}]_{\mathrm{eq},1} - (k_1 + k_{-1})[\mathrm{B}] \tag{9.10.7}$$

At equilibrium, $d[\mathrm{B}]/dt = 0$ and $[\mathrm{B}] = [\mathrm{B}]_{\mathrm{eq},2}$, allowing us to write

$$k_1[\mathrm{B}]_{\mathrm{eq},1} = (k_1 + k_{-1})[\mathrm{B}]_{\mathrm{eq},2} \tag{9.10.8}$$

Using the above equation, we can rewrite the rate equation as

$$\frac{d\mathrm{B}}{\left([\mathrm{B}]_{\mathrm{eq},2} - [\mathrm{B}]\right)} = (k_1 + k_{-1})\,dt \tag{9.10.9}$$

Integrating yields

$$-\ln\left([\mathrm{B}] - [\mathrm{B}]_{\mathrm{eq},2}\right) = -(k_1 + k_{-1})\,t + C \tag{9.10.10}$$

We can rearrange the above equation in terms of B

$$[\mathrm{B}] = Ce^{-(k_1+k_{-1})t} + [\mathrm{B}]_{\mathrm{eq},2} \tag{9.10.11}$$

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

$$[\mathrm{B}]-[\mathrm{B}]_{\mathrm{eq},2}=\left([\mathrm{B}]_{\mathrm{eq},1}-[\mathrm{B}]_{\mathrm{eq},2}\right)e^{-(k_1+k_{-1})t} \tag{9.10.12}$$

which can also be expressed as

$$\Delta[\mathrm{B}]=\Delta[\mathrm{B}]_0 e^{-(k_1+k_{-1})t}=\Delta[\mathrm{B}]_0 e^{-t/\tau} \tag{9.10.13}$$

where $\Delta[\mathrm{B}]$ is the difference in the concentration of B from the final equilibrium concentration after the perturbation, and τ is the *relaxation time*. A plot of $\ln(\Delta[\mathrm{B}]/\Delta[\mathrm{B}]_0)$ 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.

Contributors and Attributions

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9.11: Oscillating Reactions

It should be clear by now that chemical kinetics is governed by the mathematics of systems of differential equations. Thus far, we have only looked at reaction systems that give rise to purely *linear* differential equations, however, in many instances the rate equations are nonlinear. When the differential equations are nonlinear, the behavior is considerably more complex. In particular, nonlinear equations can lead to oscillatory solutions and can also exhibit the phenomenon of *chaos*. Chaotic systems are systems that are highly sensitive to small changes in the parameters of the equations or in the initial conditions. Basically, this means that the behavior of a chaotic system can be unpredictable, since such small changes can occur in the form of small errors in determining the parameters (rounding to the nearest tenth or hundredth) or in specifying the initial conditions, and these small changes can cause the system to evolve in time in a very different way.

The Iodine Clock Reaction

The iodine clock reaction is a popular chemistry experiment in which one can visualize how different rate constants in consecutive reactions affect the concentration of species during the reaction. Iodine anions (I^-) are colorless. When I^- is reacted with hydrogen peroxide and protons, triiodide is formed, which has a dark blue color. Consider the following series of irreversible reactions:

$$H_2O_2 + 3\ I^- + 2\ H^+ \xrightarrow{k_1} I_3^- + 2\ H_2O \tag{9.11.1}$$

$$I_3^- + 2\ S_2O_3^{2-} \xrightarrow{k_2} 3\ I^- + S_4O_6^{2-} \tag{9.11.2}$$

The rate laws for this system are

$$\frac{d\left[I_3^-\right]}{dt} = k_1\left[I^-\right]^3 - k_2\left[I_3^-\right]\left[S_2O_3^{2-}\right]^2 \tag{9.11.3}$$

$$\frac{d\left[I^-\right]}{dt} = -k_1\left[I^-\right]^3 + 3k_2\left[I_3^-\right]\left[S_2O_3^{2-}\right]^2 \tag{9.11.4}$$

$$\frac{d\left[S_2O_3^{2-}\right]}{dt} = -k_2\left[I_3^-\right]\left[S_2O_3^{2-}\right]^2 \tag{9.11.5}$$

In order to make the equations look a little simpler, let us introduce the variables:

$$x = \left[I^-\right], \qquad y = \left[I_3^-\right], \qquad z = \left[S_2O_3^{2-}\right] \tag{9.11.6}$$

In terms of these, the rate equations are

$$\frac{dx}{dt} = -k_1x^3 + 3k_2yz^2 \tag{9.11.7}$$

$$\frac{dy}{dt} = k_1x^3 - k_2yz^2 \tag{9.11.8}$$

$$\frac{dz}{dt} = -k_2yz^2 \tag{9.11.9}$$

If we solve these numerically, we find the following time dependence of the three concentrations: This is a clear example of nonlinearity. Note how the concentration of I_3^- remains close to 0 for a period of time and then suddenly starts to increase. In a sense, think of the "straw that broke the camel's back". As we pile straws on the back of the camel, the camel remains upright until that last straw, which suddenly breaks the back of the camel, and the camel suddenly falls to the ground. This is also an illustration of nonlinearity.

Video* $9.11.1$*: Famous iodine clock reaction: oxidation of potassium iodide by hydrogen peroxide (https://www.youtube.com/watch?v=_qhYDuJt8fI).

Despite the complexity of the rate equations, we can still analyze the approximately and predict the behavior seen in Figure $9.11.1$. In this reaction mechanism, $k_2 \gg k_1$. Given the rate law for I_3^- ,

$$\frac{d\left[I_3^-\right]}{dt} = k_1\left[I^-\right]^3 - k_2\left[I_3^-\right]\left[S_2O_3^{2-}\right]^2 \tag{9.11.10}$$

if we use the steady-state approximation, we can set the $\frac{d\left[I_3^-\right]}{dt}$ equal to 0, yielding

$$\left[I_3^-\right] = \frac{k_1}{k_2}\frac{\left[I^-\right]^3}{\left[S_2O_3^{2-}\right]^2} \tag{9.11.11}$$

Since $k_2 \gg k_1$, the concentration of $\left[I_3^-\right]$ is approximately 0 as long as there are $S_2O_3^{2-}$ ions present. As soon as all of the $S_2O_3^{2-}$ is consumed, the concentration of I_3^- can build up in the solution, changing the solution to a dark blue color. Figure $9.11.1$ displays the concentration profiles for I^-, I_3^-, and $S_3O_3^{2-}$. As can be seen from the figure, the concentration of I_3^- (red line) remains at approximately $0\ \mathrm{mol/L}$ until all of the $S_2O_3^{2-}$ (blue line) has been depleted.

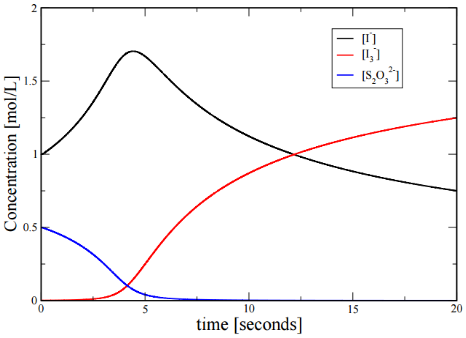

Figure 9.11.1: Concentrations as functions of time of the three species in the iodine clock reaction.

Oscillating Reactions

In all of the examples we have seen thus far, the concentration of intermediate species displays a single maximum during the course of the reaction. There is another class of reactions called *oscillating reactions* in which the concentration of intermediate species oscillates with time. Consider the following series of reactions

$$\mathrm{A} + \mathrm{Y} \xrightarrow{k_1} \mathrm{X} \tag{9.11.12}$$

$$\mathrm{X} + \mathrm{Y} \xrightarrow{k_2} \mathrm{P} \tag{9.11.13}$$

$$\mathrm{B} + \mathrm{X} \xrightarrow{k_3} 2\,\mathrm{X} + \mathrm{Z} \tag{9.11.14}$$

$$2\,\mathrm{X} \xrightarrow{k_4} \mathrm{Q} \tag{9.11.15}$$

$$\mathrm{Z} \xrightarrow{k_5} \mathrm{Y} \tag{9.11.16}$$

In the above reaction mechanism, A and B are reactants; X, Y, and Z are intermediates; and P and Q are products. The third reaction in which B and X react to form X and Z is known as an ”autocatalytic reaction” in which at least one of the reactants is also a product. Such reactions are a key feature of oscillating reactions, as will be discussed below.

Video* $\mathbf{9.11.2}$*: *The famous Belousov Zhabotinsky chemical reaction in a petri dish. The action is speeded up 8 x from real life. Pacemaker nucleation sites emit circular waves. Breaking the wavefront with a wire triggers pairs of spiral defects which emit more closely spaced waves which eventually fill the container.*

Let us assume that the concentrations of A and B are large, such that we can approximate them to be constant with time. The rate equation for species X can be written as

$$\frac{d\,[\mathrm{X}]}{dt} = k_1\,[\mathrm{A}]\,[\mathrm{Y}] - k_2\,[\mathrm{X}]\,[\mathrm{Y}] + k_3\,[\mathrm{B}]\,[\mathrm{X}] - 2k_4[\mathrm{X}]^2 \tag{9.11.17}$$

Using the steady-state approximation, we can set $d\mathrm{X}/dt = 0$ and rewrite Equation 9.11.17as

$$(-2k_4)\,[\mathrm{X}]^2 + (k_2\,[\mathrm{Y}] - k_3\,[\mathrm{B}])\,[\mathrm{X}] + k_1\,[\mathrm{A}]\,[\mathrm{Y}] = 0 \tag{9.11.18}$$

We can then use the quadratic formula to solve for X:

$$[\mathrm{X}] = -\frac{(k_2\,[\mathrm{Y}] - k_3\,[\mathrm{B}]) \pm \sqrt{(k_2\,[\mathrm{Y}] - k_3\,[\mathrm{B}])^2 - 4\,(-2k_4)\,(k_1\,[\mathrm{A}]\,[\mathrm{Y}])}}{2\,(-2k_4)} \tag{9.11.19}$$

Thus, there are two solutions for the concentration of X accessible to the reaction system. To examine solutions for $[\mathrm{X}]$, let us first assume that $[\mathrm{Y}]$ is large. Under these conditions, the first two reactions in the reaction mechanism largely determine the concentration of $[\mathrm{X}]$. We can thus approximate Equation 9.11.17as

$$0 \approx k_1\,[\mathrm{A}]\,[\mathrm{Y}] - k_2\,[\mathrm{X}]\,[\mathrm{Y}] \tag{9.11.20}$$

Solving for $[\mathrm{X}]$ yields

$$[\mathrm{X}] \approx \frac{k_1\,[\mathrm{A}]}{k_2} \tag{9.11.21}$$

As the reaction continues, species Y is depleted and the assumption that $[\mathrm{Y}]$ is large becomes invalid. Instead the 3^{rd} and 4^{th} steps of the reaction mechanism determine the concentration of X. In this limit, we can approximate Equation 9.11.17as

$$0 \approx k_3\,[\mathrm{B}]\,[\mathrm{X}] - 2k_4[\mathrm{X}]^2 \tag{9.11.22}$$

Solving for $[\mathrm{X}]$ yields

$$[\mathrm{X}] \approx \frac{k_3\,[\mathrm{B}]}{2k_4} \tag{9.11.23}$$

In the second mechanism, the autocatalytic reaction step leads to an increase in the concentration of X and Z, which in turn leads to an increase in the concentration of Y. The feedback loop between the production of species X and Y leads to oscillatory behavior in the system. This reaction mechanism is known as the Belousov-Zhabotinksii reaction first discovered in the 1950s.

- The autocatalytic reaction of X in which X reacts with B to form more X in reaction 3
- The regeneration of species Y in reaction 5
- The competition between reaction 2 and 3 for the consumption of X and the involvement of Y in reaction 2

The actual Belousov-Zhabotinskii reaction is complex, involving many individual steps, and involves the oscillation between the concentration of $HBrO_2$ and Br^-. The reaction equations are

$$BrO_3^- + Br^- + 2\,H^+ \longrightarrow HBrO_2 + HOBr \tag{9.11.24}$$

$$HBrO_2 + Br^- + H^+ \longrightarrow 2\,HOBr \tag{9.11.25}$$

$$HOBr + Br^- + H^+ \longrightarrow Br_2 + H_2O \tag{9.11.26}$$

$$2\,HBrO_2 \longrightarrow BrO_3^- + HOBr + H^+ \tag{9.11.27}$$

$$BrO_3^- + HBrO_2 + H^+ \longrightarrow 2\,BrO_2^{\cdot} + H_2O \tag{9.11.28}$$

$$BrO_2^{\cdot} + Ce^{3+} + H^+ \longrightarrow HBrO_2 + Ce^{4+} \tag{9.11.29}$$

$$BrO_2^{\cdot} + Ce^{4+} + H_2O \longrightarrow BrO_3^- + Ce^{3+} + 2\,H^+ \tag{9.11.30}$$

The essential steps in this mechanism can be reduced to the following set of reactions. Note that we leave this unbalanced and only include the species whose concentrations as functions of time we seek.

$$BrO_3^- + Br^- \xrightarrow{k_1} HBrO_2 + HOBr \tag{9.11.31}$$

$$HBrO_2 + Br^- \xrightarrow{k_2} 2\,HOBr \tag{9.11.32}$$

$$BrO_3^- + HBrO_2 \xrightarrow{k_3} 2\,HBrO_2 + 2\,Ce^{4+} \tag{9.11.33}$$

$$2\,HBrO_2 \xrightarrow{k_4} BrO_3^- + HOBr \tag{9.11.34}$$

$$Ce^{4+} \xrightarrow{k_5} f Br^- \tag{9.11.35}$$

Setting the variables as follows:

$$x = [HBrO_2], \qquad y = [Br^-], \qquad z = [Ce^{4+}] \tag{9.11.36}$$

We make the approximation that $[BrO_3^-]$ to be a constant a. In this case, the rate equations become

$$\frac{dx}{dt} = k_1 ay - k_2 xy + k_3 ax - k_4 x^2 \tag{9.11.37}$$

$$\frac{dy}{dt} = -k_1 ay - k_2 xy + f k_5 z \tag{9.11.38}$$

$$\frac{dz}{dt} = 2k_3 ax - k_5 z \tag{9.11.39}$$

Solving these equations numerically, we obtain the trajectory of two of the species show in the Figure $9.11.2$

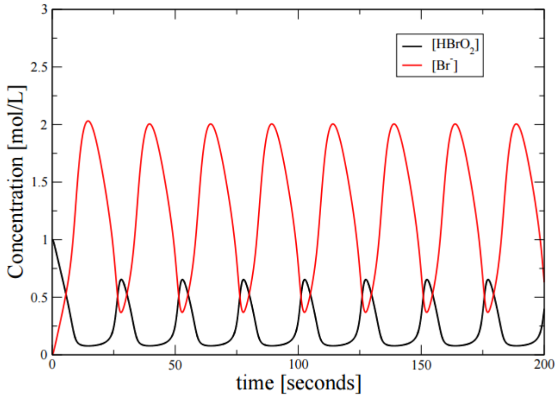

Figure 9.11.2: Oscillating pattern of the concentrations in the Belousov-Zhabotinskii reaction.

On the other hand, we can drive this system to become chaotic by changing the parameters a little. When this is done, we find the follow plot of the concentration of x:

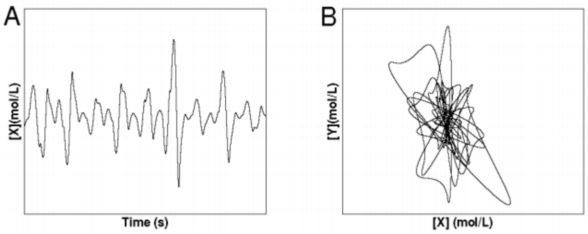

Figure 9.11.3: Chaotic behavior in the Belousov-Zhabotinskii reaction.

Contributors and Attributions

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9.E: Chemical Kinetics (Exercises)

9.1: Reaction Rates

Q9.1

Write the rate of reaction in terms of the rate of disappearance of reactant and the rate of formation of products:

a. $NO_{(g)} + O_{3(g)} \rightarrow NO_{2(g)} + O_{2(g)}$
b. $2C_2H_{6(g)} + 7O_{2(g)} \rightarrow 4CO_{2(g)} + 6H_2O_{(aq)}$
c. $H_{2(g)} + I_{2(g)} \rightarrow 2HI_{(g)}$
d. $4OH_{(g)} + H_2S_{(g)} \rightarrow SO_{2(g)} + 2H_2O_{(aq)} + H_{2(g)}$

S9.1

1. rate of reaction $= \dfrac{-\Delta[NO]}{\Delta t} = \dfrac{-\Delta[O_3]}{\Delta t} = \dfrac{\Delta[NO_2]}{\Delta t} = \dfrac{\Delta[O_2]}{\Delta t}$
2. rate of reaction $= \dfrac{-\Delta[C_2H_6]}{2\,\Delta t} = \dfrac{-\Delta[O_2]}{7\,\Delta t} = \dfrac{\Delta[CO_2]}{4\,\Delta t} = \dfrac{\Delta[H_2O]}{6\,\Delta t}$
3. rate of reaction $= \dfrac{-\Delta[H_2]}{\Delta t} = \dfrac{-\Delta[I_2]}{\Delta t} = \dfrac{\Delta[HI]}{2\,\Delta t}$
4. rate of reaction $= \dfrac{-\Delta[OH]}{4\,\Delta t} = \dfrac{-\Delta[H_2S]}{\Delta t} = \dfrac{\Delta[SO_2]}{\Delta t} = \dfrac{\Delta[H_2O]}{\Delta t} = \dfrac{\Delta[H_2]}{\Delta t}$

9.2: Reaction Order

Q9.2

Determine the value of the rate constant for the elementary reaction:

$$I_{2(g)} + H_{2(g)} \rightarrow 2HI_{(aq)} \tag{9.E.1}$$

given that when [Br_2] is 0.15 M and [H_2] is 0.2M, the rate of reaction is 0.005 M s^{-1} at 298 K.

S9.2

$$\text{rate of reaction} = k[Br_2][H_2]$$

$$0.005\ Ms^{-1} = k\ (\ 0.15M)^2(0.2M)$$

$$k = 1.11\ M^{-1}s^{-1}$$

Q9.3

Given the rate of the third order reaction:

$$A + B + C \rightarrow P \tag{9.E.2}$$

is 0.05 Ms^{-1}

If the [A] = 0.05 M, [B] = 0.01M, and [C] = 0.25M. What is the third order rate constant?

S9.3

rate of reaction = k[A][B][C]

$0.05Ms^{-1}$ =k (0.05M)(0,01M)(0.25M)

k= $0.05Ms^{-1}$/(0.05) (0.01)(0.25) M^3

k= $400M^{-2}s^{-1}$

Q9.3

What are the units of the rate constant for a second-order reaction?

S9.3

The reaction rate:

$$Rate = \frac{d[A]}{dt} = -k[A]^2 \tag{9.E.3}$$

The rate constant of a second-order reaction, k, is $M^{-1}min^{-1}$ or $M^{-1}s^{-1}$

Q9.4

Calculate the fraction of the starting quantity of A that will be used up after 60 s. Given the reaction below which is found to be the first order in A and $t_{1/2} = 40\ s$

$$A \rightarrow B + C \tag{9.E.4}$$

S9.4

with \(t_{1/2} = 40 \; s\]

$k = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{40} = 0.0173s^{-1}$

The remain of fraction A after 60 s:

$[A] = [A]_o e^{-kt}$

$\frac{[A]}{[A]_o} = e^{-(0.0173s^{-1})(60s)} = 0.354$

The fraction will be used up after 60s:

$1 - 0.354 = 0.646$

Q9.5

Given the first order reaction is completed 90% in 30 mins at 298 K. Calculate the rate constant.

S9.5

90%= 0.9

$[A] = [A]_o e^{-kt}$

$\frac{[A]}{[A]_o} = e^{-kt}$

$\ln \frac{[A]}{[A]_o} = -kt$

$\ln 0.9 = -30k$

$k = -\frac{\ln 0.9}{30} = 0.00351 min^{-1}$

Q9.6

Assume the half life of the first order decay of radioactive isotope takes about 1 year (365 days). How long will it take the radioactivity of that isotope to decay by 60%?

S9.6

$t_{1/2} = \frac{\ln 2}{k}$

$k = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{365} = 0.00189 day^{-1}$

60% is lost

100%- 60%= 40% is remained

40%= 0.4

$$\frac{[A]}{[A]_o} = 0.4$$

$$\frac{[A]}{[A]_o} = e^{-kt}$$

$$\ln\frac{[A]}{[A]_o} = -kt$$

$$t = \frac{-1}{k}\ln\frac{[A]}{[A]_o} = \frac{-1}{0.00189}\ln 0.4 = 484.81 days$$

Q9.7a

The decomposition of dinitrogen peroxide (N_2O_5) is a first-order reaction with a rate constant of 0.045 min^{-1} at 300 K.

$$2N_2O_{5(g)} \rightarrow 4NO_2(g) + O_2 \tag{9.E.5}$$

If there were initially 0.040 mol of N_2O_5, calculate the moles of N_2O_5 remaining after 5 minutes.

S9.7a

The integrated rate equation of a first-order reaction is:

$$[A] = [A]_0 e^{-kt} \tag{9.E.6}$$

Substituting concentration for moles of reactant and plugging in the known values:

$$n_A = 0.040_0 e^{-0.045*5} \tag{9.E.7}$$

$$n_A = 0.032 \tag{9.E.8}$$

Q9.7b

You forgot to do your lab assignment the day before and realize you only have 5 hours to reduce your initial concentration of your reactant by 90%. You know the half life is 2 hours and before you get out of bed, you wonder if you can even finish the lab on time. Assuming you have a first order reactant, will 5 hours be enough time for your compound to reduce by 90%?

S9.7b

First, you need to figure the half life of your compound. We do this by solving for **k**:

$$t_{1/2} = \frac{0.693}{k} \tag{9.E.9}$$

$$k = \frac{0.693}{t\frac{1}{2}} \tag{9.E.10}$$

$$k = \frac{0.693}{2hrs} = 0.3465 \tag{9.E.11}$$

with this half life, we can find the time it will take by solving for **t:**

$$ln\frac{[A]}{[A]_{\circ}} = -kt \tag{9.E.12}$$

We do not have the initial and final concentration, but that is okay.

Assuming the initial concentration is 100 g, we can assume that the final concentration is 10 g because that would be reduced 90% as stated in the problem.

$$ln\frac{[10]}{[100]} = -kt \tag{9.E.13}$$

$$\frac{ln[0.1]}{-0.3465} = t = 6.65\ hours \tag{9.E.14}$$

So 5 hours will be definitely not enough time to reduce the compound

Q9.8a

Assume you are dealing with a first order reactant. You know your rate constant is 1.5x10^{-4}/min, but your employer wants to the half-life of the reactant?

S9.8a

$$t_{1/2} = \frac{0.693}{k} \tag{9.E.15}$$

$$t_{1/2} = \frac{0.693}{1.5x10^{-4}} \tag{9.E.16}$$

$$= 4.62 \times 10^3\ mins \tag{9.E.17}$$

Q9.8b

The half-life of a second order reaction

$$2A \rightarrow P \tag{9.E.18}$$

is given by:

$$t_{1/2} = \frac{1}{k[A]_o} \tag{9.E.19}$$

Calculate the half-life of a reaction with initial reactant concentration [A] = 0.90 M and a rate constant of 0.20 M^{-1} min^{-1}.

S9.8b

$$t_{1/2} = \frac{1}{0.20 \times 0.90} = 0.18 min^{-1} \tag{9.E.20}$$

Q9.9a

A reaction

$$A \rightarrow B \tag{9.E.21}$$

is observed. You do not know the stoichiometry of the reactants or products, but observe that when you increase the initial concentration of A from 0.4 M to 0.8 M, the half-life decreased from 10 minutes to 5 minutes. Determine the reaction order and the rate constant.

S9.9a

A reaction whose half-life changes when the reactant concentration is changed is a second-order reaction.

$$t_{1/2} = \frac{1}{k[A]_o} \tag{9.E.22}$$

$$k = \frac{1}{[A]_0 t_{1/2}} \tag{9.E.23}$$

$$k = \frac{1}{(0.4M)(5min)} = 0.5M^{-1}min^{-1} \tag{9.E.24}$$

Q9.9b

You notice the initial concentration has no affect on the half-life. From this information alone, what can you determine about the the order of the reactant?

S9.9b

You can determine from this information that it would be a first order reactant. The concentration of first order reactants has not affect on the rate or half-life of the reactant. This can be seen in the formula. t_{\frac{1}{2}}=\frac{0.693}{k} This formula does not account for the initial concentration of the reactant.

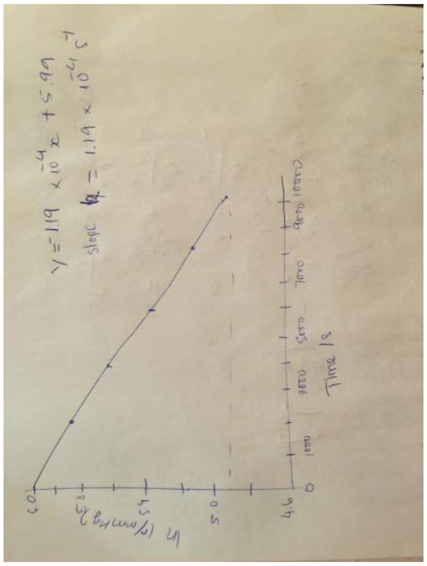
Q9.10a

Calculate the order of the reaction and the rate constant of Cytobutane decompose to ethylene based on equation

\[C_$_4$H_{8 g)} \rightarrow 2C_$_2$H_{$_4$(g)}\]

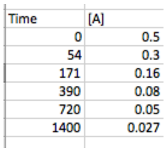
and temperature at 215^{0}C, constant volume, the pressure 200, 158, 124, 98, 77.5, 61 mmHg.

S9.10a



Q9.10b

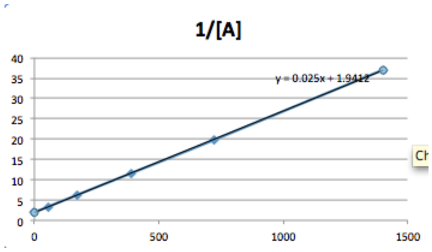
Given the following data of concentration [A] over a period of time, decide if the data represents first order or second order. Solve for K. Show graphs.



Time	[A]
0	0.5
54	0.3
171	0.16
390	0.08
720	0.05
1400	0.027

S9.10b

The data best fits a Second order graph.



The equation for a second order reaction is:

1/[A]= kt+ 1/[A_0]

When solving for K, the equation is rearranged to:

1/[A]- 1/[A_0] =k

t

Plug in the numbers given:

1/[.3]- 1/[.5]= k

(0-54)

.025=k

One, can also obtain the slop of the graph and k=.025

Q9.11a

If a compound's ½ life is 15.6 days. What is the value of k? How long will it take to decompose to 10%. Use first order reaction.

S9.11a

Equation for half-life of a First-Order Reaction is:

$$t_{½} = \frac{\ln(2)}{k} \tag{9.E.25}$$

If we plug in the information given:

$$15.6 days = \frac{\ln(2)}{k} \tag{9.E.26}$$

$$k = 4.4 \times 10^{-2}\, day^{-1} \tag{9.E.27}$$

The second equation needed is the first order reaction, which is:

$$\ln([A]/[A_0]) = -kt_{1/2}$$

so, ln $([A]/[A_0])$=.1

t=-1/k x ln($[A]/[A_0]$)

t= -1/(4.4 x 10^{-2} day^{-1}) x (.1)

t=52 days

12) In a second order reaction 2A--> products, the final concentration is .28M. What is the initial concentration if k=.32M^{-1}s^{-1} and the times is 5 seconds.

Solution:

Second order reaction equation is:

$1/[A] = kt + 1/[A_0]$

Filling the information given:

1/[.28M]=.32M^{-1}s^{-1}(5)+ 1/$[A_0]$

$1/[A_0]$= 1.97

$[A_0]$= .50M

Q9.11b

Calculate the half life of a compound if 90% of a given sample of the compound decomposed in 30min

S9.11b

$$[A]=[A]_0\ e\text{^}{-kt}$$

$$[A]_0 = 90\%$$

$$[A] = 10\%$$

$$t = 30min * 60s/1min = 1800s$$

$$[10\%]/[90\%]=e\text{^} -k*1800$$

$$\ln[10\%/90\%]/1800 = k = 3.95E\text{-}4$$

$$t1/2= \ln(2)/k$$

$$t1/2 = .693/3.95E\text{-}4= 1754s$$

1754s*1min/60s = 29 min

Q9.12

Given rate constant for second order reaction

$$2NO_{2(g)} \rightarrow 2NO_{(g)} + O_{2(g)} \tag{9.E.28}$$

is 1.08 $M^{-1}s^{-1}$ at 600 ^{0}C. Find the time that would take for the concentration of NO_2 from 1.24 M to 0.56 M?

S9.12

$$1/[A] - 1/[A]_0 = kt$$

$$t = 1/k\ (1/[A] - 1/[A]_0)$$

$$= (1/\ 1.08\ M^{-1}s^{-1})\ (1/0.56 - 1/1.24) = 7.2\ s$$

Q9.13a

Is which order of reaction half-life is independent of initial concentration?

S9.13a

First order because the half-life equation for first order is

$t_{1/2=}$ ln(2)/k, it does not have $[A_0]$

Q9.13b

The decomposition of N2) is the first order. At 365^{0}C, t1/2 is 1.79 x 10^3 min. given intial pressure of 1.05 atm.. Calculate total pressure.

S9.13b

$$\begin{aligned} P &= P_{N_2O} + P_{N_2} + P_{O_2} \qquad (9.E.29) \\ &= 0.525 + 0.525 + 0.2625 = 1.31\ atm \qquad (9.E.30) \end{aligned}$$

Q9.14a

The integrated rate law for the zero-order reaction A → B is $[A]_t = [A]_0 - kt$

a) skektch the following plots:

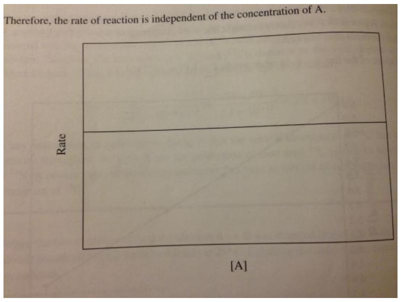
(i) rate vs. [A]

(ii) [A] vs. t

S9.14a

rate = k

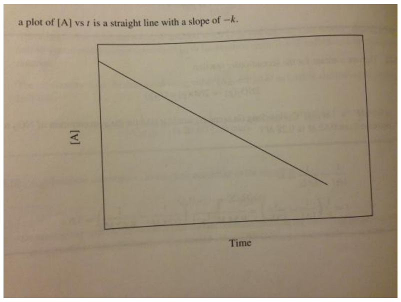
rate is independent of [A]



Therefore, the rate of reaction is independent of the concentration of A.

(ii) [A] vs. t

$[A]_t = [A]_0 - kt$


a plot of [A] vs t is a straight line with a slope of $-k$.

b) Derive an expression for the half-life of the reaction.

At t = $t_{1/2}$, [A] = $[A]_0/2$ so, $[A]_0/2$ = $[A]_0$ - $kt_{1/2}$

$t_{1/2}$ = 1/2k [A$\}_0$

c) Calculate the time in half-lives when the integrated rate law is no longer valid (that is, when [A] = 0)

$[A]_t$ = 0 = $[A]_0$ - kt

$t_{1/2}$ = 1/2k [A$\}_0$ ⇒ k = 1/2$t_{1/2}$ [A$\}_0$

Therefore, to consume all of the reactants it takes

t = [A$\}_0$/k = $[A]_0$/2 so, $[A]_0$ / (1/(2$t_{1/2}$)) $[A]_0$ = 2$t_{1/2}$

integrated rate law is no longer valid after 2 half-lives

Q9.14b

Jack, Jill, and you are in a physical chemistry class. The professor writes the following equations on the black board.

$$A \rightarrow B \tag{9.E.31}$$

$$[A] = [A_0]e^{-kt} \tag{9.E.32}$$

a. The professor assigns you to derive the first-order reaction in front of the class.
b. Jack was assigned to find the rate constant if the reaction half-life is 10 hours. Since you are a good friend of Jack, you decide to help him double check his answer by solving for the rate constant.

S9.14b

a)

$$\int_{[A]_0}^{[A]} \frac{d[A]}{[A]} = \int_0^t -kdt \tag{9.E.33}$$

$$\ln[A] \,|_{[A]_0}^{[A]} = -kt \tag{9.E.34}$$

$$\ln[A] - \ln[A]_0 = -kt \tag{9.E.35}$$

$$\ln\frac{[A]}{[A]_0} = -kt \tag{9.E.36}$$

$$\frac{[A]}{[A]_0} = e^{-kt} \tag{9.E.37}$$

$$[A] = [A_0]e^{-kt} \tag{9.E.38}$$

b)

$$t_{1/2} = \frac{\ln 2}{k} \tag{9.E.39}$$

$$10 hours = \frac{\ln 2}{k} \tag{9.E.40}$$

$$k = \frac{\ln 2}{10 hours} \times \frac{1 hour}{60 min} \times \frac{1 min}{60 secs} \tag{9.E.41}$$

$$k = \tag{9.E.42}$$

Q9.15a

In the nuclear industry, workers use a rule of thumb that the readioactivity from any sample will be relatively harmless after 10 half-lives. Calculate the fraction of a radioactive sample that remains after this time period (hint: Radioactive decay obeys first-order kinetics)

S9.15a

$[A] = [A]_o e^{-kt}$

$t_{1/2} = \ln 2 / k$

$[A] = (100)e^{-(1)(10)} = .00454$

% remaining after 10 half-lives

Q9.15b

As a school field trip to apply what you learned in physical chemistry class, you and your class went to a nuclear power plant. The plant's manager, Mr. Setsaw gives the class a tour of the facilities. When the class reaches the simulation room, a meltdown simulation is offered to the class, but only if the class can answer his questions can the class experience it.

a. Radioactive decay occurs in what order?
b. The gas used in the simulation is harmless because the fraction of the original remaining is 0.004 and the time that passed 30 years. What is the rate constant?

S9.15b

a) Radioactive decay occurs in first order.

b)

$$\frac{[A]}{[A]_0} = e^{-kt} \tag{9.E.43}$$

$$0.004 = e^{-k\,30 years} \tag{9.E.44}$$

$$\ln[0.004] = -k\,30 years \tag{9.E.45}$$

$$k = \frac{-30}{\ln[0.004]} \tag{9.E.46}$$

$$k = \tag{9.E.47}$$

Q9.16a

Many reactions involving heterogeneous catalysis are zero order; that is, rate = k. An example is the decomposition of phosphine (PH_3) over tungsten (W):

$$4\,PH_3(g) \rightarrow P_4(g) + 6\,H_2(g) \tag{9.E.48}$$

The rate for this reaction is independent of $[PH_3]$ as long as phosphine's pressure is sufficiently high (>= 1 atm). Explain.

S9.16a

With sufficient PH_3, all of the catalytic sites on the tungsten surface are occupied. Further increases in the amount of phosphine cannot affect the reaction, and the rate is independent of $[PH_3]$.

Q9.16b

Jill and you just went to an enzyme kinetic workshop. However, Jill is confused about why at high concentrations of substrates the reaction order is zero-order. Please explain to Jill in a way that anyone can understand.

S9.16b

At high concentrations of substrates, all the enzymes are working at their fastest rate. As soon as the enzyme is done converting one substrate to its product, another substrate comes into the active site. Therefore, the rate of the enzyme working is constant and this is the definition for zero-order reaction.

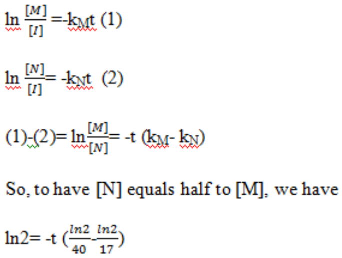
9.3: Molecularity of a Reaction

Q9.41a

A mixture of compounds M and N whose half-lives are 40 minutes and 17 minutes, respectively. They decompose by first-order kinetics. If their concentrations are equal initially, how long does concentration of N to be half that of M?

S9.41a

[I] is the initial concentration of M and N



$\ln \frac{[M]}{[I]} = -k_M t$ (1)

$\ln \frac{[N]}{[I]} = -k_N t$ (2)

(1)-(2)= $\ln \frac{[M]}{[N]} = -t\,(k_M - k_N)$

So, to have [N] equals half to [M], we have

$\ln 2 = -t\,(\frac{\ln 2}{40} - \frac{\ln 2}{17})$

-> t = 30.1 min

Q9.41b

Compounds A and B both decay by first-order kinetics. The half-life of A is 20 minutes and the half-life of B is 48 minutes. If a container initially contains equal concentrations of compounds A and B, after how long will the concentration of B be twice that of A?

S9.41b

1. Write, in mathematical terms, the information given in the problem and what the problem is asking for.

$$t_{1/2,A} = 20.0 min \tag{9.E.49}$$

$$t_{1/2,B} = 48.0 min \tag{9.E.50}$$

$$[A]_0 = [B]_0 \tag{9.E.51}$$

A and B decay by first-order, so

$$-\frac{d[A]}{dt} = k_A[A] \tag{9.E.52}$$

$$-\frac{d[B]}{dt} = k_B[B] \tag{9.E.53}$$

(Note: the rate constants for A and B are not equal, so indicate which is which with subscripts.)

Want find t at which the following is true:

$$[B] = 2[A] \tag{9.E.54}$$

2. Substitute the integrated rate equations for [A] and [B]

$$[B]_0 e^{-k_B t} = 2[A]_0 e^{-k_A t} \tag{9.E.55}$$

3. Write expressions for the rate constants in terms of half-lives, and substitute into the equation.

$$t_{1/2,A} = \frac{ln2}{k_A} \Rightarrow k_A = \frac{ln2}{t_{1/2,A}} \tag{9.E.56}$$

$$t_{1/2,B} = \frac{ln2}{k_B} \Rightarrow k_B = \frac{ln2}{t_{1/2,B}} \tag{9.E.57}$$

$$[B]_0 e^{-\frac{ln2}{t_{1/2,B}} t} = 2[A]_0 e^{-\frac{ln2}{t_{1/2,B}} t} \tag{9.E.58}$$

4. Solve for t

Since initial concentrations of A and B are equal:

$$e^{-\frac{ln2}{t_{1/2,B}} t} = 2e^{-\frac{ln2}{t_{1/2,B}} t} \tag{9.E.59}$$

Take natural log of both sides:

$$-\frac{t}{t_{1/2,B}} ln2 = \left(1 - \frac{t}{t_{1/2,A}}\right) ln2 \tag{9.E.60}$$

$$t = \frac{1}{\frac{1}{t_{1/2,A}} - \frac{1}{t_{1/2,B}}} \tag{9.E.61}$$

5. Plug in values for half-lives

\[t = \dfrac{1}{\dfrac{1}{20.0 min} - \dfrac{1}{48.0 min}} = 34.2\ min \]

Answer: 34.2 minutes

Q9.42a

In Q3 thermodynamics and in Q9 chemical kinetics, the term “reversible “ is used. How do you understand this term? (it has a same meaning in these two chapters)

S9.42a

Actually, this word is used to describe a “reversible” reaction in which both forward and backward reactions can happen in kinetics. In thermodynamics, “reversible” is used to describe a process that is in equilibrium along the pathway from the initial to final states.

Q9.42b

If a reaction has come to thermodynamic equilibrium, can we say anything in particular about the system's kinetics?

S9.42b

Equilibrium occurs when all reactants and products are being consumed at the same rate that they are created. Take the simple example:

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B \tag{9.E.62}$$

When the system is at equilibrium,

$$\frac{d[A]}{dt} = \frac{d[B]}{dt} = 0 \tag{9.E.63}$$

$$k_{-1}[A] = k_1[B] \tag{9.E.64}$$

$$\frac{k_{-1}}{k_1} = \frac{[B]}{[A]} \tag{9.E.65}$$

$$K_{eq} = \frac{k_{-1}}{k_1} \tag{9.E.66}$$

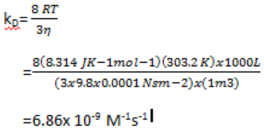
Q9.43a

The recombination of bromine atoms in an organic solvent, like carbon tetrafloride, is considered as a diffusion-controlled process

$$Br + Br \rightarrow Br_2 \tag{9.E.67}$$

we have the viscosity of CF_4 is 9.80 x 10^{-4} Nsm^{-2} at 30^oC, what is the rate of recombination at 30^oC?

S9.43a



$$k_D = \frac{8\,RT}{3\eta}$$

$$= \frac{8(8.314\ JK-1mol-1)(303.2\ K)x1000L}{(3x9.8x0.0001\ Nsm-2)x(1m3)}$$

$$= 6.86x\ 10^{-9}\ M^{-1}s^{-1}$$

Q9.43b

Calculate the rate constant of the diffusion-controlled reaction

$$2I \rightarrow I_2 \tag{9.E.68}$$

in dichloromethane at 15°C, which has a viscosity of 0.449 mPa·s at 15°C.

S9.43b

1. Use equation 9.50 to calculate the rate constant.

$$k_D = \frac{8}{3}\frac{RT}{\eta} \tag{9.E.69}$$

$$k_D = \frac{8}{3}\frac{8.314\frac{J}{mol\ K} \times 288\ K \times \frac{N\ m}{J}}{0.449\ mPa\ s \times \frac{Pa}{1000\ mPa} \times \frac{N/m^2}{Pa}} \times \frac{1000\ L}{m^3} \tag{9.E.70}$$

Answer:

$$k_D = 1.42 \times 10^{10} M^{-1} s^{-1} \tag{9.E.71}$$

Q9.52

Japanese survivors have been exposed to the risk of radiation after the atomic bomb. One man was measured to have iodine-131 levels at 9.7 mC. Calculate the number of atoms of I-131 to which this radioactivity corresponds.

S9.52

First, convert the rate mCi s^{-1}

1 mCi=1.10X10^{-3} Ci

1 Ci=3.7 X 10^{10} s^{-1}

The rate (r can be derived as such

$$r = (9.7\ Ci)\left(\frac{1\ Ci}{1000\ mCi}\right)\left(\frac{3.7 \times 10^{10}\ s^{-1}}{1\ Ci}\right) = 3.59 \times 10^8 s^{-1} \tag{9.E.72}$$

The accepted value for the half life of I-131 is 8.02 days. Using this information, the number of I-131 atoms can be calculated using the nuclear decay equation. Use the

Nuclear Decay Equation:

$$\lambda N = \frac{\ln 2}{t_{1/2}} N \tag{9.E.73}$$

or

$$N = \frac{\ln 2}{t_{1/2}} r \tag{9.E.74}$$

The half-life for the radioactive beta decay of iodine is 8.02 days

$$^{131}_{53}\text{I} \rightarrow {}^{131}_{54}\text{Xe} + \beta + \bar{\nu_e} \tag{9.E.75}$$

therefore, the rate is

$$r = 3.59 \times 10^8 s^{-1} \tag{9.E.76}$$

Plug into the equation and convert days to seconds.

(8.02 days/ln2)(24 hours/1 day)(3600 seconds/1 hour)(3.59X 10^{-8}) = 2.49 X 10^{14} I-131 atoms.

N= (

Q9.54

Calculate the rate law for the following acid-catalyzed reaction:

$$CH_3COCH_3 + Br_2 \xrightarrow{H^+} CH_3COCH_2Br + H^+ + Br^- \tag{9.E.77}$$

Expt. #	$[CH_3COCH_3]_o$/ M	$[Br_2]_o$ /M	$[H^+]_o$ /M	Rate of Disappearance Br_2/ M*s^{-1}
1	0.3	0.05	0.05	5.7×10^{-5}
2	0.3	0.1	0.05	5.7×10^{-5}
3	0.3	0.05	0.05	1.2×10^{-4}
4	0.4	0.05	0.2	3.1×10^{-4}
5	0.4	0.05	0.05	7.6×10^{-5}

S9.54

Find the rate law.
rate = k[CH3COCH3]^x [Br2]^y [H+]^z

[exp 1] / [exp 5]:
5.7e-5 / 7.6e-5 = (0.30/0.40)^x (0.050/0.050)^y (0.050/0.050)^z
3/4 = (3/4)^x
x = 1

[exp 1] / [exp 2]:
5.7e-5 / 5.7e-5 = (0.30/0.30) (0.050/0.10)^y (0.050/0.050)^z
1 = (1/2)^y
y = 0

[exp 1] / [exp 3]:
5.7e-5 / 1.2e-4 = (0.30/0.30) (0.050/0.10)^z
19/40 = (1/2)^z

z ≈ 1

Use [exp 1] to find rate constant.
5.7e-5 M/s = k(0.30 M)(0.050 M)
k = 3.8e-3 M^(-1)-s^(-1)

"calculate the rate of disappearance of bromine if the initial concentration are .600mol/L, 0.200 mol/L, and .10 mol/L for propanone, bromine and H+."
rate = (3.8e-3 M^(-1)-s^(-1))(0.600 M)(0.10 M)
rate = 2.28e-4 M/s

Q9.55

Determine the rate law for the following reaction:

$$N_2O_2 + H_2 \rightarrow H_2O + N_2O \tag{9.E.78}$$

In addition, determine which of the following actions would alter the value of k?

a. Increase in pressure of N_2O_2
b. Increase in volume size of container
c. Increase in temperature
d. Addition of catalyst to the container.
e. None of the above ;a rate constant is always constant.

Q9.56

Consider the mechanism for the association of iodine atoms to create molecular iodine.

$$2I_{(g)} \rightleftharpoons I^*_{2(g)} \tag{9.E.79}$$

$$I^*_2(g) + M(g) \rightarrow I_{2(g)} + M_{(g)} \tag{9.E.80}$$

With the respect of the first step is at equilibrium, determine the expected rate law (d/dt)[I2(g)] in terms of k1, k-1, k2, [I], and [M].

Q9.57

Consider the following reaction:

$$C_3H_{8(g)} + 5O_{2(g)} -> 3CO_{2(g)} + 4H_2O_{(g)} \tag{9.E.81}$$

If propane (C3H8) is burning at a rate of 0.15 M/s^-1, calculate the rate of formation of CO2.

9.4: More Complex Reactions

S9.57

First, express the reaction with the differential rate equation for the reactants and products involved.

-(d/dt)[C3H8] = (1/3)(d/dt)[CO2]

Then, use the given burning rate of propane and plug it into the differential equation.

(d/dt)[CO2] = 3(0.15M/s^-1)

(d/dt)[CO2] = 0.45 M/s^-1

9.5: The Effect of Temperature on Reaction Rates

Q9.26

If kept in a refrigerator, fresh fish will last for 3 days. If kept in a freezer, it will last for 6 months. Assuming that the temperature in the refrigerator is 5°C, and the temperature in the freezer is -10°C, calculate the activation energy for the bacterial spoiling of fish. Assume that the spoiling time is the 1/e lifetime instead of the half-life.

Q9.27

Find the activation energy of a reaction whose rate constant is multiplied by 6.50 when T is increased from 300.0 K to 310.0 K. For a reaction with E_a = 19 kJ/mol, by what factor is k multiplied when T increases from 300.0 K to 310.0 K?

Q9.28

The kinetics of the browning of juice from Golden Delicious apples was studied; at 20°C $k=7.87\times10^{-3}$/week, and at 37°C $k=0.139$/week. What is the activation energy for the browning of Golden Delicious apple juice?

9.6: Potential Energy Surfaces

9.7: Theories of Reaction Rates

9.8: Isotope Effects in Chemical Reactions

9.9: Reactions in Solution

9.10: Fast Reactions in Solution

9.11: Oscillating Reactions

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CHAPTER OVERVIEW

10: Enzyme Kinetics

Enzyme kinetics is the study of the chemical reactions that are catalyzed by enzymes. In enzyme kinetics, the reaction rate is measured and the effects of varying the conditions of the reaction are investigated.

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10.1: General Principles of Catalysis

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. *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 $10.1.1$ shows a comparison of energy profiles of a reaction in the absence and presence of a catalyst.

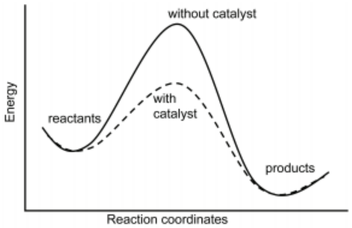


Figure 10.1.1: Comparison of energy profiles with and without catalyst present.

Consider a non-catalyzed elementary reaction

$$\mathrm{A} \xrightarrow{k} \mathrm{P} \tag{10.1.1}$$

which proceeds at rate k at a certain temperature. The reaction rate can be expressed as

$$\frac{d[\mathrm{A}]}{dt} = -k[\mathrm{A}] \tag{10.1.2}$$

In the presence of a catalyst C, we can write the reaction as

$$\mathrm{A} + \mathrm{C} \xrightarrow{k_{\text{cat}}} \mathrm{P} + \mathrm{C} \tag{10.1.3}$$

and the reaction rate as

$$\frac{d[\mathrm{A}]}{dt} = -k[\mathrm{A}] - k_{\text{cat}}[\mathrm{A}][\mathrm{C}] \tag{10.1.4}$$

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. $k_{\text{cat}} \gg k$), the first term can often be ignored.

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

$$\frac{d[\mathrm{P}]}{dt} = k[\mathrm{S}] \tag{10.1.5}$$

The purpose of an enzyme is to enhance the rate of production of the product P. The equations of the acid-catalyzed reaction are

$$\mathrm{S} + \mathrm{A}H \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{S}H^+ + \mathrm{A}^- \tag{10.1.6}$$

$$\mathrm{S}H^+ + H_2O \xrightarrow{k_2} \mathrm{P} + H_3O^+ \tag{10.1.7}$$

$$H_3O^+ + \mathrm{A}^- \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \mathrm{A}H + H_2O \tag{10.1.8}$$

The full set of kinetic equations is

$$\frac{d[\mathrm{S}]}{dt} = -k_1[\mathrm{S}][\mathrm{A}H] + k_{-1}\left[SH^+\right]\left[\mathrm{A}^-\right] \tag{10.1.9}$$

$$\frac{d[\mathrm{A}H]}{dt} = -k_1[\mathrm{S}][\mathrm{A}H] + k_{-1}\left[SH^+\right]\left[\mathrm{A}^-\right] - k_{-3}[\mathrm{A}H] + k_3\left[H_3O^+\right]\left[\mathrm{A}^-\right] \tag{10.1.10}$$

$$\frac{d\left[\mathrm{S}H^+\right]}{dt} = k_1[\mathrm{S}][\mathrm{A}H] - k_{-1}\left[SH^+\right]\left[\mathrm{A}^-\right] - k_2\left[SH^+\right] \tag{10.1.11}$$

$$\frac{d\left[\mathrm{A}^-\right]}{dt} = k_1[\mathrm{S}][\mathrm{A}H] - k_{-1}\left[SH^+\right]\left[\mathrm{A}^-\right] - k_2\left[\mathrm{A}^-\right]\left[H_3O^+\right] + k_{-3}[\mathrm{A}H] \tag{10.1.12}$$

$$\frac{d[\mathrm{P}]}{dt} = k_2\left[SH^+\right] \tag{10.1.13}$$

$$\frac{d\left[H_3O^+\right]}{dt} = -k_2\left[SH^+\right] - k_3\left[H_3O^+\right]\left[\mathrm{A}^-\right] + k_{-3}[\mathrm{A}H] \tag{10.1.14}$$

We cannot easily solve these, as they are nonlinear. However, let us consider two cases $k_2 \gg k_{-1}\left[\mathrm{A}^-\right]$ and $k_2 \ll k_{-1}\left[\mathrm{A}^-\right]$. In both cases, $\mathrm{S}H^+$ is consumed quickly, and we can apply a steady-state approximation:

$$\frac{d\left[\mathrm{S}H^+\right]}{dt} = k_1[\mathrm{S}][\mathrm{A}H] - k_{-1}\left[\mathrm{A}^-\right]\left[\mathrm{S}H^+\right] - k_2\left[\mathrm{S}H^+\right] = 0 \tag{10.1.15}$$

Rearranging in terms of $\mathrm{S}H^+$ yields

$$\left[SH^+\right] = \frac{k_1[\mathrm{S}][\mathrm{A}H]}{k_{-1}\left[\mathrm{A}^-\right] + k_2} \tag{10.1.16}$$

and the rate of production of P can be written as

$$\frac{d[\mathrm{P}]}{dt} = k_2\left[SH^+\right] = \frac{k_1 k_2[\mathrm{S}][\mathrm{A}H]}{k_{-1}\left[\mathrm{A}^-\right] + k_2} \tag{10.1.17}$$

In the case where $k_2 \gg k_{-1}\left[\mathrm{A}^-\right]$, Equation 10.1.17can be written as

$$\frac{d[\mathrm{P}]}{dt} = k_1[\mathrm{S}][\mathrm{A}H] \tag{10.1.18}$$

which is known as a general acid-catalyzed reaction. On the other hand, if $k_2 \ll k_{-1}\left[\mathrm{A}^-\right]$, we can use an equilibrium approximation to write the rate of production of P as

$$\frac{d[\mathrm{P}]}{dt} = \frac{k_1 k_2[\mathrm{S}][\mathrm{A}H]}{k_{-1}\left[\mathrm{A}^-\right]} = \frac{k_1 k_2}{k_{-1}K}[\mathrm{S}]\left[H^+\right] \tag{10.1.19}$$

where K is the acid dissociation constant:

$$K = \frac{\left[\mathrm{A}^-\right]\left[H^+\right]}{[\mathrm{A}H]} \tag{10.1.20}$$

In this case, the reaction is hydrogen ion-catalyzed.

Enzyme Catalysis

To live, grow, and reproduce, microorganisms undergo a variety of chemical changes. They alter nutrients so they can enter the cell and they change them once they enter in order to synthesize cell parts and obtain energy.

Metabolism refers to all of the organized chemical reactions in a cell. Reactions in which chemical compounds are broken down are called **catabolic reactions** while reactions in which chemical compounds are synthesized are termed **anabolic reactions**. All of these reactions are under the control of enzymes.

Enzymes are substances present in the cell in small amounts that function to **speed up or catalyze chemical reactions**. On the surface of the enzyme is usually a small crevice that functions as an **active site** or catalytic site to which one or two specific substrates are able to bind. (Anything that an enzyme normally combines with is called a

substrate.) The binding of the substrate to the enzyme causes the flexible enzyme to change its shape slightly through a process called **induced fit** to form a tempore intermediate called an **enzyme-substrate complex** (Figure 1).

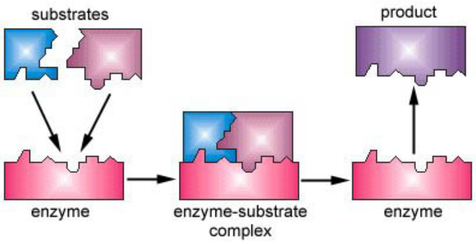


Figure 10.1.2 : Enzymes are substances present in the cell in small amounts which speed up or catalyze chemical reactions. Enzymes speed up the rate of chemical reactions because they lower the energy of activation, the energy that must be supplied in order for molecules to react with one another. Enzymes lower the energy of activation by forming an enzyme-substrate complex.

Enzymes speed up the rate of chemical reactions because they lower the energy of activation, the energy that must be supplied in order for molecules to react with one another (Figure 10.1.3). Like homogeneous catalysts discussed above, enzymes lower the energy of activation by forming an enzyme-substrate complex allowing products of the enzyme reaction to be formed and released (Figure 10.1.2).

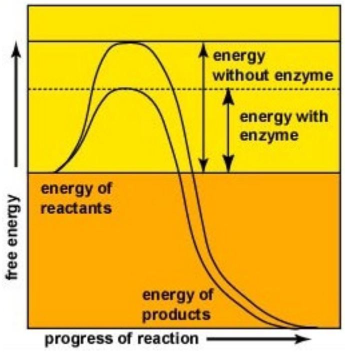
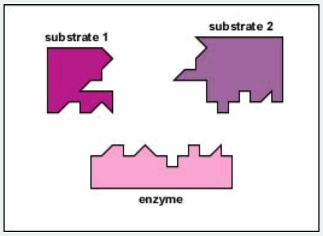


Figure 10.1.3 : An enzyme speeds up a chemical reaction by lowering its energy of activation, the energy that must be supplied in order for molecules to react with one another.

Enzyme-Substrate Reactions

Enzymes are substances present in the cell in small amounts which speed up or catalyze chemical reactions. Enzymes speed up the rate of chemical reactions because they lower the energy of activation, the energy that must be supplied in order for molecules to react with one another. Enzymes lower the energy of activation by forming an enzyme-substrate complex.



Many enzymes require a nonprotein **cofactor** to assist them in their reaction. In this case, the protein portion of the enzyme, called an **apoenzyme**, combines with the cofactor to form the whole enzyme or **haloenzyme** (Figure 10.1.4). Some cofactors are ions such as Ca^{++}, Mg^{++}, and K^{+}; other cofactors are organic molecules called **coenzymes** which serve as carriers for chemical groups or electrons. NAD^{+}, $NADP^{+}$, FAD, and coenzyme A (CoA) are examples of coenzymes.

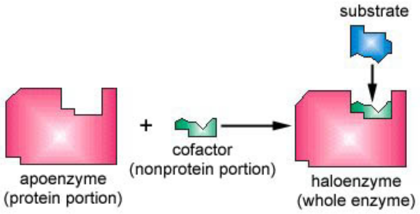


Figure 10.1.4 : An apoenzyme and cofactor combine to form a haloenzyme. If the cofactor is an organic molecule, it is called a coenzyme.

Enzymes are generally globular proteins. (Some RNA molecules called ribozymes can also be enzymes. These are usually found in the nuclear region of cells and catalyze the splitting of RNA molecules.). Enzymes are catalysts that breakdown or synthesize more complex chemical compounds. They allow chemical reactions to occur fast enough to support life. Enzymes speed up the rate of chemical reactions because they lower the energy of activation, the energy that must be supplied in order for molecules to react with one another. Anything that an enzyme normally combines with is called a substrate. Enzymes are very efficient with a typically enzyme generally able to catalyze between 1 and 10,000 molecules of substrate per second. The means that enzymes are only have to be present in small amounts in the cell since. They are not altered during their reaction and are highly specific for their substrate, with generally one specific enzyme dedicated for each specific chemical reaction.

Factors that affect the rate of enzyme reactions

Enzyme activity is affected by a number of factors including:

a. **The concentration of enzyme**: Assuming a sufficient concentration of substrate is available, increasing enzyme concentration will increase the enzyme reaction rate.
b. **The concentration of substrate**: At a constant enzyme concentration and at lower concentrations of substrates, the substrate concentration is the limiting factor. As the substrate concentration increases, the enzyme reaction rate increases. However, at very high substrate concentrations, the enzymes become saturated with substrate and a higher concentration of substrate does not increase the reaction rate.
c. **Inhibitors:** inhibitors will inhibit the activity of enzyme and decrease the rate of reaction. Enzyme inhibitors will bind to enzyme active sites and could modify the chemistry of an active site which can stop a substrate from entering.
d. **The temperature**: Each enzyme has an optimum temperature at which it works best. A higher temperature generally results in an increase in enzyme activity (Arrhenius kinetics). As the temperature increases, molecular motion increases resulting in more molecular collisions. If, however, the temperature rises above a certain point, the heat will denature the enzyme, causing it to lose its three-dimensional functional shape by denaturing its hydrogen bonds. Cold temperature, on the other hand, slows down enzyme activity by decreasing molecular motion.
e. **The pH**: Each enzyme has an optimal pH that helps maintain its three-dimensional shape. Changes in pH may denature enzymes by altering the enzyme's charge. This alters the ionic bonds of the enzyme that contribute to its functional shape.
f. **The salt concentration**: Each enzyme has an optimal salt concentration. Changes in the salt concentration may also denature enzymes.

Applications of Enzymes

Enzymes are essential to maintain homeostasis because any malfunction of an enzyme could lead to diseases. Therefore, pharmaceutical companies study enzyme to manipulate and synthesis new medicine. Besides their medicinal applications, enzymes in industry are important because enzymes help breaking down cellulose, wastes, etc. Enzymes are essential in the process of making new products in many industries such as pharmaceutical, food, paper, wine, etc.

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10.2: The Equations of Enzyme 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.

Michaelis-Menten Enzyme Kinetics

Enzymes are highly specific catalysts for biochemical reactions, with each enzyme showing a selectivity for a single reactant, or **substrate**. For example, the enzyme acetylcholinesterase catalyzes the decomposition of the neurotransmitter acetylcholine to choline and acetic acid. Many enzyme–substrate reactions follow a simple mechanism that consists of the initial formation of an enzyme–substrate complex, ES, which subsequently decomposes to form product, releasing the enzyme to react again.

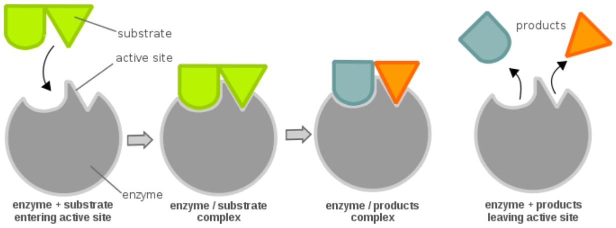


Figure 10.2.1: An enzyme catalyzes the reaction of two substrates and to form one product. from Wikipedia.

This is described within the following multi-step mechanism

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} E + P \tag{10.2.1}$$

where k_1, k_{-1}, k_2, and k_{-2} are rate constants. The reaction's rate law for generating the product $[P]$ is

$$rate = \frac{d[P]}{dt} = k_2[ES] - k_{-2}[E][P] \tag{10.2.2}$$

However, if we make measurement early in the reaction, the concentration of products is negligible, i.e.,

$$[P] \approx 0 \tag{10.2.3}$$

and we can ignore the back reaction (second term in right side of Equation 10.2.2). Then under these conditions, the reaction's rate is

$$rate = \frac{d[P]}{dt} = k_2[ES] \tag{10.2.4}$$

To be analytically useful we need to write Equation 10.2.4 in terms of the reactants (e.g., the concentrations of enzyme and substrate). To do this we use the **steady-state approximation**, in which we assume that the concentration of ES remains essentially constant. Following an initial period, during which the enzyme–substrate complex first forms, the rate at which ES forms

$$\frac{d[ES]}{dt} = k_1[E][S] = k_1([E]_0 - [ES])[S] \tag{10.2.5}$$

is equal to the rate at which it disappears

$$-\frac{d[ES]}{dt} = k_{-1}[ES] + k_2[ES] \tag{10.2.6}$$

where $[E]_0$ is the enzyme's original concentration. Combining Equations 10.2.5 and 10.2.6 gives

$$k_1([E]_0 - [ES])[S] = k_{-1}[ES] + k_2[ES] \tag{10.2.7}$$

which we solve for the concentration of the enzyme–substrate complex

$$[ES] = \frac{[E]_0[S]}{\frac{k_{-1}+k_2}{k_1}+[S]} = \frac{[E]_0[S]}{K_m+[S]} \tag{10.2.8}$$

where K_m is the **Michaelis constant**. Substituting Equation 10.2.8 into Equation 10.2.4 leaves us with our final rate equation.

$$\frac{d[P]}{dt} = \frac{k_2[E]_0[S]}{K_m+[S]} \tag{10.2.9}$$

A plot of Equation 10.2.9, as shown in Figure 10.2.1, is instructive for defining conditions where we can use the rate of an enzymatic reaction for the quantitative analysis of an enzyme or substrate.

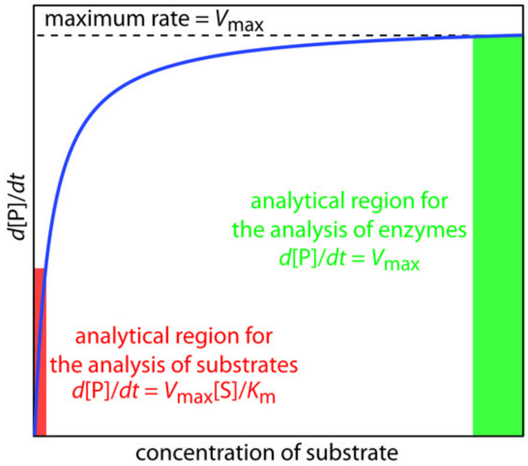


Figure 10.2.1 : Plot of Equation 10.2.9 showing limits for the analysis of substrates and enzymes in an enzyme-catalyzed chemical kinetic method of analysis. The curve in the region highlighted in red obeys equation 10.2.11 and the curve in the area highlighted in green follows Equation 10.2.10.

For high substrate concentrations, where $[S] \gg K_m$, Equation 10.2.9 simplifies to

$$\frac{d[P]}{dt} = \frac{k_2[E]_0[S]}{K_m+[S]} \approx \frac{k_2[E]_0[S]}{[S]} = k_2[E]_0 = V_{max} \tag{10.2.10}$$

where V_{max} is the maximum rate for the catalyzed reaction. Under these conditions the reaction is zero-order in substrate and we can use V_{max} to calculate the enzyme's concentration, typically using a variable-time method. At lower substrate concentrations, where $[S] \ll K_m$, Equation 10.2.9 becomes

$$\frac{d[P]}{dt} = \frac{k_2[E]_0[S]}{K_m+[S]} \approx \frac{k_2[E]_0[S]}{K_m} = \frac{V_{max}[S]}{K_m} \tag{10.2.11}$$

The reaction is now first-order in substrate, and we can use the rate of the reaction to determine the substrate's concentration by a fixed-time method.

The Michaelis constant K_m is the substrate concentration at which the reaction rate is at half-maximum, and is an inverse measure of the substrate's affinity for the enzyme—as a small K_m indicates high affinity, meaning that the rate will approach V_{max} more quickly. The value of K_m is dependent on both the enzyme and the substrate, as well as conditions such as temperature and pH.

> *The Michaelis constant K_m is the substrate concentration at which the reaction rate is at half-maximum.*

From the last two terms in Equation 10.2.11, we can express V_{max} in terms of a **turnover number** (k_{cat}):

$$V_{max} = k_{cat}[E]_o \tag{10.2.12}$$

where $[E]_0$ is the enzyme concentration and k_{cat} is the turnover number, defined as the maximum number of substrate molecules converted to product per enzyme molecule per second. Hence, the turnover number is defined as the maximum number of chemical conversions of substrate molecules per second that a single catalytic site will execute for a given enzyme concentration $[E]_o$.

✓ Example 10.2.1: Turnover number of acetylcholinesterase

Acetylcholinesterase (AChE) may be one of the fastest enzymes. It hydrolyzes acetylcholine to choline and an acetate group. One of the earliest values of the turnover number was 3×10^7 (molecules of acetylcholine) per minute per molecule of enzyme. A more recent value at 25°C, pH = 7.0, acetylcholine concentration of $2.5 \times 10^{-3}\ M$, was found to be $7.4 \times 10^5\ min^{-1}$ (*J Biol Chem.* ***236*** *(8): 2292–5.*).

There may be some 30 active centers per molecule. AChE is a serine hydrolase that reacts with acetylcholine at close to **the diffusion-controlled rate**. A diffusion-controlled reaction occurs so quickly that the reaction rate is the rate of transport of the reactants through the solution; as quickly as the reactants encounter each other, they react.

The Significance of K_M and V_{max}

The Michaelis-Menten model is used in a variety of biochemical situations other than enzyme-substrate interaction, including antigen-antibody binding, DNA-DNA hybridization, and protein-protein interaction. It can be used to characterize a generic biochemical reaction, in the same way that the **Langmuir equation** can be used to model generic adsorption of biomolecular species. When an empirical equation of this form is applied to microbial growth. The experimentally determined parameters values vary wildly between enzymes (Table 10.2.1):

Table 10.2.1: Enzyme Kinetic parameters

Enzyme	K_m (M)	k_{cat} (1/s)	k_{cat}/K_m (1/M.s)
Chymotrypsin	1.5×10^{-2}	0.14	9.3
Pepsin	3.0×10^{-4}	0.50	1.7×10^3
Tyrosyl-tRNA synthetase	9.0×10^{-4}	7.6	8.4×10^3
Ribonuclease	7.9×10^{-3}	7.9×10^2	1.0×10^5
Carbonic anhydrase	2.6×10^{-2}	4.0×10^5	1.5×10^7
Fumarase	5.0×10^{-6}	8.0×10^2	1.6×10^8

While K_m is equal to the substrate concentration at which the enzyme converts substrates into products at half its maximal rate and hence is related to the affinity of the substrate for the enzyme. The catalytic rate k_{cat} is the rate of product formation when the enzyme is saturated with substrate and therefore reflects the enzyme's maximum rate. The rate of product formation is dependent on both how well the enzyme binds substrate and how fast the enzyme converts substrate into product once substrate is bound. For a kinetically perfect enzyme, every encounter between enzyme and substrate leads to product and hence the reaction velocity is only limited by the rate the enzyme encounters substrate in solution. From Equation 10.2.8, the catalytic efficiency of a protein can be evaluated.

$$\frac{k_{cat}}{K_m} = \frac{k_2}{K_m} = \frac{k_1 k_2}{k_{-1} + k_2} \tag{10.2.13}$$

This k_{cat}/K_m ratio is called the specificity constant measure of how efficiently an enzyme converts a substrate into product. It has a theoretical upper limit of $10^8 - 10^{10}$ /M.s; enzymes working close to this, such as fumarase, are termed superefficient (Table 10.2.1).

Determining V_m and K_m from experimental data can be difficult and the most common way is to determine initial rates, v_0, from experimental values of $[P]$ or $[S]$ as a function of time. Hyperbolic graphs of v_0 vs. $[S]$ can be fit or transformed as we explored with the different mathematical transformations of the hyperbolic binding equation to determine K_d. These included:

- nonlinear hyperbolic fit (e.g., Figure 10.2.1)
- double reciprocal plot (e.g., Lineweaver–Burk plot discussed below
- Eadie-Hofstee plot

Lineweaver–Burk plot

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 $1/[\mathrm{S}]$. Rearranging Equation 10.2.10,

$$\frac{1}{r}=\frac{K_M+[\mathrm{S}]}{k_2[\mathrm{E}]_0[\mathrm{S}]}=\frac{K_M}{k_2[\mathrm{E}]_0}\frac{1}{[\mathrm{S}]}+\frac{1}{k_2[\mathrm{E}]_0} \tag{10.2.14}$$

Tthe Lineweaver–Burk plot (or double reciprocal plot) is a graphical representation of the Lineweaver–Burk equation of enzyme kinetics, described by Hans Lineweaver and Dean Burk in 1934 (Figure 10.2.2). The Lineweaver-Burk plot results in a straight line with the slope equal to $K_M/k_2[\mathrm{E}]_0$ and y-intercept equal to $1/k_2[\mathrm{E}]_0$ which is $1/V_{max}$ via Equation 10.2.10.

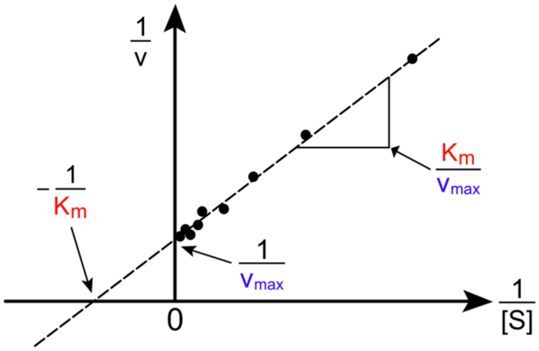


Figure 10.2.2 : Lineweaver–Burk plot of Michaelis–Menten kineitcs.

The plot provides a useful graphical method for analysis of the Michaelis–Menten equation:

$$V=\frac{V_{\max}[S]}{K_m+[S]} \tag{10.2.15}$$

Taking the reciprocal gives

$$\frac{1}{V}=\frac{K_m+[S]}{V_{max}[S]}=\frac{K_m}{V_{max}}\frac{1}{[S]}+\frac{1}{V_{max}} \tag{10.2.16}$$

where

- V is the reaction velocity (the reaction rate),
- K_m is the Michaelis–Menten constant,
- V_{max} is the maximum reaction velocity, and
- $[S]$ is the substrate concentration.

The Lineweaver–Burk plot was widely used to determine important terms in enzyme kinetics, such as K_m and V_{max}, before the wide availability of powerful computers and non-linear regression software. The y-intercept of such a graph is equivalent to the inverse of V_{max}; the x-intercept of the graph represents $-1/K_m$. It also gives a quick, visual impression of the different forms of enzyme inhibition.

✓ Example 10.2.2

The reaction between nicotineamide mononucleotide and ATP to form nicotineamide–adenine dinucleotide and pyrophosphate is catalyzed by the enzyme nicotinamide mononucleotide adenylyltransferase. The following table provides typical data obtained at a pH of 4.95. The substrate, S, is nicotinamide mononucleotide and the initial rate, *v*, is the µmol of nicotinamide–adenine dinucleotide formed in a 3-min reaction period.

[S] (mM)	v (µmol)	[S] (mM)	v (µmol)
0.138	0.148	0.560	0.324
0.220	0.171	0.766	0.390
0.291	0.234	1.460	0.493

Determine values for V_{max} and K_m.

Solution

Figure 13.12 shows the Lineweaver–Burk plot for this data and the resulting regression equation. Using the *y*-intercept, we calculate V_{max} as

$$V_{max} = 1 / y\text{−intercept} = 1 / 1.708 \text{ mol} = 0.585 \text{ mol}$$

and using the slope we find that K_m is

$$K_m = \text{slope} \times V_{max} = 0.7528 \text{ molimM} \times 0.585 \text{ mol} = 0.440 \text{ mM}$$

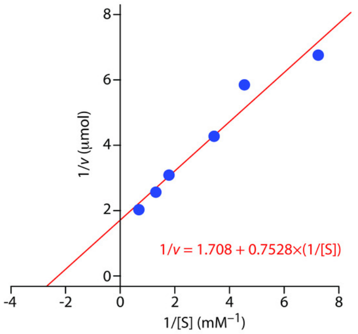
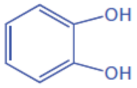


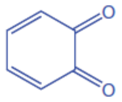
Figure 13.12: Linweaver–Burk plot and regression equation for the data in Example 13.6.

-diphenyl oxidase

The following data are for the oxidation of catechol (the substrate) to *o*-quinone by the enzyme *o*-diphenyl oxidase. The reaction is followed by monitoring the change in absorbance at 540 nm. The data in this exercise are adapted from jkimball.



catechol



o-quinone

[catechol] (mM)	0.3	0.6	1.2	4.8
rate (ΔAU/min)	0.020	0.035	0.048	0.081

Determine values for V_{max} and K_m.

Click here to review your answer to this exercise.

The double reciprocal plot distorts the error structure of the data, and it is therefore unreliable for the determination of enzyme kinetic parameters. Although it is still used for representation of kinetic data, non-linear regression or alternative linear forms of the Michaelis–Menten equation such as the **Hanes-Woolf plot** or **Eadie–Hofstee plot** are generally used for the calculation of parameters.

Problems with the Method

The Lineweaver–Burk plot is classically used in older texts, but is prone to error, as the *y*-axis takes the reciprocal of the rate of reaction – in turn increasing any small errors in measurement. Also, most points on the plot are found far to the right of the *y*-axis (due to limiting solubility not allowing for large values of $[S]$ and hence no small values for $1/[S]$), calling for a large extrapolation back to obtain *x*- and *y*-intercepts.

When used for determining the type of enzyme inhibition, the Lineweaver–Burk plot can distinguish competitive, non-competitive and uncompetitive inhibitors. Competitive inhibitors have the same y-intercept as uninhibited enzyme (since V_{max} is unaffected by competitive inhibitors the inverse of V_{max} also doesn't change) but there are different slopes and x-intercepts between the two data sets. Non-competitive inhibition produces plots with the same x-intercept as uninhibited enzyme (K_m is unaffected) but different slopes and y-intercepts. Uncompetitive inhibition causes different intercepts on both the y- and x-axes but the same slope.

Eadie–Hofstee Plot

The Eadie–Hofstee plot is a graphical representation of enzyme kinetics in which reaction rate is plotted as a function of the ratio between rate and substrate concentration and can be derived from the Michaelis–Menten equation (10.2.9) by inverting and multiplying with V_{max}:

$$\frac{V_{max}}{v} = \frac{V_{max}(K_m + [S])}{V_{max}[S]} = \frac{K_m + [S]}{[S]} \tag{10.2.17}$$

Rearrange:

$$V_{max} = \frac{vK_m}{[S]} + \frac{v[S]}{[S]} = \frac{vK_m}{[S]} + v \tag{10.2.18}$$

Isolate v:

$$v = -K_m \frac{v}{[S]} + V_{max} \tag{10.2.19}$$

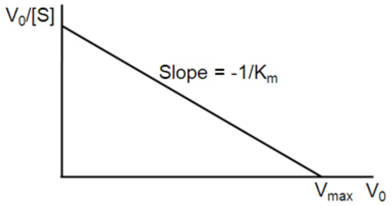


Figure 10.2.3 : The Eadie-Hofstee plot is a more accurate linear plotting method with v is plotted against v/[S].

A plot of v against $v/[S]$ will hence yield V_{max} as the y-intercept, V_{max}/K_m as the x-intercept, and K_m as the negative slope (Figure 10.2.3). Like other techniques that linearize the Michaelis–Menten equation, the Eadie-Hofstee plot was used historically for rapid identification of important kinetic terms like K_m and V_{max}, but has been superseded by nonlinear regression methods that are significantly more accurate and no longer computationally inaccessible. It is also more robust against error-prone data than the Lineweaver–Burk plot, particularly because it gives equal weight to data points in any range of substrate concentration or reaction rate (the Lineweaver–Burk plot unevenly weights such points). Both Eadie-Hofstee and Lineweaver–Burk plots remain useful as a means to present data graphically.

Problems with the Method

One drawback from the Eadie–Hofstee approach is that neither ordinate nor abscissa represent independent variables: both are dependent on reaction rate. Thus any experimental error will be present in both axes. Also, experimental error or uncertainty will propagate unevenly and become larger over the abscissa thereby giving more weight to smaller values of v/[S]. Therefore, the typical measure of goodness of fit for linear regression, the correlation coefficient R, is not applicable.

Contributors and Attributions

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10.3: Chymotrypsin- A Case Study

Chymotrypsin is a digestive enzyme belonging to a super family of enzymes called serine proteases. It uses an active serine residue to perform hydrolysis on the C-terminus of the aromatic amino acids of other proteins. Chymotrypsin is a protease enzyme that cleaves on the C-terminal phenylalanine (F), tryptophan (W), and tyrosine (Y) on peptide chains. It shows specificity for aromatic amino acids because of its hydrophobic pocket.

Introduction

Chymotrypsin is one of the most studied enzymes due to its two phase kinetics: pre-steady-state and steady state. The study of these two kinetic states gives evidence of the "Ping-Pong" mechanism, the formation of covalent complexes leading to covalent hydrolysis reactions, and the rate of the catalyzed reactions. Synthesis of chymotrypsin occurs primarily in the pancreas. Instead of the active form, however, it is produced as an inactive zymogen called chymotrypsinogen to prevent its protease activity from digesting the pancreas. Upon secretion into the lumen of the small intestine, it is converted to its active form by another enzyme called trypsin. This dependence of a different enzyme for the activation of a protease is a common way for the body to prevent the digestion of organs and other harmful enzymatic side-effects.

Chymotrypsin operates through a general mechanism known as the ping-pong mechanism (Figure 10.3.1) whereby the enzyme reacts with a substrate to form an enzyme intermediate. This intermediate has different properties than the initial enzyme, so to regenerate the initial enzymatic activity, it must react with a secondary substrate. This process is illustrated below:

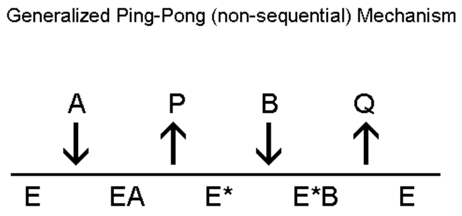
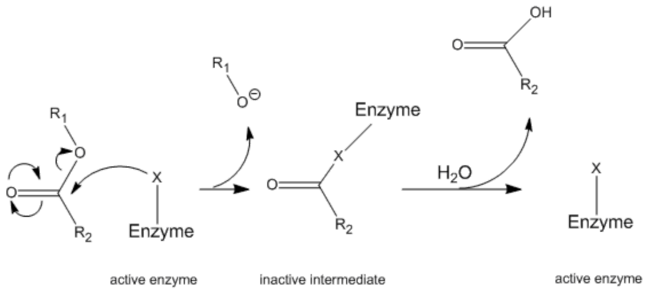


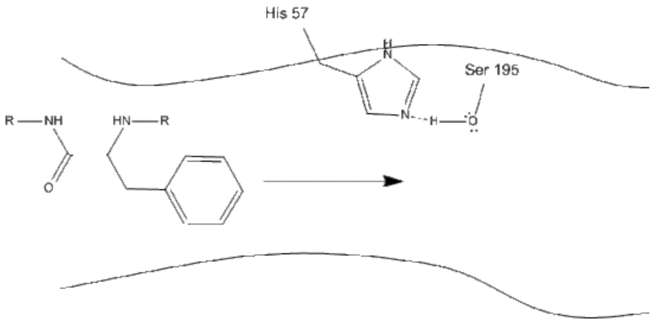
Figure 10.3.1: Generic Ping-Pong Mechanism

More specifically, chymotrypsin operates through a particular type of ping-pong mechanism called covalent hydrolysis. This means that the enzyme first forms a covalent bond with the target substrate, displacing the more stable moiety into solution. This enzyme-substrate complex is called the enzyme intermediate. The intermediate then reacts with water, which displaces the remaining part of the initial substrate and reforms the initial enzyme.

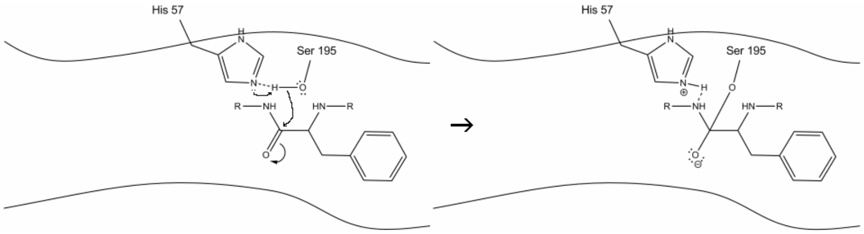


Chymotrypsin, like most enzymes, is specific in the types of substrates with which it reacts. As a protease, it cleaves polypeptides, and its inherent specificity allows it to act only on the carboxy-terminal of aromatic residues. It is a somewhat complicated mechanism, and is best explained in a series of steps.

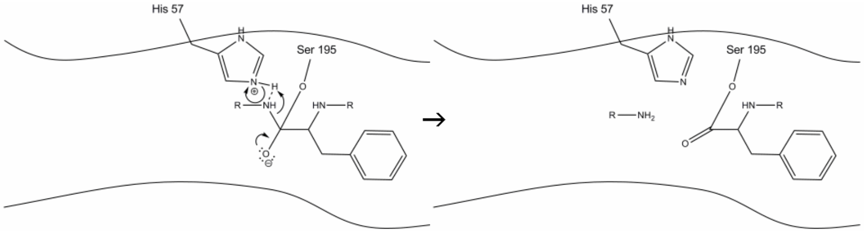
Step 1: The target enters the active site of chymotrypsin, and it is held there by hydrophobic interactions between exposed non-polar groups of enzyme residues and the non-polar aromatic side-chain of the substrate. It is important to note the hydrogen bond between the Schiff nitrogen on histidine-57 and the oxygen side-chain of serine-195.



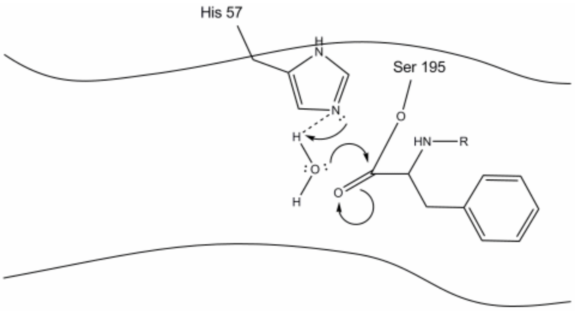
Step 2: Aided by the histidine-serine hydrogen bonding, the hydroxyl group on serine-195 performs a nucleophilic attack on the carbonyl carbon of an aromatic amino acid while simultaneously transferring the hydroxyl hydrogen to the histidine Schiff nitrogen. This attack pushes the pi carbonyl electrons onto the carbonyl oxygen, forming a short-lived intermediate consisting of a c-terminal carbon with four single bonds: an oxygen anion, the beta-carbon of the aromatic amino acid, the n-terminus of the subsequent amino acid of the substrate protein, and the serine-195 side-chain oxygen.



Step 3: This intermediate is short-lived, as the oxyanion electrons reform the pi bond with the c-terminus of the aromatic amino acid. The bond between the carboxy-terminus of the aromatic amino acid and the n-terminus of the subsequent residue is cleaved, and its electrons are used to extract the hydrogen of the protonated Schiff nitrogen on histidine-57. The bonds between the carbonyl carbon and the serine-195 oxygen remain in an ester configuration. This is called the acyl-enzyme intermediate. The c-terminal side of the polypeptide is now free to dissociate from the active site of the enzyme.

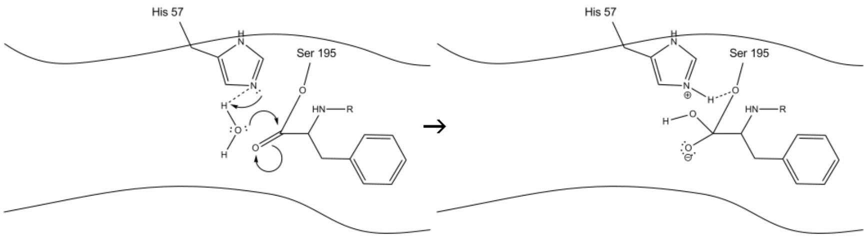


Step 4: Water molecules are now able to enter and bind to active site through hydrogen bonding between the hydrogen atoms of water and the histidine-57 Schiff nitrogen.

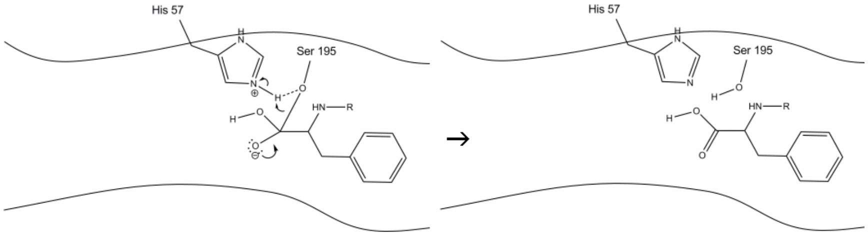


Step 5: The water oxygen now makes a nucleophilic attack on the carbonyl carbon of the acyl-enzyme intermediate, pushing the carbonyl's pi electrons onto the carbonyl carbon as histidine-57 extracts one proton from water. This forms another quaternary

carbon covalently bonded with serine, a hydroxyl, an oxyanion, and the aromatic amino acid. The proton on the recently protonated histidine-57 is now able to make a hydrogen bond with the serine oxygen.



Step 6: The oxyanion electrons reform the carbonyl pi bond, cleaving the bond between the carbonyl carbon and the serine hydroxyl. The electrons in this bond are used by the serine oxygen to deprotonate the histidine Schiff nitrogen and reform the original enzyme. The substrate no longer has affinity for the active site, and it soon dissociates from the complex.



Kinetics

Experiments were conducted in 1953 by B.S. Hartley and B.A. Kilby to investigate the kinetics of chymotrypsin-catalyzed hydrolysis. Instead of using a poly-peptide chain as a substrate, they used a nitro-phenyl ester, p-nitrophenyl acetate, that resembles an aromatic amino acid. Hydrolysis of this compound by chymotrypsin at the carbonyl group yields acetate and nitrophenolate, the latter of which absorbs near 400 nm light and its concentration can thus be measured by spectrophotometry (Figure 10.3.2).

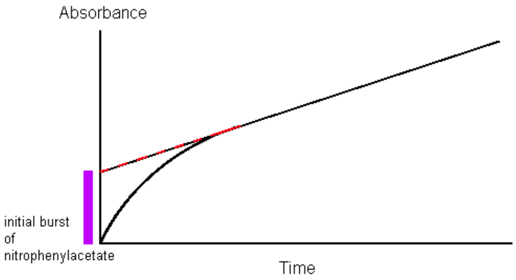
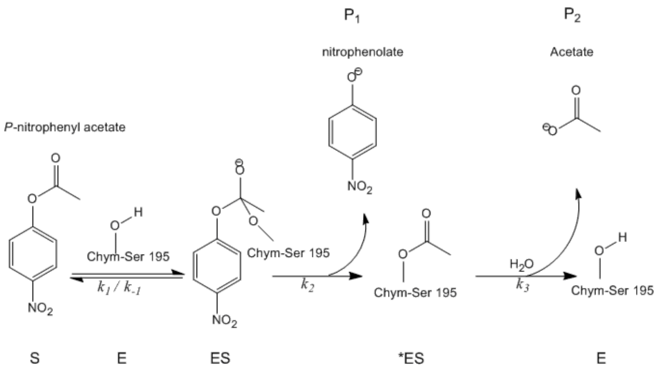


Figure 10.3.2*: Catalytic activity of he hydrolysis of p-nitropenolate under*

Spectrophotometric analysis of chymotrypsin acting on nitrophenylacetate showed that nitrophenolate was produced at a rate independent of substrate concentration, proving that the only factor contributing to the rate of product formation is the concentration of enzyme; this is typical for enzyme-substrate kinetics. However, when the slope of the 0-order absorbance plot was traced back to the starting point (time = 0), it was found that the initial concentration of nitrophenolate was not 0. In fact, it showed a 1:1 stoichiometric ratio with the amount of chymotrypsin used in the assay. This can only be explained by the fact that hydrolysis by chymotrypsin is biphasic in nature, meaning that it proceeds in two distinct steps.

1. The first step, which describes the **initial burst** of nitrophenolate seen in Hartley and Kilby's absorbance plot, is the fastest. The attack of the nitrophenyl acetate substrate by chymotrypsin immediately cleaves the nitrophenolate moiety and leaves the acetate group attached to chymotrypsin, rendering the enzyme inactive.
2. The second step has been deduced to involve the hydrolysis of the acetate group from the inactivated chymotrypsin to regenerate the original enzyme.

To analytically determine the rate of catalysis, all substrates, products, and intermediates must be defined. Refer to the figure below:



Using these abbreviations, kinetic analysis becomes less cumbersome.

1. The initial amount of enzyme can be represented as the sum of the free enzyme, the bound enzyme, and the inactive intermediate.

$$[E]_o = [ES] + [^*ES] + [E]$$

2. Assuming the initial step is the faster than the subsequent steps, the rate of nitrophenolate production can be described as:

$$\frac{d[P_1]}{dt} = k_2[ES]$$

3. Likewise, the rate of acetate formation can be represented by the equation:

$$\frac{d[P_2]}{dt} = k_3[^*ES]$$

4. Therefore, the net change in concentration of the inactive intermediate can be deduced:

$$\frac{d[*ES]}{dt} = k_2[ES] - k_3[^*ES]$$

5. The last inference that can be made from analysis of the measured kinetics data (Figure $10.3.2$) is that the first step of the reaction equilibrates rapidly, and thus the change in bound substrate can be described in the following equation. This is a principal tenet in analyzing **the kinetics of chymotrypsin and is a ubiquitous mechanism in biological enzyme** catalysis.

$$\frac{d[ES]}{dt} = k_1[E][S] - k_{-1}[ES] = 0$$

6. Where:

$$\frac{k_{-1}}{k_1} = K_s = \frac{[E][S]}{[ES]}$$

7. Combining all of these quantities, we can deduce the catalytic rate constant as:

$$k_{cat} = \frac{k_2 k_3}{k_2 + k_3}$$

8. In ester hydrolysis, $k_3 >> k_2$, so the resultant catalytic rate constant simplifies to:

$$k_{cat} = k_2$$

which is in agreement with the observed zeroth-order kinetics of Figure $10.3.2$

Table 10.3.1: Kinetic Constants of the Chymotrypsin-Catalyzed Hydrolysis of p-Nitrophenyl Trimethylacetate at pH 8.2. 0.01 M tris-HCL buffer, ionic strength 0.06, 25.6 ± 0.1 °C, 1.8% (v/v) acetonitrile-water. From M.L. Bender, F.J. Kezdy and F.C. Wedler, J. Chem. Educ. 44, 84 (1967

k_2	$0.37 \pm 0.11\ s^{-1}$
k_3	$(1.3 \pm 0.02) \times 10^{-4}\ s^{-1}$
K_s	$(1.6 \pm 0.5) \times 10^{-3}$
k_{cat}	1.3 × 10-4 s^{-1}
K_M	5.6×10^{-7}

? Exercise 10.3.1

Speculate on how the catalytic rate constant can be determined from the spectrophotogram.

Answer

The catalytic rate constant can be deduced from the graph by simply determining the slope of the line where the reaction demonstrates 0-order kinetics (the linear part)

? Exercise 10.3.2

How can product be consistently produced if the rate of change of the ES complex is 0?

Answer

This is pre-equilibrium kinetics in action. The ES complex is formed from E and S at a faster rate than any other step in the reaction. As soon as ES is converted to *ES, another mole of ES is produced from an infinite supply of E + S. This means that the amount of ES and E + S is constantly at equilibrium, and thus the change of either with respect to time is 0.

? Exercise 10.3.3

How would the rate of product formation change if:

a. the substrate concentration was doubled.
b. the enzyme concentration was doubled.
c. The reaction was carried out in mono-deuterated water instead of H2O (comment qualitatively).

Answer

a. No change.
b. Two fold increase.
c. Since water is involved in the final, slowest step of the mechanism, deuterating the water would decrease the rate of the overall reaction from 5 to 30-fold.

? Exercise 10.3.4

Explain the role of hydrogen bonding in protein hydrolysis catalyzed by chymotrypsin.

Answer

Initially, hydrogen bonding between the enzymes histidine and serine side chains weakens the bond of serine’s O-H. This allows for a facilitated nucleophilic attack of the hydroxyl Oxygen on the substrates carbonyl group. Conversely, in the final step of the reaction, the bound serine oxygen forms a hydrogen bond with a protonated histidine, which allows for easier cleavage from the substrate.

? Exercise 10.3.5

What would the spectrophotogram look like if the reaction proceeded via a steady-state mechanism instead of pre-equilibrium.

Answer

The graph would show similar 0-order kinetics, but the line would intercept the Y-axis at an absorbance of 0 instead of the 1:1 mole ratio of nitrophenolate to enzyme.

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10.4: Multisubstrate Systems

The Michaelis –Menten model of enzyme kinetics was derived for single substrate reactions. Enzymatic reactions requiring multiple substrates and yielding multiple products are more common and yielding multiple products are more common than single-substrate reaction. In these types of reactions, the all the substrates involved are bound to the enzyme before catalysis of the reaction takes place to release the products. Sequential reactions can be either ordered or random. In contrast to the Michealis-Menton kinetics where a binary Enzyme-Substrate complex is generated in the mechanism ($[ES]$, in bisubstrate enzyme reactions, a ternary complex of the enzyme and two substrates is generated:

$$A + B \overset{E}{\rightleftharpoons} P + Q \tag{10.4.1}$$

Bisubstrate reactions account for ~ 60% of the known enzymatic reactions. Multi-substrate reactions follow complex rate equations that describe how the substrates bind and in what sequence. The analysis of these reactions is much simpler if the concentration of substrate A is kept constant and substrate B varied. Under these conditions, the enzyme behaves just like a single-substrate enzyme and a plot of v by $[S]$ gives apparent K_M and V_{max} constants for substrate B. If a set of these measurements is performed at different fixed concentrations of A, these data can be used to work out what the mechanism of the reaction is. For an enzyme that takes two substrates A and B and turns them into two products P and Q, there are two types of mechanism: ternary complex and ping–pong.

How do you resolve the enzymes kinetics of these more complicated systems? The answer is fairly straightforward. You keep one of the substrates (B, for example) fixed, and vary the other substrate (A) and obtain a **series** of hyperbolic plots of v_o vs A at different fixed B concentrations. This would give a series of linear $1/v$ vs. $1/A$ double-reciprocal plots (Lineweaver-Burk plots) as well. The pattern of Lineweaver-Burk plots depends on how the reactants and products interact with the enzyme.

Sequential Mechanism

In this mechanism, both substrates must bind to the enzyme before any products are made and released.The substrates might bind to the enzyme in a random fashion (A first then B or vice-versa) or in an ordered fashion (A first followed by B). An abbreviated notation scheme developed by W.W. Cleland is shown in Figure 10.4.1 for the sequential random and sequential ordered mechanisms (Figure 10.4.1). For both mechanisms, Lineweaver-Burk plots at varying A and different fixed values of B give a series of intersecting lines. Derivative curves can be solved to obtain appropriate kinetic constants. In ordered sequential reactions, all the substrates are first bound to the enzyme in a **defined order or sequence**. The products, too, are released after catalysis in a defined order or sequence.

An example is the lactate dehydrogenase enzyme, which is a protein that catalyzes glucose metabolism. In this ordered mechanism, the coenzyme, NADH, always binds first, with pyruvate binding afterward. During the reaction, the pyruvate is reduced to lactate while NADH is oxidized to NAD$^+$ by the enzyme. Lactate is then released first, followed by the release of NAD$^+$.

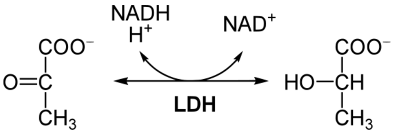

Figure 10.4.2 **:** *Reaction of the lactate dehydrogenase: pyruvate (left) is oxidized to lactate (right) by expense of NADH*

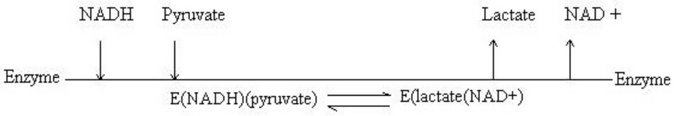

Figure 10.4.3 **:** Ordered Sequential Mechanism for the lactate dehydrogenase enzyme

This is a characteristic of a ternary complex, which consists of three molecules that are bound together. Before catalysis, the substrates and coenzyme are bound to the enzyme. After catalysis, the complex consists of the enzyme and products, NAD$^+$ and lactate.

In random sequential reactions, the substrates and products are bound and then released in no preferred order, or "random" order (Figure 10.4.1). An example is the creatine kinase enzyme, which catalyzes creatine and ATP (the two substrates) to form phosphocreatine and ADP (teh Products) in Figure 10.4.4 In this case, **either** substrates may bind first and either products may be released first. A ternary complex is still observed for random sequential reactions. Before catalysis, the complex is generated that includes the enzyme, ATP, and creatine. After catalysis, the complex consists of the enzyme, ADP, and phosphocreatine.

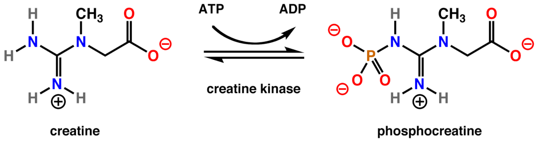

Figure 10.4.4: The metabolism of creatine follows a random sequential mechanism.

Ping-Pong Mechanism

In this mechanism, one substrate bind first to the enzyme followed by product P release. Typically, product P is a fragment of the original substrate A.The rest of the substrate is covalently attached to the enzyme E, which is designated as E'. Now the second reactant, B, binds and reacts with the enzyme to form a covalent adduct with the A as it is covalentattached to the enzyme to form product Q. This is now released and the enzyme is restored to its initial form, E. This represents a ping-pong mechanism. An abbreviated notation scheme is shown below for the ping-pong mechanisms. For this mechanism, Lineweaver-Burk plots at varying A and different fixed values of B give a series of parallel lines. An example of this type of reaction might be low molecular weight protein tyrosine phosphatase against the small substrate p-initrophenylphosphate (A) which binds to the enzyme covalently with the expulsion of the product P, the p-nitrophenol leaving group. Water (B) then comes in and covalently attacks the enzyme, forming an adduct with the covalently bound phosphate releasing it as inorganic phosphate. In this particular example, however, you cannot vary the water concentration and it would be impossible to generate the parallel **Lineweaver-Burk** plots characteristic of ping-pong kinetics.

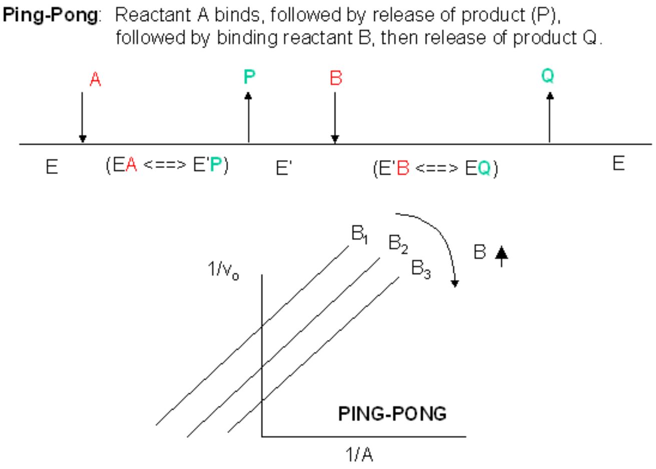

Figure 10.4.5): The Ping-Pong mechanism and associated **Lineweaver-Burk**.

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10.5: Enzyme Inhibition

Enzymes can be regulated in ways that either promote or reduce their activity. There are many different kinds of molecules that inhibit or promote enzyme function, and various mechanisms exist for doing so. In some cases of enzyme inhibition, for example, an inhibitor molecule is similar enough to a substrate that it can bind to the active site and simply block the substrate from binding. When this happens, the enzyme is inhibited through competitive inhibition, because an inhibitor molecule competes with the substrate for active site binding. On the other hand, in noncompetitive inhibition, an inhibitor molecule binds to the enzyme in a location other than an allosteric site and still manages to block substrate binding to the active site.

Elucidating Mechanisms for the Inhibition of Enzyme Catalysis

When an **inhibitor** interacts with an enzyme it decreases the enzyme's catalytic efficiency. An irreversible inhibitor covalently binds to the enzyme's active site, producing a permanent loss in catalytic efficiency even if we decrease the inhibitor's concentration. A reversible inhibitor forms a noncovalent complex with the enzyme, resulting in a temporary decrease in catalytic efficiency. If we remove the inhibitor, the enzyme's catalytic efficiency returns to its normal level.

There are several pathways for the reversible binding of an inhibitor to an enzyme, as shown in Figure 10.5.1. In **competitive inhibition** the substrate and the inhibitor compete for the same active site on the enzyme. Because the substrate cannot bind to an enzyme–inhibitor complex, EI, the enzyme's catalytic efficiency for the substrate decreases. With **noncompetitive inhibition** the substrate and the inhibitor bind to different active sites on the enzyme, forming an enzyme–substrate–inhibitor, or ESI complex. The formation of an ESI complex decreases catalytic efficiency because only the enzyme–substrate complex reacts to form the product. Finally, in **uncompetitive inhibition** the inhibitor binds to the enzyme–substrate complex, forming an inactive ESI complex.

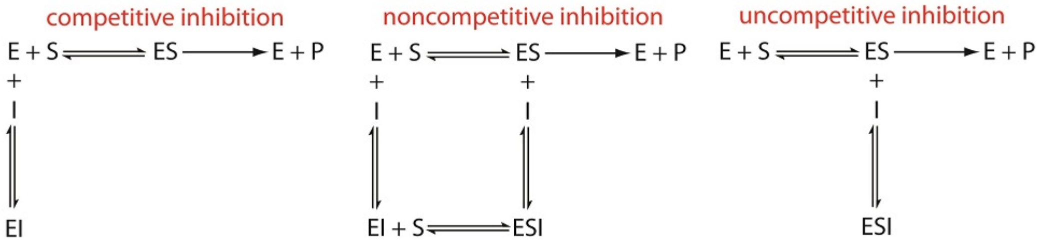

Figure 10.5.1 : Mechanisms for the reversible inhibition of enzyme catalysis. E: enzyme, S: substrate, P: product, I: inhibitor, ES: enzyme–substrate complex, EI: enzyme–inhibitor complex, ESI: enzyme–substrate–inhibitor complex.

We can identify the type of reversible inhibition by observing how a change in the inhibitor's concentration affects the relationship between the rate of reaction and the substrate's concentration. As shown in Figure 13.14, when we display kinetic data using as a Lineweaver-Burk plot it is easy to determine which mechanism is in effect. For example, an increase in slope, a decrease in the *x*-intercept, and no change in the *y*-intercept indicates competitive inhibition. Because the inhibitor's binding is reversible, we can still obtain the same maximum velocity—thus the constant value for the *y*-intercept—by adding enough substrate to completely displace the inhibitor. Because it takes more substrate, the value of K_m increases, which explains the increase in the slope and the decrease in the *x*-intercept's value.

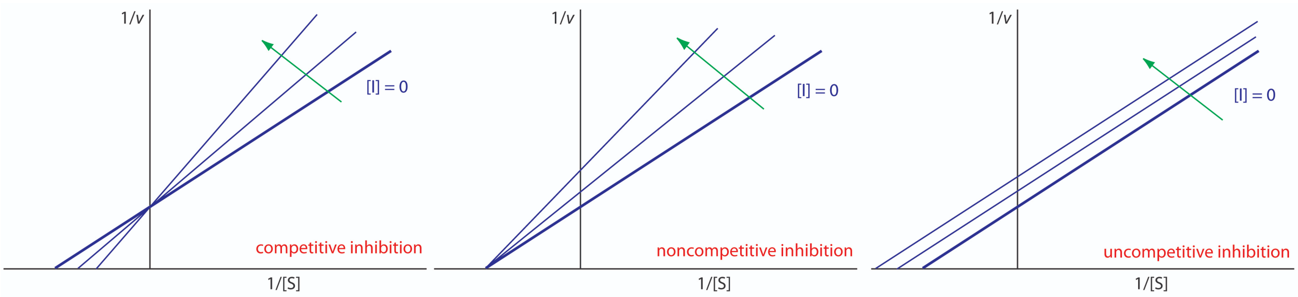

Figure 10.5.2: Linweaver–Burk plots for competitive inhibition, noncompetitive inhibition, and uncompetitive inhibition. The thick blue line in each plot shows the kinetic behavior in the absence of inhibitor, and the thin blue lines in each plot show the change in behavior for increasing concentrations of the inhibitor. In each plot, the inhibitor's concentration increases in the direction of the green arrow.

Example 10.5.1

Practice Exercise 13.3 provides kinetic data for the oxidation of catechol (the substrate) to *o*-quinone by the enzyme *o*-diphenyl oxidase in the absence of an inhibitor. The following additional data are available when the reaction is run in the presence of *p*-hydroxybenzoic acid, PBHA. Is PBHA an inhibitor for this reaction and, if so, what type of inhibitor is it?

[catechol] (mM)	0.3	0.6	1.2	4.8
rate (ΔAU/min)	0.011	0.019	0.022	0.060

Solution

Figure $10.5.3$ shows the resulting Lineweaver–Burk plot for the data in Practice Exercise 13.3 and Example 13.7. Although the *y*-intercepts are not identical in value—the result of uncertainty in measuring the rates—the plot suggests that PBHA is a competitive inhibitor for the enzyme's reaction with catechol.

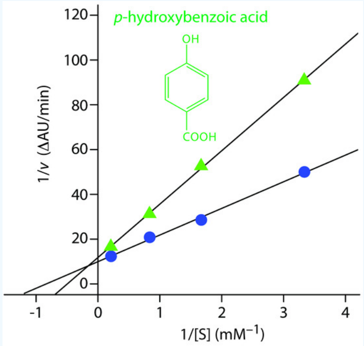

Figure 10.5.3: Lineweaver–Burk plots for the data in Practice Exercise 13.3 and Example 13.7.

Exercise 10.5.1

Practice Exercise 13.3 provides kinetic data for the oxidation of catechol (the substrate) to *o*-quinone by the enzyme *o*-diphenyl oxidase in the absence of an inhibitor. The following additional data are available when the reaction is run in the presence of phenylthiourea. Is phenylthiourea an inhibitor for this reaction and, if so, what type of inhibitor is it? The data in this exercise are adapted from jkimball.

[catechol] (mM)	0.3	0.6	1.2	4.8
rate (ΔAU/min)	0.010	0.016	0.024	0.040

Click here to review your answer to this exercise.

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10.6: Allosteric Interactions

Learning Objectives

- When a substrate binds to one enzymatic subunit, the rest of the subunits are stimulated and become active. Ligands can either have non-cooperativity, positive cooperativity or negative cooperativity.

A significant portion of enzymes function such that their properties can be studied using the Michaelis-Menten equation. However, a particular class of enzymes exhibit kinetic properties that cannot be studied using the Michaelis-Menten equation. The rate equation of these unique enzymes is characterized by an “S-shaped” sigmoidal curve, which is different from the majority of enzymes whose rate equation exhibits hyberbolic curves. Allosteric regulation is the regulation of an enzyme or other protein by binding an effector molecule at the protein's allosteric site (that is, a site other than the protein's active site). Effectors that enhance the protein's activity are referred to as allosteric activators, whereas those that decrease the protein's activity are called allosteric inhibitors. The term allostery refers to the fact that the regulatory site of an allosteric protein is **physically distinct** from its active site. Allosteric regulations are a natural example of control loops, such as feedback from downstream products or feedforward from upstream substrates. Long-range allostery is especially important in cell signaling.

Allosteric Modulation (Cooperativity)

Cooperativity is a phenomenon displayed by enzymes or receptors that have multiple binding sites where the affinity of the binding sites for a ligand is increased, positive cooperativity, or decreased, negative cooperativity, upon the binding of a ligand to a binding site. We also see cooperativity in large chain molecules made of many identical (or nearly identical) subunits (such as DNA, proteins, and phospholipids), when such molecules undergo phase transitions such as melting, unfolding or unwinding. This is referred to as subunit cooperativity (discussed below).

An example of positive cooperativity is the binding of oxygen to hemoglobin. One oxygen molecule can bind to the ferrous iron of a heme molecule in each of the four chains of a hemoglobin molecule. Deoxy-hemoglobin has a relatively low affinity for oxygen, but when one molecule binds to a single heme, the oxygen affinity increases, allowing the second molecule to bind more easily, and the third and fourth even more easily. The oxygen affinity of 3-oxy-hemoglobin is ~300 times greater than that of deoxy-hemoglobin. This behavior leads the affinity curve of hemoglobin to be sigmoidal, rather than hyperbolic as with the monomeric myoglobin. By the same process, the ability for hemoglobin to lose oxygen increases as fewer oxygen molecules are bound.

Negative allosteric modulation (also known as allosteric inhibition) occurs when the binding of one ligand **decreases** the affinity for substrate at other active sites. For example, when 2,3-BPG binds to an allosteric site on hemoglobin, the affinity for oxygen of all subunits decreases. This is when a regulator is absent from the binding site.

Another instance in which negative allosteric modulation can be seen is between ATP and the enzyme Phosphofructokinase within the negative feedback loop that regulates glycolysis. Phosphofructokinase (generally referred to as PFK) is an enzyme that catalyses the third step of glycolysis: the phosphorylation of Fructose-6-phosphate into Fructose 1,6-bisphosphate. PFK can be allosterically inhibited by high levels of ATP within the cell. When ATP levels are high, ATP will bind to an allosteric site on phosphofructokinase, causing a change in the enzyme's three-dimensional shape. This change causes its affinity for substrate (fructose-6-phosphate and ATP) at the active site to decrease, and the enzyme is deemed inactive. This causes glycolysis to cease when ATP levels are high, thus conserving the body's glucose and maintaining balanced levels of cellular ATP. In this way, ATP serves as a negative allosteric modulator for PFK, despite the fact that it is also a substrate of the enzyme.

Sigmoidal kinetic profiles are the result of enzymes that demonstrate positive cooperative binding. cooperativity refers to the observation that binding of the substrate or ligand at one binding site affects the affinity of other sites for their substrates. For enzymatic reactions with multiple substrate binding sites, this increased affinity for the substrate causes a rapid and coordinated increase in the velocity of the reaction at higher $[S]$ until V_{max} is achieved. Plotting the V_0 vs. $[S]$ for a cooperative enzyme, we observe the characteristic sigmoidal shape with low enzyme activity at low substrate concentration and a rapid and immediate increase in enzyme activity to V_{max} as $[S]$ increases. The phenomenon of cooperativity was initially observed in the oxygen-hemoglobin interaction that functions in carrying oxygen in blood. Positive cooperativity implies allosteric binding – binding of the ligand at one site increases the enzyme’s affinity for another ligand at a site different from the other site. Enzymes that demonstrate cooperativity are defined as allosteric. There are several types of allosteric interactions: homotropic (positive) and heterotropic (negative).

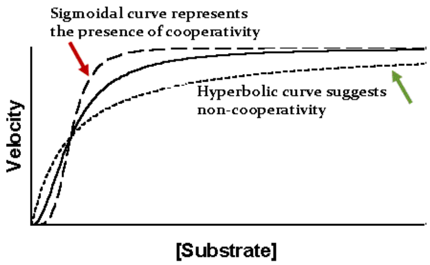


Figure 10.6.1: Rate of Reaction (velocity) vs. Substrate Concentration.

Positive and negative allosteric interactions (as illustrated through the phenomenon of cooperativity) refer to the enzyme's binding affinity for other ligands at other sites, as a result of ligand binding at the initial binding site. When the ligands interacting are all the same compounds, the effect of the allosteric interaction is considered homotropic. When the ligands interacting are different, the effect of the allosteric interaction is considered heterotropic. It is also very important to remember that allosteric interactions tend to be driven by ATP hydrolysis.

The Hill Equation

The degree of cooperativity is determined by Hill equation (Equation 10.6.1) for non-Michaelis-Menten kinetics. The Hill equation accounts for allosteric binding at sites other than the active site. n is the "**Hill coefficient**."

$$\theta = \frac{[L]^n}{K_d + [L]^n} = \frac{[L]^n}{K_a^n + [L]^n} \tag{10.6.1}$$

where

- θ is the fraction of ligand binding sites filled
- $[L]$ is the ligand concentration
- K_d is the apparent dissociation constant derived from the law of mass action (equilibrium constant for dissociation)
- K_a is the ligand concentration producing half occupation (ligand concentration occupying half of the binding sides), that is also the microscopic dissociation constant
- n is the Hill coefficient that describes the cooperativity

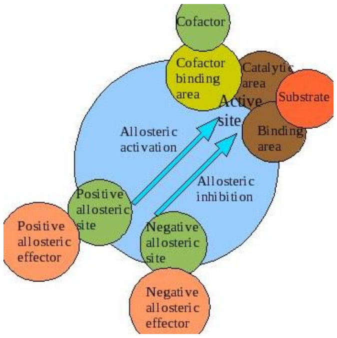
Taking the logarithm of both sides of the equation leads to an alternative formulation of the Hill Equation.

$$\log\left(\frac{\theta}{1-\theta}\right) = n\log[L] - \log K_d \tag{10.6.2}$$

- when $n < 1$, there is negative cooperativity
- when $n = 1$, there is no cooperativity
- when $n > 1$, there is positive cooperativity

Allosteric Models

Currently, there are 2 models for illustrating cooperativity: the concerted model and the sequential model. Most allosteric effects can be explained by the concerted MWC model put forth by Monod, Wyman, and Changeux, or by the sequential model described by Koshland, Nemethy, and Filmer. Both postulate that enzyme subunits exist in one of two conformations, tensed (T) or relaxed (R), and that relaxed subunits bind substrate more readily than those in the tense state. The two models differ most in their assumptions about subunit interaction and the preexistence of both states.



The Concerted model

The concerted model of allostery, also referred to as the symmetry model or MWC model, postulates that enzyme subunits are connected in such a way that a conformational change in one subunit is necessarily conferred to all other subunits. Thus, all subunits must exist in the same conformation. The model further holds that, in the absence of any ligand (substrate or otherwise), the equilibrium favours one of the conformational states, T or R. The equilibrium can be shifted to the R or T state through the binding of one ligand (the allosteric effector or ligand) to a site that is different from the active site (the allosteric site).

The Sequential model

The sequential model of allosteric regulation holds that subunits are not connected in such a way that a conformational change in one induces a similar change in the others. Thus, all enzyme subunits do not necessitate the same conformation. Moreover, the sequential model dictates that molecules of substrate bind via an induced fit protocol. In general, when a subunit randomly collides with a molecule of substrate, the active site, in essence, forms a glove around its substrate. While such an induced fit converts a subunit from the tensed state to relaxed state, it does not propagate the conformational change to adjacent subunits. Instead, substrate-binding at one subunit only slightly alters the structure of other subunits so that their binding sites are more receptive to substrate. To summarize:

- subunits need not exist in the same conformation
- molecules of substrate bind via induced-fit protocol
- conformational changes are not propagated to all subunits

Note: Allosteric database

Allostery is a direct and efficient means for regulation of biological macromolecule function, produced by the binding of a ligand at an allosteric site topographically distinct from the orthosteric site. Due to the often high receptor selectivity and lower target-based toxicity, allosteric regulation is also expected to play an increasing role in drug discovery and bioengineering. The AlloSteric Database (ASD, provides a central resource for the display, search and analysis of the structure, function and related annotation for allosteric molecules. Currently, ASD contains allosteric proteins from more than 100 species and modulators in three categories (activators, inhibitors, and regulators). Each protein is annotated with detailed description of allostery, biological process and related diseases, and each modulator with binding affinity, physicochemical properties and therapeutic area. Integrating the information of allosteric proteins in ASD should allow the prediction of allostery for unknown proteins, to be followed with experimental validation. In addition, modulators curated in ASD can be used to investigate potential allosteric targets for a query compound, and can help chemists to implement structure modifications for novel allosteric drug design.

Summary

Allosteric enzymes are an exception to the Michaelis-Menten model. Because they have more than two subunits and active sites, they do not obey the Michaelis-Menten kinetics, but instead have sigmoidal kinetics. Since allosteric enzymes are cooperative, a sigmoidal plot of V_0 versus $[S]$ results: There are distinct properties of Allosteric Enzymes that makes it different compared to other enzymes.

1. One is that allosteric enzymes do not follow the Michaelis-Menten Kinetics. This is because allosteric enzymes have multiple active sites. These multiple active sites exhibit the property of cooperativity, where the binding of one active site affects the affinity of other active sites on the enzyme. As mentioned earlier, it is these other affected active sites that result in a sigmoidal curve for allosteric enzymes.

2. Allosteric Enzymes are influenced by substrate concentration. For example, at high concentrations of substrate, more enzymes are found in the R state. The T state is favorite when there is an insufficient amount of substrate to bind to the enzyme. In other words, the T and R state equilibrium depends on the concentration of the substrate.
3. Allosteric Enzymes are regulated by other molecules. This is seen when the molecules 2,3-BPG, pH, and CO2 modulates the binding affinity of hemoglobin to oxygen. 2,3-BPG reduces binding affinity of O2 to hemoglobin by stabilizing the T- state. Lowering the pH from physiological pH=7.4 to 7.2 (pH in the muscles and tissues) favors the release of O_2. Hemoglobin is more likely to release oxygen in CO_2 rich areas in the body.

There are two primary models for illustrating cooperativity. **The concerted model** (also called the **Monod-Wyman-Changeux** model) illustrates cooperativity by assuming that proteins have two or more subunits, and that each part of the protein molecule is able to exist in either the relaxed (R) state or the tense (T) state - the tense state of a protein molecule is favored when it doesn't have any substrates bound. All aspects, including binding and dissociation constants are the same for each ligand at the respective binding sites. **The sequential model** aims to demonstrate cooperativity by assuming that the enzyme/protein molecule affinity is relative and changes as substrates bind. Unlike the concerted model, the sequential model accounts for different species of the protein molecule.

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10.7: The Effect of pH on Enzyme Kinetics

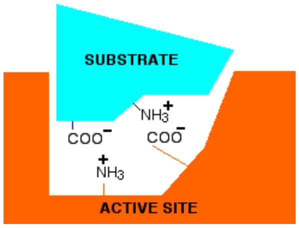
In the same way that every enzyme has an optimum temperature, so each enzyme also has an optimum pH at which it works best. For example, trypsin and pepsin are both enzymes in the digestive system which break protein chains in the food into smaller bits - either into smaller peptide chains or into individual amino acids. Pepsin works in the highly acidic conditions of the stomach. It has an optimum pH of about 1.5. On the other hand, trypsin works in the small intestine, parts of which have a pH of around 7.5. Trypsin's optimum pH is about 8.

Table 10.7.1: pH for Optimum Activity

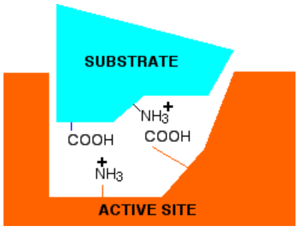
Enzyme	Optimal pH	Enzyme	Optimal pH
Lipase (pancreas)	8.0	Invertase	4.5
Lipase (stomach)	4.0 - 5.0	Maltase	6.1 - 6.8
Lipase (castor oil)	4.7	Amylase (pancreas)	6.7 - 7.0
Pepsin	1.5 - 1.6	Amylase (malt)	4.6 - 5.2
Trypsin	7.8 - 8.7	Catalase	7.0
Urease	7.0		

If you think about the structure of an enzyme molecule, and the sorts of bonds that it may form with its substrate, it isn't surprising that pH should matter. Suppose an enzyme has an optimum pH around 7. Imagine that at a pH of around 7, a substrate attaches itself to the enzyme via two ionic bonds. In the diagram below, the groups allowing ionic bonding are caused by the transfer of a hydrogen ion from a -COOH group in the side chain of one amino acid residue to an $-NH_2$ group in the side chain of another.

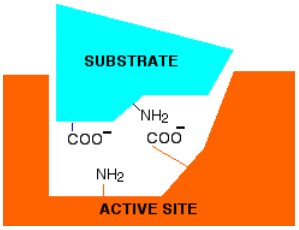
In this simplified example, that is equally true in both the substrate and the enzyme.



Now think about what happens at a lower pH - in other words under acidic conditions. It won't affect the $-NH_3^+$ group, but the $-COO^-$ will pick up a hydrogen ion. What you will have will be this:



You no longer have the ability to form ionic bonds between the substrate and the enzyme. If those bonds were necessary to attach the substrate and activate it in some way, then at this lower pH, the enzyme won't work. What if you have a pH higher than 7 - in other words under alkaline conditions. This time, the $-COO^-$ group won't be affected, but the $-NH_3^+$ group will lose a hydrogen ion. That leaves . . .



Again, there is no possibility of forming ionic bonds, and so the enzyme probably won't work this time either. At extreme pH's, something more drastic can happen. Remember that the tertiary structure of the protein is in part held together by ionic bonds just like those we've looked at between the enzyme and its substrate. At very high or very low pH's, these bonds within the enzyme can be disrupted, and it can lose its shape. If it loses its shape, the active site will probably be lost completely. This is essentially the same as denaturing the protein by heating it too much.

Kinetics

The rates of enzyme-catalysed reactions vary with pH and often pass through a maximum as the pH is varied. If the enzyme obeys Michaelis-Menten kinetics the kinetic parameters k_0 and k_A often behave similarly. The pH at which the rate or a suitable parameter is a maximum is called the *pH optimum* and the plot of rate or parameter against pH is called a *pH profile.* Neither the pH optimum nor the pH profile of an enzyme has any absolute significance and both may vary according to which parameter is plotted and according to the conditions of the measurements.

If the pH is changed and then brought back to its original value, the behavior is said to be *reversible* if the original properties of the enzyme are restored; otherwise it is *irreversible.* Reversible pH behavior may occur over a narrow range of pH, but effects of large changes in pH are in most cases irreversible. The diminution in rate as the pH is taken to the acid side of the optimum can be regarded as inhibition by hydrogen ions. The diminution in rate on the alkaline side can be regarded as inhibition by hydroxide ions. The equations describing pH effects are therefore analogous to inhibition equations. For single-substrate reactions the pH behavior of the parameters k_0 and k_A can sometimes be represented by an equation of the form

$$k=\frac{k_{opt}}{1+\dfrac{[H^+]}{K_1}+\dfrac{K_2}{[H^+]}} \tag{10.7.1}$$

in which k represents k_0 or k_A, and k_{opt} is the value of the same parameter that would be observed if the enzyme existed entirely in the optimal state of protonation; it may be called the *pH-independent* value of the parameter. The constants K_1 and K_2 can sometimes be identified as acid dissociation constants for the enzyme. substrates or other species in the reaction mixture. The identification is, however, never straight forward and has to be justified by independent evidence. The behavior is frequently much more complicated than represented by Equation 10.7.1.

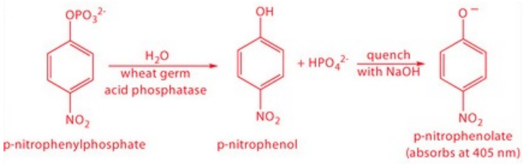
It is not accidental that this section has referred exclusively to pH dependences of k_0 and k_A. The pH dependence of the initial rate or, worse, the extent of reaction after a given time is rarely meaningful; the pH dependence of the Michaelis constant is often too complex to be readily interpretable.

> *The pH dependence of the Michaelis constant is often too complex to be readily interpretable.*

Quenching Enzyme Activity

In principle, we can use any of the range of possible analytical techniques to follow a reaction’s kinetics provided that the reaction does not proceed to any appreciable extent during the time it takes to make a measurement. As you might expect, this requirement places a serious limitation on kinetic methods of analysis. If the reaction’s kinetics are slow relative to the analysis time, then we can make our measurements without the analyte undergoing a significant change in concentration. When the reaction’s rate is too fast—which often is the case—then we introduce a significant error if our analysis time is too long.

One solution to this problem is to stop, or **quench** the reaction by adjusting experimental conditions. For example, many reactions show a strong pH dependency, and may be quenched by adding a strong acid or a strong base. Figure 13.7 shows a typical example for the enzymatic analysis of *p*-nitrophenylphosphate using the enzyme wheat germ acid phosphatase to hydrolyze the analyte to *p*-nitrophenol.



The reaction has a maximum rate at a pH of 5. Increasing the pH by adding NaOH quenches the reaction and converts the colorless *p*-nitrophenol to the yellow-colored *p*-nitrophenolate, which absorbs at 405 nm.

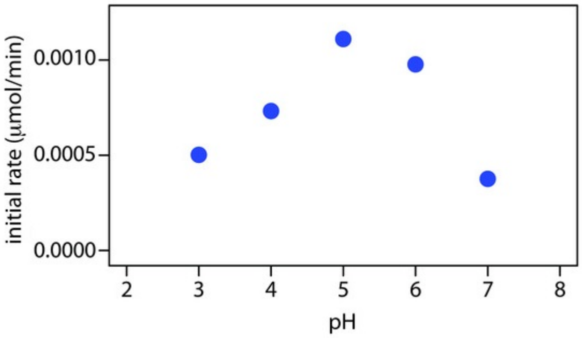


Figure 13.7: Initial rate for the enzymatic hydrolysis of p-nitrophenylphosphate using wheat germ acid phosphatase. Increasing the pH quenches the reaction and coverts colorless p-nitrophenol to the yellow-colored p-nitrophenolate, which absorbs at 405 nm. The data are adapted from socrates.hunter.cuny.edu.

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10.8: The Effect of Temperature on Enzyme Kinetics

Enzymes are generally globular proteins, acting alone or in larger complexes. Like all proteins, enzymes are linear chains of amino acids that fold to produce a three-dimensional structure. The sequence of the amino acids specifies the structure which in turn determines the catalytic activity of the enzyme. Although structure determines function, a novel enzyme's activity **cannot** yet be predicted from its structure alone. Enzyme structures unfold (denature) when heated or exposed to chemical denaturants and this disruption to the structure typically causes a loss of activity.

Protein folding is key to whether a globular protein or a membrane protein can do its job correctly. It must be folded into the right shape to function. But hydrogen bonds, which play a big part in folding, are rather weak, and it does not take much heat, acidity, or other stress to break some and form others, denaturing the protein. This is one reason why tight homeostasis is physiologically necessary in many life forms.

Denaturation

Denaturation is a process in which proteins or nucleic acids lose the quaternary structure, tertiary structure and secondary structure which is present in their native state, by application of some external stress or compound such as a strong acid or base, a concentrated inorganic salt, an organic solvent (e.g., alcohol or chloroform), radiation or heat. If proteins in a living cell are denatured, this results in disruption of cell activity and possibly cell death. Denatured proteins can exhibit a wide range of characteristics, from conformational change and loss of solubility to aggregation due to the exposure of hydrophobic groups.

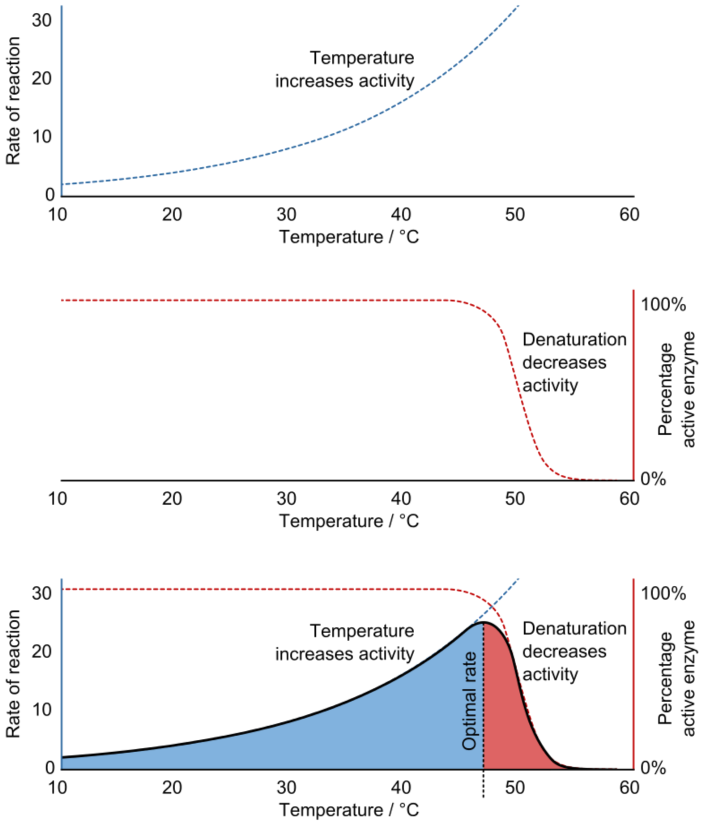

Figure 10.8.1: Enzyme activity initially increases with temperature until the enzyme's structure unfolds (denaturation), leading to an optimal rate of reaction at an intermediate temperature. (CC-BY-SA-4.0; Thomas Shafee)

Enzyme denaturation is normally linked to temperatures above a species' normal level; as a result, enzymes from bacteria living in volcanic environments such as hot springs are prized by industrial users for their ability to function at high temperatures, allowing enzyme-catalyzed reactions to be operated at a very high rate.

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10.E: Exercises

10.1: General Principles of Catalysis

Q10.1a

One day in class about enzyme kinetics, Jack comes over to you and asks, "I know enzymes are biological catalysts, but I do not understand how it works. Can you explain how enzymes make reactions go faster? And is it only faster in one direction?"

S10.1a

Because the activation energy is the energy hill between reactants and products, enzymes decreasing the size of the hill also decreases the amount of energy needed for reactions to go in either direction. A smaller energy hill allows reactants and products to overcome the barrier quicker, resulting a faster reaction rate.

Q10.1b

If your student colleagues argues that a catalysts affects only the rate of only one direction of a reaction. Explain why he is correct or not.

S10.1b

False. Catalysts affect rate by providing an alternative mechanism which has a lower transition state energy. It's impossible to lower transition state energy for only one direction of a reaction. (It'd be like making a hill shorter from the north, but keeping it the same height from the south.)

Q10.1c

How does the enzyme catalysis affect both forward and reverse reaction?

S10.1c

The enzyme catalyst lowers the Gibb energy of transition state, which reduces the activation energy of both reactions. Therefore, it makes reactions occur faster.

Q10.2a

Given enzyme-catalyzed reaction k_1 = 4x10^6 M^{-1} s^{-1} , k_{-1} =6x10^4 s^{-1} and k_2= 2.0x10^3 s^{-1}. Determine if the enzyme –substrate binding follow the equilibrium or not ?

S10.2a

The dissociation constant $k_s = k_{-1} / k_1$ =6x10^4 s^{-1}/ 4x10^6 M^{-1} s^{-1} = 0.15 M

The Michaelis constant $k_M = k_{-1} + k_2 / k_{1=}$ 6x10^4 s^{-1}+ 2.0x10^3 s^{-1}/ 4x10^6 M^{-1} s^{-1} =0.155M

The two constant are not equal. Therefore, the binding does not follow the equilibrium scheme.

Q10.2b

Is it appropriate to use the rapid equilibrium scheme to model the kinetics of a catalyzed reaction with the following rate constants?

$$k_1 = 7 \times 10^7\ M^{-1}\ s^{-1} \tag{10.E.1}$$

$$k_{-1} = 8 \times 10^5\ s^{-1} \tag{10.E.2}$$

$$k_2 = 5 \times 10^4\ s^{-1} \tag{10.E.3}$$

S10.2b

Assuming rapid equilibrium is appropriate when $k_{-1} \gg k_2$, so that $K_M = K_S$. In this case, the values of k_{-1} and k_2 are not dramatically different, so we can calculate K_S and K_M and compare.

1. Calculate K_M:

$$K_M = \frac{k_{-1} + k_2}{k_1} \tag{10.E.4}$$

$$K_M = \frac{8\times 10^5\ s^{-1} + 5\times 10^4\ s^{-1}}{7\times 10^7\ M^{-1}\ s^{-1}} \tag{10.E.5}$$

$$K_M = 0.01\ M \tag{10.E.6}$$

2. Calculate K_S:

$$K_S = \frac{k_{-1}}{k_1} \tag{10.E.7}$$

$$K_M = \frac{8\times 10^5\ s^{-1}}{7\times 10^7\ M^{-1}\ s^{-1}} \tag{10.E.8}$$

$$K_M = 0.01\ M \tag{10.E.9}$$

Since $K_M = K_S$, it is appropriate to assume rapid equilibrium.

Q10.2c

Given k_1= 7 x 10^6 M-1s-1, k_{-1}=6 x 10^4 s^{-1}, k_3= 2 x 10^3 s^{-1}, determine if the enzyme substance binding follow the equilibrium or steady state scheme?

$$K_s = \frac{k_{-1}}{k_1} \tag{10.E.10}$$

$$= \frac{6\times 10^4\ s^{-1}}{7\times 10^6 M^{-1} s^{-1}} \tag{10.E.11}$$

$$= 8.8\times 10^{-3} M \tag{10.E.12}$$

$$K_M = k_{-1} + k_2 \tag{10.E.13}$$

$$= \frac{6\times 10^4 s^{-1} + 2\times 10^3 s^{-1}}{7\times 10^6 M^{-1} s^{-1}} \tag{10.E.14}$$

$$= 8.9\times 10^{-3} M \tag{10.E.15}$$

Q10.3a

The substrate N-acetylglycine ethyl ester can be catalyzed by the enzyme carbonic anhydrase. This enzyme has a turnover rate of 30,000 s^{-1}. Determine how long it will take carbonic anhydrase to cleave the substrate.

S10.3a

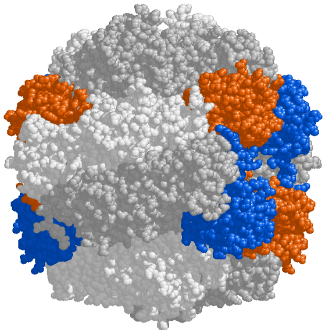
We already know the turnover number (k_{cat}). The amount of time necessary to cleave the substrate is the reciprocal of the turnover rate.

$$t = \frac{1}{k} = \frac{1}{30,000\ s^{-1}} = 3.33\times 10^{-5} \tag{10.E.16}$$

$$(5\ minutes)(7.1\times 10^{-6}) = 3.5\times 10^{-5} \tag{10.E.17}$$

Q10.3b

RuBisCO is an enzyme in the Calvin cycle that fixes atmospheric carbon and has a turnover rate of 3.3 s^{-1}. How long does it take RuBisCO to fix one molecule of carbon dioxide?



Spacefilling structure of RuBisCO created using Rasmol and the 8RUC file from the Protein Data Bank.

S10.3b

The turnover number is the number of molecules of substrate per unit time (when the enzyme is fully saturated). So simply take the reciprocal to find the time per molecule of substrate.

$$\frac{1}{3.3\ s^{-1}} = 0.30\ s \tag{10.E.18}$$

Note: RuBisCO is a notoriously slow enzyme.

Q10.3c

The catalyze of acetylcholine has a rate 50000 s^{-1} . Calculate the time for the enzyme to cleave one Ach molecule.

S10.3c

$t = 1/k_2 = 1/ 50000 = 2.0 \text{ x}10^{-5}s$

Q10.3d

Carbonic anhydrase, an enzyme that catalyzes the dehydration of carbonic acid to form carbonic acid, has the turnover rate of k_{cat} 4.0x 10^5 s^{-1}. Calculate how long does it take does it take for the enzyme to cleave one molecule carbonic acid?

S10.3d

The time required for the enzyme to cleave one molecule carbonic acid:

$t=1/k_{cat} = 1/ 4\text{x}10^5 s^{-1} = 2.5\text{x}10^{-6}s = 2.5\mu s$

Q10.3e

p-nitrophenyl acetate(PNPA) is catalyzed by chymotrypsin to yield p-nitrophenolate ion and acetate ion. The turnover rate of that enzyme is 40,000 s^{-1}. How long will it take for the enzyme to produce 1 mole of Nitrophenyl acetate?

S10.3e

It takes 1 second to convert all 40,000 molecule substrate into the product, so: $t = \frac{40,000}{9.5x10^5}$ = 3.8 sec.

10.2: The Equations of Enzyme Kinetics

Q10.4

What is plotted on the x and y axes on a Lineweaver-Burk plot? Show how to derive the equation for the plot from the equation

$$v_0 = \frac{V_{max}[S]}{K_M + [S]} \tag{10.E.19}$$

and explain how V_{max} and K_M can be found from the graph's intercepts. *Hint: A Lineweaver-Burk plot is also sometimes called a double reciprocal plot.*

S10.4

The x-axis is $1/v_0$, and the x-axis is $1/V_{max}$.

1. Take the reciprocal of both sides of the equation.

$$\frac{1}{v_0} = \frac{K_M + [S]}{V_{max}[S]} \tag{10.E.20}$$

$$\frac{1}{v_0} = \frac{K_M}{V_{max}}\frac{1}{[S]} + \frac{1}{V_{max}} \tag{10.E.21}$$

2. Set $1/[S] = 0$ to find the y-intercept, and show that it relates to V_{max}.

$$Yint = \frac{1}{V_{max}} \tag{10.E.22}$$

$$V_{max} = \frac{1}{Yint} \tag{10.E.23}$$

3. Set $1/v_0 = 0$ to find the x-intercept, and show that it relates to K_M.

$$0 = \frac{K_M}{V_{max}}Xint + \frac{1}{V_{max}} \tag{10.E.24}$$

$$\frac{K_M}{V_{max}}Xint = -\frac{1}{V_{max}} \tag{10.E.25}$$

$$Xint = -\frac{1}{K_M} \tag{10.E.26}$$

$$K_M = -\frac{1}{Xint} \tag{10.E.27}$$

Q10.4a

Derive the Michaelis-Menten equation by assuming rapid equilibrium.

$$E + S \overset{K_1}{\rightleftharpoons} ES \overset{K_2}{\rightarrow} E + P \tag{10.E.28}$$

$$v_0 = \frac{V_{max}[S]}{K_M + [S]} \tag{10.E.29}$$

S10.4a

$$\frac{[E][S]}{dt} = K_{-1}[ES] \quad \frac{[ES]}{dt} = K_1[E][S] \quad \frac{[E][S]}{dt} = \frac{[ES]}{dt} \quad K_{-1}[ES] = K_1[E][S] \quad K_M\frac{k_{-1}}{K_1} = \frac{[E][S]}{[ES]}$$

given that $[E]_0 = [E] + [ES]$

$$K_M = \frac{[E]_0 - [ES][S]}{[ES]} \quad K_M = \frac{[E]_0[S] - [ES][S]}{[ES]} \quad K_M \times [ES] = [E]_0[S] - [ES][S] \quad K_M \times [ES] + [ES][S] = [E]_0[S]$$

$$(K_M + [S])[ES] = [E_0][S] \quad [ES] = \frac{[E_0][S]}{K_M + [S]}$$

since $\frac{d[P]}{dt} = k_2[ES]$

$$v_0 = \frac{K_2[E_0][S]}{K_M + [S]}$$

since $v_{max} = k_2[E]_0$

$$v_0 = \frac{V_{max}[S]}{K_M + [S]}$$

Q10.4b

We know that the Michaelis Menten derivation for the following reaction:

$$\mathrm{E+S \rightleftharpoons ES \longrightarrow E+P} \tag{10.E.30}$$

However, what if the reaction took place in a different scenario whereby:

$$\mathrm{E+S \rightleftharpoons ES_1 \longrightarrow ES_2 \longrightarrow E+P} \tag{10.E.31}$$

What would be the corresponding Michaelis-Menten Ebe quation now?

S10.4b

This is the an outline for determining an expression for the rate of substrate conversion in the given case:

1. Set up the reaction with rate constants, assuming $k_{-2} \approx k_{-3} \approx 0$:

$$\mathrm{E+S} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{ES_1} \xrightarrow{k_2} \mathrm{ES_2} \xrightarrow{k_3} \mathrm{E+P} \tag{10.E.32}$$

2. Set up the differential equations describing the reaction, i.e. the rate of change for each component with time. The rate of substrate change, for example, will be

$$\frac{d[\mathrm{S}]}{dt} = -k_1[\mathrm{E}][\mathrm{S}] + k_{-1}[\mathrm{ES_1}] \tag{10.E.33}$$

3. Choose initial conditions and set up two equations for conservation of mass. For example, the initial concentration of enzyme must equal the sum of the concentrations of E, $\mathrm{ES_1}$ and $\mathrm{ES_2}$.
4. Make the *steady-state assumpt*: assume that the concentrations of the intermediate complexes do not change on the time-scale of product formation, i.e.

$$\frac{d[\mathrm{ES_1}]}{dt} \approx \frac{d[\mathrm{ES_2}]}{dt} \approx 0 \tag{10.E.34}$$

5. Solve for $-r_S$, the negative rate of substrate conversion, obtaining the Michaelis-Menten expression describing the kinetics of the given situtation.

Q10.4c

Prove that K_s equals the concentration S when the initial rate is half its maximum value.

S10.4c

We have: $v_o = \frac{V_{max}[S]}{K_M + [S]}$

Divided both said by 1 $\frac{1}{v_o} = \frac{K_M + [S]}{V_{max}[S]}$

$$\frac{1}{v_o} = \frac{K_M}{V_{max}[S]} + \frac{[S]}{V_{max}[S]}$$

$$\frac{1}{v_o} = \frac{K_M}{V_{max}[S]} + \frac{1}{V_{max}}$$

When the initial rate is half its maximum value: $v_o = \frac{V_{max}}{2}$

$$\frac{2}{V_{max}} = \frac{K_M}{V_{max}[S]} + \frac{1}{V_{max}}$$

$$\frac{2}{V_{max}} - \frac{1}{V_{max}} = \frac{K_M}{V_{max}[S]}$$

$$\frac{1}{V_{max}} = \frac{K_M}{V_{max}[S]}$$

$\frac{V_{max}}{V_{max}} = \frac{K_M}{[S]}$

$[S] = K_M$

Q10.5a

An enzyme that has a K_m value of $4.6 \times 10^{-5}\ M$ is studied at an initial substrate concentration of 0.041 M. After a minute, it is found that 7.3 uM of product has been produced. Calculate the value of Vmax and the amount of product formed after 4.5 minutes.

Q10.5b

An solution initially contains a catalytic amount of an enzyme with K_M = 1.5 mM, 0.25 M of substrate, and no product. After 45 seconds, the solution contains 25 µM of product. Find V_{max} and the concentration of product after 2.0 minutes.

Hint: [S] >> K_M

S10.5b

1. Find the initial velocity.

$$v_0 = \frac{25\ \mu M}{0.75\ min} \tag{10.E.35}$$

$$v_0 = 33.3\ \mu M/min \tag{10.E.36}$$

2. Use v_0, [S], and K_M to solve for V_{max}.

$$v_0 = \frac{V_{max}[S]}{K_M + [S]} \tag{10.E.37}$$

$$V_{max} = v_0 \left(\frac{K_M}{[S]} + 1 \right) \tag{10.E.38}$$

$$V_{max} = 33.3\ \mu M/min \left(\frac{1.5\ mM}{0.25\ M} \times \frac{M}{1000\ mM} + 1 \right) \tag{10.E.39}$$

$$V_{max} = 33.3\ \mu M/min \tag{10.E.40}$$

Notice that $v_0 = V_{max}$. Since [S] >>K_M, the reaction will continue with a velocity of V_{max} for the remainder of the two minutes.

3. Predict [P] after 2.0 minutes at the rate V_{max}.

$$[P] = V_{max} \times t \tag{10.E.41}$$

$$[P] = 33.3\ \mu M/min \times 2.0\ min \tag{10.E.42}$$

$$[P] = 66.6\ \mu M \tag{10.E.43}$$

Q10.5c

A particular enzyme at a research facility is being studied by a group of graduate students. This enzyme has a K_m value of 5.0 X 10^{-6} M. The students study this enzyme with an initial substrate concentration of 0.055 M. At one minute, 7 µM of product was made. What is the amount of product produced after 5 minutes. What is the V_{max} ?

S10.5c

$V_o = V_{max}[substrate]/K_m + [substrate]$ 7.0 X 10^{-6} M = V_{max} (0.055 M) / (5.0 X 10^{-6} M + .055 M) V_{max} = 7.1 X 10^{-6} M/min At 5 minutes the amount of product formed is:

Q10.5d

Calculate the value v_o if an enzyme has $K_M = 5.4 * 10^{-4}$, value $V_{max} = 48 \mu M min^{-1}$ and $[S] = 0.001 M$

S10.5d

We have: $v_o = \frac{V_{max}\,[S]}{K_M + [S]}$

$$v_o = \frac{48 * 0.001}{5.4 * 10^{-4} + 0.001} = 31\mu M min^{-1}$$

Q10.6a

Given the values, [S]/10^-4 M 3.0 4.6 10.5 16.5

vo/10^-6 M * min^-1. 2.64 3.5 6.2 7.8

construct a Lineweaver-Burk plot, and assuming Michaelis-Menten kinetics, calculate the values of Vmax, Km, and k2 using the constructed plot.

Q10.6b

The data below represents the data recorded after the hydrolysis of a substrate by an enzyme.

[S]/10-4 M	2.1	4.2	9.3	14.2
vo / 10-6 M · min-1	1.2	3.1	6.3	9.1

Calculate V_{max}, K_m and K_2 using a Lineweaver-Burk plot. Assume Michaelis. Given $[E\}_0$ is 5.0 X 10^{-6} M

S10.6b

(1/[S])/10-3 M-1	(1/vo)/ 10-5 M-1 · min
4.8	8.3
2.4	3.2
1.1	1.6
0.7	1.1

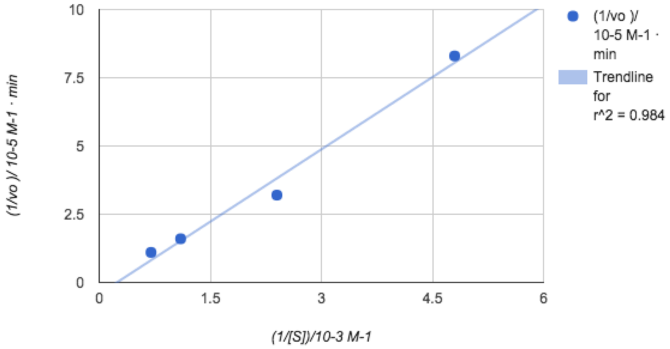


Figure: Lineweaver-Burk Plot

The linear equation for the graph above is: y=176x+4.23X10^4 To solve for V_{max} use: Intercept= 1/V_{max} V_{max} = 1/(.4.23X10^4) = 2.36 X 10^{-5} To solve for K_m use Slope= K_m/V_{max} (176)(2.36 X 10^{-5}) = 4.2 X 10^{-5} To solve for K_2 use K_2 = V_{max}/ $[E\}_0$ = (2.36 X 10^{-5})(5.0 X 10^{-6} M)= 4.72 min^{-1}

Q10.6c

Using the table below, calculate the K_M, V_{max}, and slope.

$$\frac{1}{V_0}(10^{-3}\frac{sec}{M^{-1}}) \tag{10.E.44}$$	$$\frac{1}{[S]}(10^2 M^{-1}) \tag{10.E.45}$$
2.9	0.3
3.2	1.2

$\frac{1}{V_0}(10^{-3}\frac{sec}{M^{-1}})$ (10.E.44)	$\frac{1}{[S]}(10^2 M^{-1})$ (10.E.45)
4.4	1.8
5.1	3.3

S10.6c

slope=$\frac{5.1\times10^{-3}-2.9\times10^{-3}}{3.3\times10^2-0.3\times10^2}=6.73\times10^{-6}$ $6.73\times10^{-6}\times0.3\times10^2+\frac{1}{V_{max}}=2.9\times10^{-3}$ $\frac{1}{V_{max}}=0.00270$
$V_{max}=370.62Ms^{-1}$ $6.73\times10^{-6}\times\frac{-1}{K_M}+0.00270=0$ $\frac{-1}{K_M}=-0.00943$ $K_M=106.044$

Q10.6d

Given the value $[S]$= 0.00032 and $K_M=3.5*10^{-5}$. Find the ratio between v_o and V_{max}

S10.6d

$$v_o=\frac{V_{max}[S]}{K_M+[S]}$$

Divided both side by 1: $\frac{1}{v_o}=\frac{K_M}{V_{max}[S]}+\frac{1}{V_{max}}$

Divided both side by 1 again: $v_o=\frac{V_{max}[S]}{K_{max}}+V_{max}$

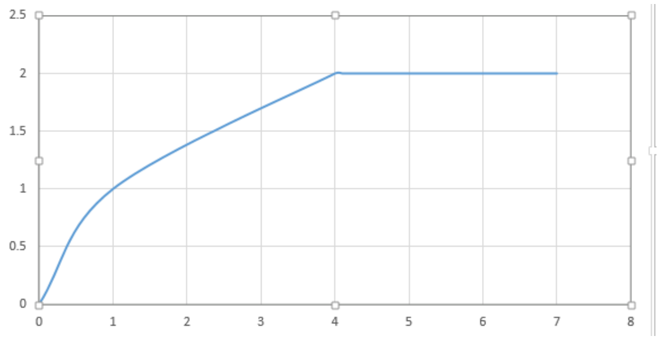
$$v_o=V_{max}\left(\frac{[S]}{K_{max}}+1\right)$$

$$\frac{v_o}{V_{max}}=\frac{[S]}{K_M}+1$$

$$\frac{v_o}{V_{max}}=\frac{0.00032}{3.5*10^{-5}}+1=\frac{71}{7}=10.14$$

Q10.7a

From this graph determine the K_M and V_{max}?



S10.7b

From his graph we can see that the value K_M is 2. Then we look to see where K_M is half. At that point, we see that K_M/2 is 1 and the x-value for that coordinate is 1. This means V_{max} is 1.

Q10.7b

Neutral sphingomyelinase 2 converts sphingomyelin into ceramide and phosphocholine. Assume its V_{max} is 35 μM min^{-1}. When you provide 3 x 10^{-5} M of sphingomyelin, you observe an initial velocity of 6.0 μM min^{-1}. Calculate the K_M for this reaction, rounding to 3 significant figures.

S10.7b

$$\frac{1}{V_o} = \frac{K_M}{V_{max}[S]} + \frac{1}{V_{max}} \tag{10.E.46}$$

$$\frac{1}{6.0} = \frac{K_M}{(35)(30)} + \frac{1}{35} \tag{10.E.47}$$

$$\frac{1}{6} - \frac{1}{35} = \frac{K_M}{1050} \tag{10.E.48}$$

K_M = 145 µM

Q10.8a

We are given a second order equation: r=k[A][B]. The concentration of A is 0.05g and the concentration of B is 2.5g. We decide this difference is great enough to treat this as a pseudo first reaction? What concentration is held constant and why? Write the new equation.

S10.8a

We hold B constant because the concentration is so much larger, so it should be close to constant for the reaction. The new equation would be r=k'[a]

Q10.9a

Name and briefly describe two types of reactions that do not follow Michaelis-Menten kinetics.

S10.9a

Irreversible inhibition - the inhibitor binds covalently and irreversibly to the enzyme Allosteric interactions - the binding of effectors at allosteric sites (away from the active site) influence substrate binding.

Q10.9b

For the reaction mechanism below, how does the concentration of C affect the concentration of B?

$$A \leftrightharpoons B \rightarrow C \tag{10.E.49}$$

S10.9b

Because the second state is *irreversible* (i.e., since arrow), it does not matter if you have a large or little concentration of C, it would not affect B and hence the kinetics of the reaction. However, the concentration of A\0wouldclearlyaffecttheconcentrationof\(B.

10.3: Chymotrypsin: A Case Study

Q1

1. Speculate on how the catalytic rate constant can be determined from the spectrophotogram.
2. How can product be consistently produced if the rate of change of the ES complex is 0?
3. How would the rate of product formation change if:
    a. the substrate concentration were doubled?
    b. the enzyme concentration were doubled?
    c. The reaction was carried out in mono-deuterated water instead of H_2O (comment qualitatively)?
4. Explain the role of hydrogen bonding in protein hydrolysis catalyzed by chymotrypsin.
5. What would the spectrophotogram look like if the reaction proceeded via a steady-state mechanism instead of pre-equilibrium.

S2

1. The catalytic rate constant can be deduced from the graph by simply determining the slope of the line where the reaction demonstrates 0-order kinetics (the linear part).
2. This is pre-equilibrium kinetics in action. The ES complex is formed from E and S at a faster rate than any other step in the reaction. As soon as ES is converted to *ES, another mole of ES is produced from an infinite supply of E + S. This means that the amount of ES and E + S is constantly at equilibrium, and thus the change of either with respect to time is 0.

   a. No change.
   b. Two-fold increase.
   c. Because water is involved in the final, slowest step of the mechanism, deuterating the water would decrease the rate of the overall reaction from 5- to 30-fold.
3. Initially, hydrogen bonding between the enzymes histidine and serine side chains weakens the bond of serine’s O-H. This allows a facilitated nucleophilic attack of the hydroxyl oxygen on the substrates carbonyl group. Conversely, in the final step of the reaction, the bound serine oxygen forms a hydrogen bond with a protonated histidine, which allows for easier cleavage from the substrate.
4. The graph would show similar 0-order kinetics, but the line would intercept the Y-axis at an absorbance of 0 instead of the 1:1 mole ratio of nitrophenolate to enzyme.

10.4: Multisubstrate Systems

10.5: Enzyme Inhibition

10.6: Allosteric Interactions

10.7: The Effect of pH on Enzyme Kinetics

10.4: Multisubstrate Systems

10.5: Enzyme Inhibition

10.6: Allosteric Interactions

10.7: The Effect of pH on Enzyme Kinetics

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CHAPTER OVERVIEW

11: Quantum Mechanics and Atomic Structure

Quantum mechanics is a fundamental branch of physics concerned with processes involving small particles (e.g, atoms and photons). Such processes as said to be quantized with properties that are observed in only in integer multiples of the Planck constant. This is utterly inexplicable in classical physics which is a continuum approach.

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11.1: The Wave Theory of Light

Learning Objectives

- to learn about the characteristics of electromagnetic waves. Light, X-Rays, infrared and microwaves among the types of electromagnetic waves.

Scientists discovered much of what we know about the structure of the atom by observing the interaction of atoms with various forms of radiant, or transmitted, energy, such as the energy associated with the visible light we detect with our eyes, the infrared radiation we feel as heat, the ultraviolet light that causes sunburn, and the x-rays that produce images of our teeth or bones. All these forms of radiant energy should be familiar to you. We begin our discussion of the development of our current atomic model by describing the properties of waves and the various forms of electromagnetic radiation.

Figure 1.1.1 A Wave in Water When a drop of water falls onto a smooth water surface, it generates a set of waves that travel outward in a circular direction.

Properties of Waves

A wave is a periodic oscillation that transmits energy through space. Anyone who has visited a beach or dropped a stone into a puddle has observed waves traveling through water (Figure 1.1.1). These waves are produced when wind, a stone, or some other disturbance, such as a passing boat, transfers energy to the water, causing the surface to oscillate up and down as the energy travels outward from its point of origin. As a wave passes a particular point on the surface of the water, anything floating there moves up and down.

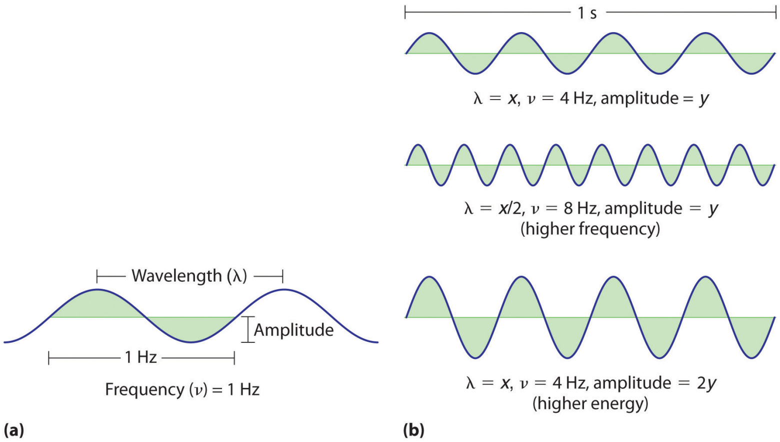

Figure 1.1.2: Important Properties of Waves (a) Wavelength (λ in meters), frequency (ν, in Hz), and amplitude are indicated on this drawing of a wave. (b) The wave with the shortest wavelength has the greatest number of wavelengths per unit time (i.e., the highest frequency). If two waves have the same frequency and speed, the one with the greater amplitude has the higher energy.

Waves have characteristic properties (Figure 1.1.2). As you may have noticed in Figure 1.1.1, waves are periodic, that is, they repeat regularly in both space and time. The distance between two corresponding points in a wave—between the midpoints of two peaks, for example, or two troughs—is the wavelength (λ), distance between two corresponding points in a wave—between the midpoints of two peaks or two troughs. λ is the lowercase Greek lambda, and ν is the lowercase Greek nu. Wavelengths are described by a unit of distance, typically meters. The frequency (ν), the number of oscillations (i.e., of a wave) that pass a particular point in a given period of time. of a wave is the number of oscillations that pass a particular point in a given period of time. The usual units are oscillations persecond (1/s = s^{-1}), which in the SI system is called the hertz (Hz). It is named after German physicist Heinrich Hertz (1857–1894),a pioneer in the field of electromagnetic radiation. The amplitude (the vertical height of a wave, which is defined as half the peak-to-trough height), or vertical height, of a wave is defined as half the peak-to-trough height; as the amplitude of a wave with a given frequency increases, so does its energy. As you can see in Figure 1.1.2 , two waves can have the same amplitude but different wavelengths and vice versa. The distance traveled by a wave per unit time is its speed (v), the distance traveled by a wave per unit time, which is typically measured in meters per second (m/s). The speed of a wave is equal to the product of its wavelength and frequency:

(wavelength)(frequency) = speed

$$\lambda \nu = v \tag{1.1.1a}$$

$$\left(\frac{meters}{\cancel{wave}}\right)\left(\frac{\cancel{wave}}{second}\right) = \frac{meters}{second} \tag{1.1.1b}$$

Be careful not to confuse the symbols for the speed, v, with the frequency, ν. Water waves are slow compared to sound waves, which can travel through solids, liquids, and gases. Whereas water waves may travel a few meters per second, the speed of sound in dry air at 20°C is 343.5 m/s. Ultrasonic waves, which travel at an even higher speed (>1500 m/s) and have a greater frequency, are used in such diverse applications as locating underwater objects and the medical imaging of internal organs.

Electromagnetic Radiation

Water waves transmit energy through space by the periodic oscillation of matter (the water). In contrast, energy that is transmitted, or radiated, through space in the form of periodic oscillations of electric and magnetic fields is known as electromagnetic radiation, which is energy that is transmitted, or radiated, through space in the form of periodic oscillations of electric and magnetic fields. (Figure 1.1.3). Some forms of electromagnetic radiation are shown in Figure 1.1.4. In a vacuum, all forms of electromagnetic radiation—whether microwaves, visible light, or gamma rays—travel at the speed of light (c), which is the speed with which all forms of electromagnetic radiation travel in a vacuum, a fundamental physical constant with a value of 2.99792458 × 10^8 m/s (which is about 3.00 ×10^8 m/s or 1.86 × 10^5 mi/s). This is about a million times faster than the speed of sound.

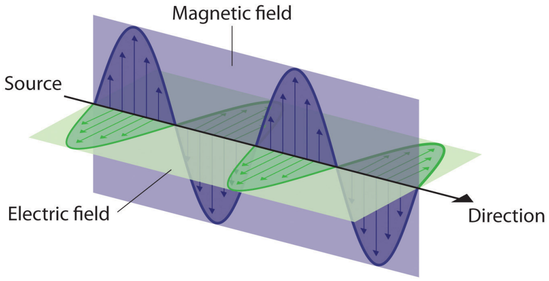

Figure 1.1.3: The Nature of Electromagnetic Radiation. All forms of electromagnetic radiation consist of perpendicular oscillating electric and magnetic fields.

Because the various kinds of electromagnetic radiation all have the same speed (c), they differ in only wavelength and frequency. As shown in Figure 1.1.4 and Table 1.1.1 , the wavelengths of familiar electromagnetic radiation range from 10^1 m for radio waves to 10^{-12} m for gamma rays, which are emitted by nuclear reactions. By replacing v with c in Equation 6.1.1, we can show that the frequency of electromagnetic radiation is inversely proportional to its wavelength:

$$\begin{gathered} c = \lambda \nu \\ \nu = \frac{c}{\lambda} \end{gathered} \tag{1.1.2}$$

For example, the frequency of radio waves is about 10^8 Hz, whereas the frequency of gamma rays is about 10^{20} Hz. Visible light, which is electromagnetic radiation that can be detected by the human eye, has wavelengths between about 7 × 10^{-7} m (700 nm, or 4.3 × 10^{14} Hz) and 4 × 10^{-7} m (400 nm, or 7.5 × 10^{14} Hz). Note that when frequency increases, wavelength decreases; c being a constant stays the same. Similarly when frequency decreases, the wavelength increases.

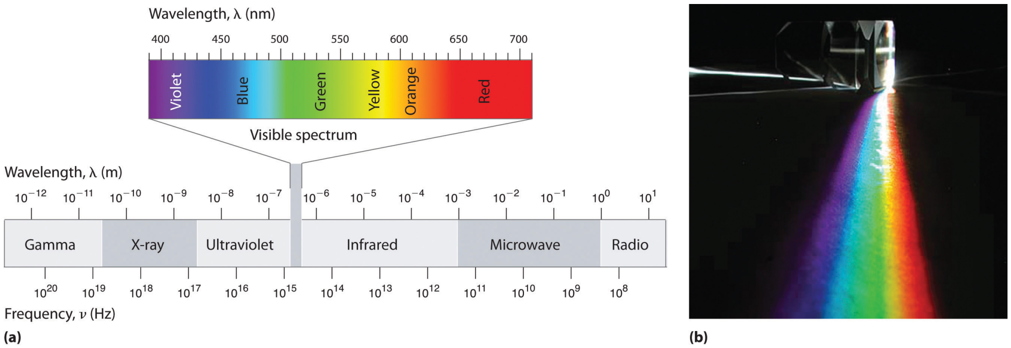

Figure 1.1.4: The Electromagnetic Spectrum. (a) This diagram shows the wavelength and frequency ranges of electromagnetic radiation. The visible portion of the electromagnetic spectrum is the narrow region with wavelengths between about 400 and 700 nm. (b) When white light is passed through a prism, it is split into light of different wavelengths, whose colors correspond to the visible spectrum.

Within this visible range our eyes perceive radiation of different wavelengths (or frequencies) as light of different colors, ranging from red to violet in order of decreasing wavelength. The components of white light—a mixture of all the frequencies of visible light—can be separated by a prism, as shown in part (b) in Figure 1.1.4. A similar phenomenon creates a rainbow, where water droplets suspended in the air act as tiny prisms.

Table 1.1.1: Common Wavelength Units for Electromagnetic Radiation

Unit	Symbol	Wavelength (m)	Type of Radiation
picometer	pm	10^{-12}	gamma ray
angstrom	Å	10^{-10}	x-ray
nanometer	nm	10^{-9}	x-ray
micrometer	μm	10^{-6}	infrared
millimeter	mm	10^{-3}	infrared
centimeter	cm	10^{-2}	microwave
meter	m	10^{0}	radio

As you will soon see, the energy of electromagnetic radiation is directly proportional to its frequency and inversely proportional to its wavelength:

$$E \propto \nu \tag{1.1.3}$$

$$E \propto \frac{1}{\lambda} \tag{1.1.4}$$

Whereas visible light is essentially harmless to our skin, ultraviolet light, with wavelengths of ≤ 400 nm, has enough energy to cause severe damage to our skin in the form of sunburn. Because the ozone layer absorbs sunlight with wavelengths less than 350 nm, it protects us from the damaging effects of highly energetic ultraviolet radiation.

> The energy of electromagnetic radiation **increases** with **increasing** frequency and **decreasing** wavelength.

Example 1.1.1

Your favorite FM radio station, WXYZ, broadcasts at a frequency of 101.1 MHz. What is the wavelength of this radiation?

Given: frequency

Asked for: wavelength

Strategy:

Substitute the value for the speed of light in meters per second into Equation 1.1.2 to calculate the wavelength in meters.

Solution:

From Equation 1.1.2 , we know that the product of the wavelength and the frequency is the speed of the wave, which for electromagnetic radiation is 2.998 × 10^8 m/s:

$$\lambda\nu = c = 2.998 \times 10^8 m/s$$

Thus the wavelength λ is given by

$$\lambda = \frac{c}{\nu} = \left(\frac{2.988 \times 10^8 \ m/\cancel{s}}{101.1 \ \cancel{MHz}}\right)\left(\frac{1 \ \cancel{MHz}}{10^6 \ \cancel{s^{-1}}}\right) = 2.965 \ m$$

Exercise 1.1.1

As the police officer was writing up your speeding ticket, she mentioned that she was using a state-of-the-art radar gun operating at 35.5 GHz. What is the wavelength of the radiation emitted by the radar gun?

Click to Check Answer

8.45 mm

External Videos & Examples

- **Light Speed, Wavelength and Frequency by Doc Schuster - Explains wavelength and frequency**
- **Waves in General by JaHu Productions - a bit faster. Also discusses sound waves**
- **Calculating Frequency Given Wavelength - Johnny Cantrell**
- **Wavelength Frequency Problems - Cayer Chem**
- **Quantum Chemistry - Ohio State**
- **Quantum Chemistry Quizzes - mhe education**
- **AP Chemistry Chapter 7 Review - Science Geek**
- **Quantum Theory of the Atom Practice Quiz - Northrup**

Answers for these quizzes are included. There are also questions covering more topics in Chapter 6.

Summary

- Understanding the electronic structure of atoms requires an understanding of the properties of waves and electromagnetic radiation.

A basic knowledge of the electronic structure of atoms requires an understanding of the properties of waves and electromagnetic radiation. A wave is a periodic oscillation by which energy is transmitted through space. All waves are periodic, repeating regularly in both space and time. Waves are characterized by several interrelated properties: wavelength (λ), the distance between successive waves; frequency (ν), the number of waves that pass a fixed point per unit time; speed (v), the rate at which the wave propagates through space; and amplitude, the magnitude of the oscillation about the mean position. The speed of a wave is equal to the product of its wavelength and frequency. Electromagnetic radiation consists of two perpendicular waves, one electric and one magnetic, propagating at the speed of light (c). Electromagnetic radiation is radiant energy that includes radio waves, microwaves, visible light, x-rays, and gamma rays, which differ in their frequencies and wavelengths.

Contributors

- Modified by Joshua Halpern (Howard University)

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11.2: Planck's Quantum Theory

Learning Objectives

- To understand how energy is quantized in blackbody radiation

By the late 19th century, many physicists thought their discipline was well on the way to explaining most natural phenomena. They could calculate the motions of material objects using Newton's laws of classical mechanics, and they could describe the properties of radiant energy using mathematical relationships known as Maxwell's equations, developed in 1873 by James Clerk Maxwell, a Scottish physicist. The universe appeared to be a simple and orderly place, containing matter, which consisted of particles that had mass and whose location and motion could be accurately described, and electromagnetic radiation, which was viewed as having no mass and whose exact position in space could not be fixed. Thus matter and energy were considered distinct and unrelated phenomena. Soon, however, scientists began to look more closely at a few inconvenient phenomena that could not be explained by the theories available at the time.

One experimental phenomenon that could not be adequately explained by classical physics was blackbody radiation (Figure 1.2.1). Attempts to explain or calculate this spectral distribution from classical theory were complete failures. A theory developed by Rayleigh and Jeans predicted that the intensity should go to infinity at short wavelengths. Since the intensity actually drops to zero at short wavelengths, the Rayleigh-Jeans result was called the **ultraviolet catastrophe** (Figure 1.2.1 dashed line). There was no agreement between theory and experiment in the ultraviolet region of the blackbody spectrum.

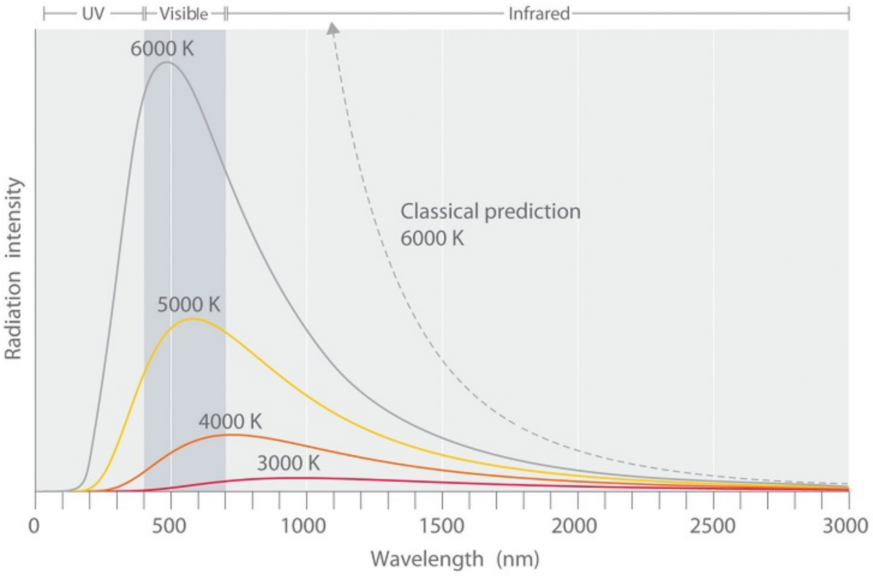


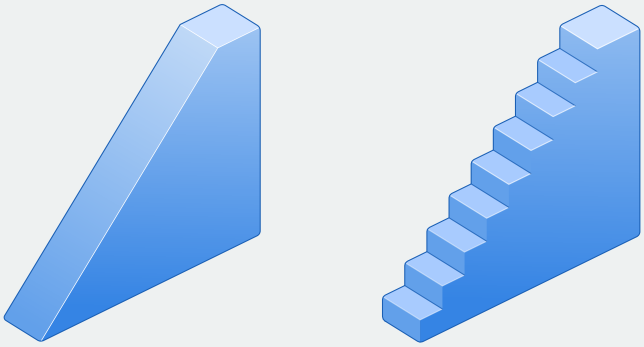
Figure 1.2.1 : Relationship between the temperature of an object and the spectrum of blackbody radiation it emits. At relatively low temperatures, most radiation is emitted at wavelengths longer than 700 nm, which is in the infrared portion of the spectrum. As the temperature of the object increases, the maximum intensity shifts to shorter wavelengths, successively resulting in orange, yellow, and finally white light. At high temperatures, all wavelengths of visible light are emitted with approximately equal intensities. The white light spectrum shown for an object at 6000 K closely approximates the spectrum of light emitted by the sun. Note the sharp decrease in the intensity of radiation emitted at wavelengths below 400 nm, which constituted the ultraviolet catastrophe. The classical prediction fails to fit the experimental curves entirely and does not have a maximum intensity. (CC BY-SA-NC; anonymous).

Quantizing Electrons in the Radiator

In 1900, the German physicist Max Planck (1858–1947) explained the ultraviolet catastrophe by proposing that the energy of electromagnetic waves is *quantized* rather than continuous. This means that for each temperature, there is a maximum intensity of radiation that is emitted in a blackbody object, corresponding to the peaks in Figure 1.2.1 , so the intensity does not follow a smooth curve as the temperature increases, as predicted by classical physics. Thus energy could be gained or lost only in integral multiples of some smallest unit of energy, a quantum (the smallest possible unit of energy). Energy can be gained or lost only in integral multiples of a quantum.

Quantization

Although quantization may seem to be an unfamiliar concept, we encounter it frequently in quantum mechanics (hence the name). For example, US money is integral multiples of pennies. Similarly, musical instruments like a piano or a trumpet can produce only certain musical notes, such as C or F sharp. Because these instruments cannot produce a continuous range of frequencies, their frequencies are quantized. It is also similar to going up and down a hill using discrete stair steps rather than being able to move up and down a continuous slope. Your potential energy takes on discrete values as you move from step to step. Even electrical charge is quantized: an ion may have a charge of −1 or −2, but *not* −1.33 electron charges.



A continuous vs. a quantized (gravitationaly) potential energy system. In the continuous case (left) a system can have any potential energy, but in the quantized case (right), a system can only have certain values (other values are not allowed). (CC BY-NC; Ümit Kaya via LibreTexts)

Planck's quantization of energy is described by the his famous equation:

$$E = h\nu \tag{11.2.1}$$

where the proportionality constant h is called **Planck’s constant**, one of the most accurately known fundamental constants in science

$$h = 6.626070040(81) \times 10^{-34}\, J \cdot s$$

However, for our purposes, its value to four significant figures is sufficient:

$$h = 6.626 \times 10^{-34}\, J \cdot s$$

As the frequency of electromagnetic radiation increases, the magnitude of the associated quantum of radiant energy increases. By assuming that energy can be emitted by an object only in integral multiples of $h\nu$, Planck devised an equation that fit the experimental data shown in Figure 1.2.1 . We can understand Planck’s explanation of the ultraviolet catastrophe qualitatively as follows: At low temperatures, radiation with only relatively low frequencies is emitted, corresponding to low-energy quanta. As the temperature of an object increases, there is an increased probability of emitting radiation with higher frequencies, corresponding to higher-energy quanta. At any temperature, however, it is simply more probable for an object to lose energy by emitting a large number of lower-energy quanta than a single very high-energy quantum that corresponds to ultraviolet radiation. The result is a maximum in the plot of intensity of emitted radiation versus wavelength, as shown in Figure 1.2.1 , and a shift in the position of the maximum to lower wavelength (higher frequency) with increasing temperature.

At the time he proposed his radical hypothesis, Planck could not explain *why* energies should be quantized. Initially, his hypothesis explained only one set of experimental data—blackbody radiation. If quantization were observed for a large number of different phenomena, then quantization would become a law. In time, a theory might be developed to explain that law. As things turned out, Planck’s hypothesis was the seed from which modern physics grew.

Max Planck explain the spectral distribution of blackbody radiation as result from oscillations of electrons. Similarly, oscillations of electrons in an antenna produce radio waves. Max Planck concentrated on modeling the oscillating charges that must exist in the oven walls, radiating heat inwards and—in thermodynamic equilibrium—themselves being driven by the radiation field. He found he could account for the observed curve if he required these oscillators not to radiate energy continuously, as the classical theory would demand, but they could **only** lose or gain energy in chunks, called **quanta**, of size $h\nu$, for an oscillator of frequency ν (Equation 11.2.1).

With that assumption, Planck calculated the following formula for the radiation energy density inside the oven:

$$d\rho(\nu,T) = \rho_\nu(T)d\nu \tag{11.2.2}$$

$$= \frac{2h\nu^3}{c^2} \cdot \frac{1}{\exp\left(\frac{h\nu}{k_BT}\right) - 1} d\nu \tag{11.2.3}$$

with

- $\pi = 3.14159$
- $h = 6.626 \times 10^{-34} J \cdot s$
- $c = 3.00 \times 10^8 \, m/s$
- $\nu = 1/s$
- $k_B = 1.38 \times 10^{-23} J/K$
- T is absolute temperature (in Kelvin)

Planck's radiation energy density (Equation 11.2.3) can also be expressed in terms of wavelength λ.

$$\rho(\lambda,T) = \frac{2hc^2}{\lambda^5} \left(\frac{1}{e^{\frac{hc}{\lambda k_B T}} - 1} \right) \tag{11.2.4}$$

With a wavelength of maximum energy density at:

$$\lambda_{max} = \frac{hc}{4.965kT}$$

Planck's equation (Equation 11.2.4) gave an excellent agreement with the experimental observations for all temperatures (Figure 1.2.2).

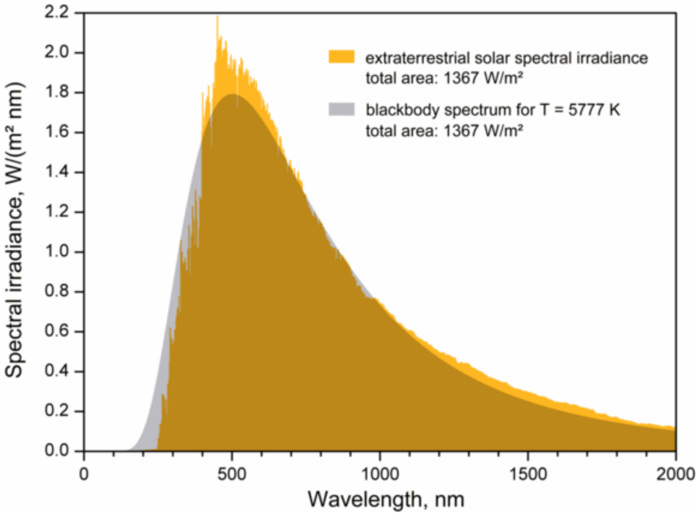


Figure 1.2.2 : The Sun is an excellent approximation of a blackbody. Its effective temperature is ~5777 K. (CC-SA-BY 3.0; Sch).

Max Planck (1858–1947)

Planck made many substantial contributions to theoretical physics, but his fame as a physicist rests primarily on his role as the originator of quantum theory. In addition to being a physicist, Planck was a gifted pianist, who at one time considered music as a career. During the 1930s, Planck felt it was his duty to remain in Germany, despite his open opposition to the policies of the Nazi government.

(left) The German physicist Max Planck had a major influence on the early development of quantum mechanics, being the first to recognize that energy is sometimes quantized. Planck also made important contributions to special relativity and classical physics. (Public Domain; Library of Congress via Wikimedia) (left) The society's logo features Minerva, the Roman goddess of wisdom. (Fair use)

One of his sons was executed in 1944 for his part in an unsuccessful attempt to assassinate Hitler and bombing during the last weeks of World War II destroyed Planck's home. After WWII, the major German scientific research organization was renamed the Max Planck Society.

? Exercise 1.2.1

Use Equation 11.2.4to show that the units of $\rho(\lambda, T)\, d\lambda$ are J/m^3 as expected for an energy density.

The near perfect agreement of this formula with precise experiments (e.g., Figure 1.2.3), and the consequent necessity of energy quantization, was the most important advance in physics in the century. His blackbody curve was completely accepted as the correct one: more and more accurate experiments confirmed it time and again, yet the radical nature of the quantum assumption did not sink in. Planck was not too upset—he didn't believe it either, he saw it as a technical fix that (he hoped) would eventually prove unnecessary.

> *Part of the problem was that Planck's route to the formula was long, difficult and implausible—he even made contradictory assumptions at different stages, as Einstein pointed out later. However, the result was correct anyway!*

The mathematics implied that the energy given off by a blackbody was not continuous, but given off at certain specific wavelengths, in regular increments. If Planck assumed that the energy of blackbody radiation was in the form

$$E = nh\nu$$

where n is an integer, then he could explain what the mathematics represented. This was indeed difficult for Planck to accept, because at the time, there was no reason to presume that the energy should only be radiated at specific frequencies. Nothing in Maxwell's laws suggested such a thing. It was as if the vibrations of a mass on the end of a spring could only occur at specific energies. Imagine the mass slowly coming to rest due to friction, but not in a continuous manner. Instead, the mass jumps from one fixed quantity of energy to another without passing through the intermediate energies.

> *To use a different analogy, it is as if what we had always imagined as smooth inclined planes were, in fact, a series of closely spaced steps that only presented the illusion of continuity.*

Summary

The agreement between Planck's theory and the experimental observation provided strong evidence that the energy of electron motion in matter is quantized. In the next two sections, we will see that the energy carried by light also is quantized in units of $h\bar{\nu}$. These packets of energy are called "photons."

Contributors and Attributions

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11.3: The Photoelectric Effect

Learning Objectives

- To be familiar with the photoelectron effect for bulk materials
- Understand how the photoelectron kinetic energy and intensity vary as a function of incident light wavelength
- Understand how the photoelectron kinetic energy and intensity vary as a function of incident light intensity
- Describe what a workfunction is and relate it to ionization energy
- Describe the photoelectric effect with Einstein's quantized photon model of light

Nature, it seemed, was quantized (non-continuous, or discrete). If this was so, how could Maxwell's equations correctly predict the result of the blackbody radiator? Planck spent a good deal of time attempting to reconcile the behavior of electromagnetic waves with the discrete nature of the blackbody radiation, to no avail. It was not until 1905, with yet another paper published by Albert Einstein, that the wave nature of light was expanded to include the particle interpretation of light which adequately explained Planck's equation.

The photoelectric effect was first documented in 1887 by the German physicist Heinrich Hertz and is therefore sometimes referred to as the Hertz effect. While working with a spark-gap transmitter (a primitive radio-broadcasting device), Hertz discovered that upon absorption of certain frequencies of light, substances would give off a visible spark. In 1899, this spark was identified as light-excited electrons (called **photoelectrons**) leaving the metal's surface by J.J. Thomson (Figure 1.3.1).

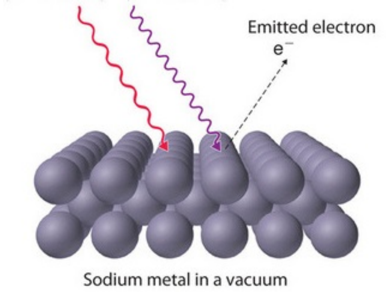

Figure 1.3.1 : The photoelectric effect involves irradiating a metal surface with photons of sufficiently high energy to cause the electrons to be ejected from the metal. (CC BY-SA-NC; anonymous)

The classical picture underlying the photoelectron effect was that the atoms in the metal contained electrons, that were shaken and caused to vibrate by the oscillating electric field of the incident radiation. Eventually some of them would be shaken loose, and would be ejected from the cathode. It is worthwhile considering carefully how the *number* and *speed* of electrons emitted would be expected to vary with the *intensity* and *color* of the incident radiation along with the time needed to observe the photoelectrons.

- Increasing the intensity of radiation would shake the electrons more violently, so one would expect more to be emitted, and they would shoot out at greater speed, on average.
- Increasing the frequency of the radiation would shake the electrons faster, so it might cause the electrons to come out faster. For very dim light, it would take some time for an electron to work up to a sufficient amplitude of vibration to shake loose.

Lenard's Experimental Results (Intensity Dependence)

In 1902, Hertz's student, Philipp Lenard, studied how the energy of the emitted photoelectrons varied with the intensity of the light. He used a carbon arc light and could increase the intensity a thousand-fold. The ejected electrons hit another metal plate, the collector, which was connected to the cathode by a wire with a sensitive ammeter, to measure the current produced by the illumination (Figure 1.3.2). To measure the energy of the ejected electrons, Lenard charged the collector plate negatively, to repel the electrons coming towards it. Thus, only electrons ejected with enough kinetic energy to get up this potential hill would contribute to the current.

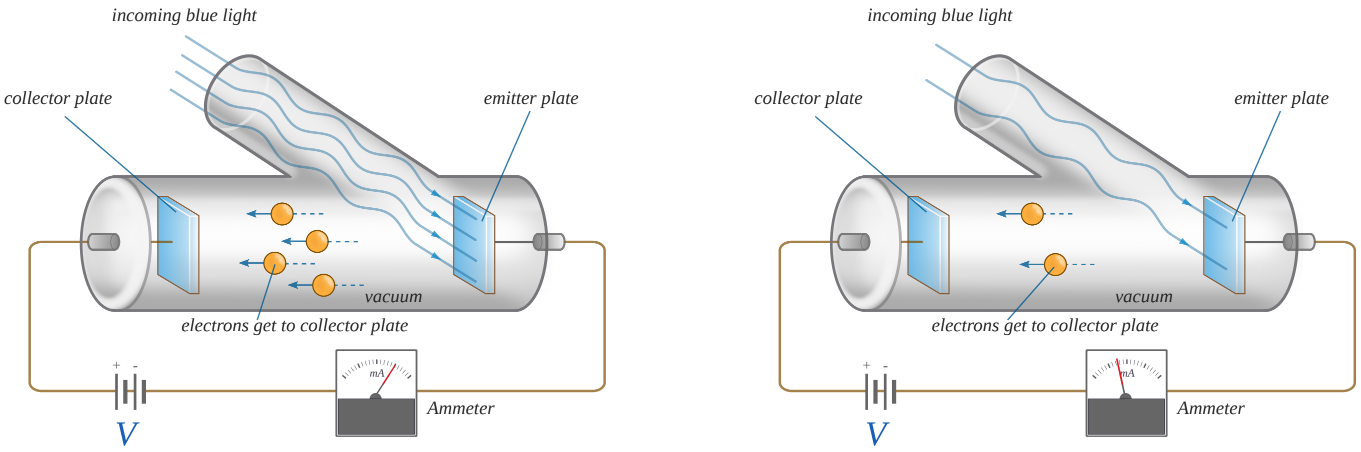

Figure 11.3.2: Lenard's photoelectric experiment. (left) High light intensity increase photocurrent (number of collected photoelectrons). (right) Low light intensity has reduced photocurrent. However, the kinetic energy of the ejected electrons is independent of incident light intensity. (CC BY-NC; Ümit Kaya via LibreTexts)

Lenard discovered that there was a well defined minimum voltage that stopped any electrons getting through (V_{stop}). To Lenard's surprise, he found that V_{stop} did not depend at all on the intensity of the light! Doubling the light intensity doubled the *number* of electrons emitted, but did not affect the *kinetic energies* of the emitted electrons. The more powerful oscillating field ejected more electrons, but the maximum individual energy of the ejected electrons was the same as for the weaker field (Figure 1.3.2).

Millikan's Experimental Results (Wavelength Dependence)

The American experimental physicist Robert Millikan followed up on Lenard's experiments and using a powerful arc lamp, he was able to generate sufficient light intensity to separate out the colors and check the photoelectric effect using light of different colors. He found that the maximum energy of the ejected electrons *did* depend on the color - the shorter wavelength, higher frequency light eject photoelectrons with greater kinetic energy (Figures 1.3.3).

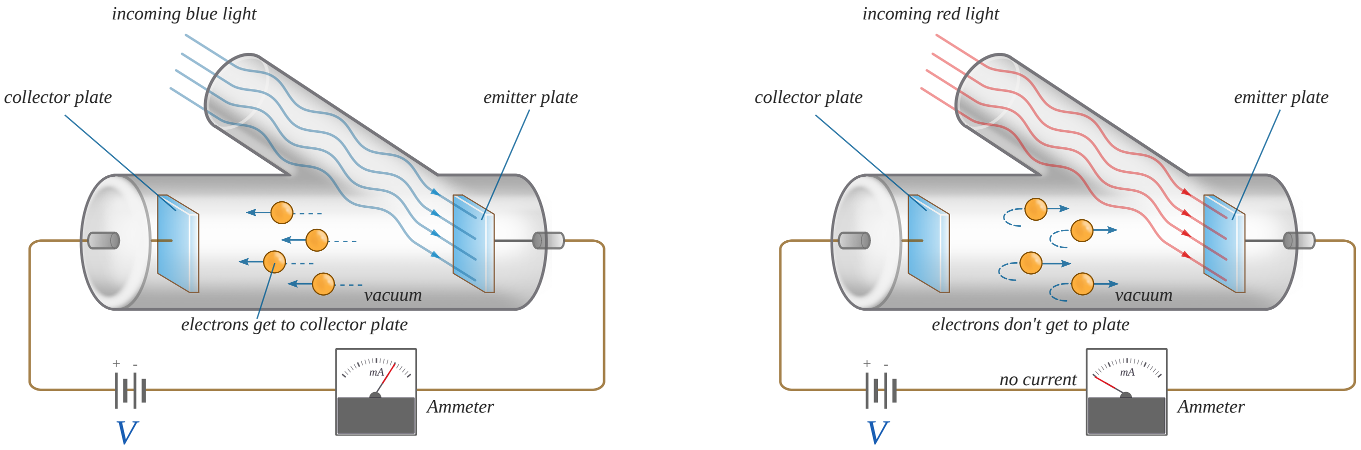

Figure 1.3.3 : Millikan's photoelectric experiment. (left) Incident high-energy blue light. The battery represents the potential Lenard used to charge the collector plate negatively, which would actually be a variable voltage source. Since the electrons ejected by the blue light are getting to the collector plate, the potential supplied by the battery is less than V_{stop}, for blue light. (right) Indicent low-energy red light. Since the electrons ejected by the red light are not getting to the collector plate, the potential supplied by the battery exceeds V_{stop} for red light. (CC BY-NC; Ümit Kaya via LibreTexts)

As shown in Figure 1.3.4 , just the opposite behavior from classical is observed from Lenard's and Millikan's experiments. The intensity affects the number of electrons, and the frequency affects the kinetic energy of the emitted electrons. From these sketches, we see that

- the kinetic energy of the electrons is linearly proportional to the frequency of the incident radiation above a threshold value of ν_0 (no current is observed below ν_0), and the kinetic energy is independent of the intensity of the radiation, and
- the number of electrons (i.e. the electric current) is proportional to the intensity and independent of the frequency of the incident radiation above the threshold value of ν_0 (i.e., no current is observed below ν_0).

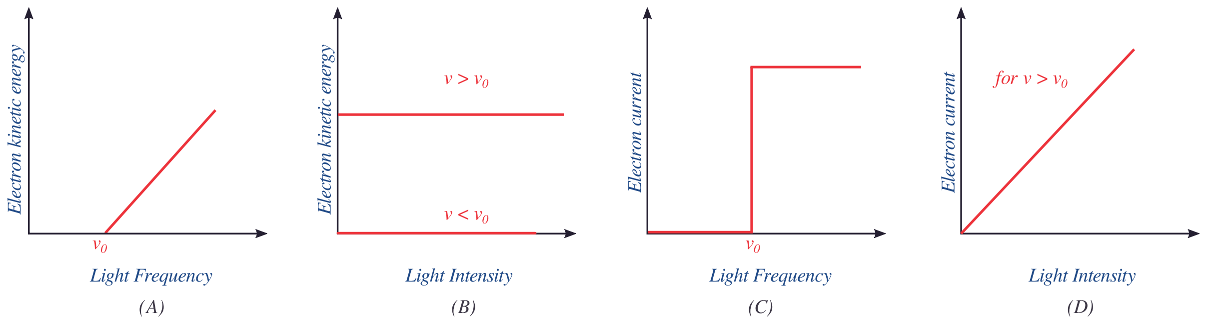

Figure 1.3.4 : Schematic drawings showing the characteristics of the photoelectric effect from Lenard's and Millikan's experiments. (A) The kinetic energy of any single emitted electron increases linearly with frequency above some threshold value (B) The electron kinetic energy is independent of the light intensity above the threshold frequency and zero below. (C) The number of electrons emitted per second (i.e. the electric current) is independent of light frequency above the threshhold frequency and zero below. (D) The number of electrons increases linearly with the light intensity. (CC BY-NC; Ümit Kaya via LibreTexts)

Classical Theory does not Describe Experiment

Classical theory predicts that energy carried by light is proportional to its amplitude independent of its frequency, and this fails to correctly explain the observed wavelength dependence in Lenard's and Millikan's observations.

As with most of the experimental results we discuss in this text, the behavior described above is a simplification of the true experimental results observed in the laboratory. A more complex description involves a greater introduction of more complex physics and instrumentation, which will be ignored for now.

Einstein's Quantum Picture

In 1905 Einstein gave a very simple interpretation of Lenard's results and borrowed Planck's hypothesis about the quantized energy from his blackbody research and assumed that the incoming radiation should be thought of as quanta of energy $h\nu$, with ν the frequency. In photoemission, one such quantum is absorbed by one electron. If the electron is some distance into the material of the cathode, some energy will be lost as it moves towards the surface. There will always be some electrostatic cost as the electron leaves the surface, which is the workfunction, Φ. The most energetic electrons emitted will be those very close to the surface, and they will leave the cathode with kinetic energy

$$KE = h\nu - \Phi \tag{11.3.1}$$

On cranking up the negative voltage on the collector plate until the current just stops, that is, to V_{stop}, the highest kinetic energy electrons (KE_e) must have had energy eV_{stop} upon leaving the cathode. Thus,

$$eV_{stop} = h\nu - \Phi \tag{11.3.2}$$

Thus, Einstein's theory makes a very definite quantitative prediction: if the frequency of the incident light is varied, and V_{stop} plotted as a function of frequency, the slope of the line should be $\frac{h}{e}$ (Figure $11.3.4A$). It is also clear that there is a minimum light frequency for a given metal ν_o, that for which the quantum of energy is equal to Φ (Equation 11.3.1). Light below that frequency, no matter how bright, will not eject electrons.

> *According to both Planck and Einstein, the energy of light is proportional to its frequency rather than its amplitude, there will be a minimum frequency ν_0 needed to eject an electron with no residual energy.*

Since every photon of sufficient energy excites only one electron, increasing the light's intensity (i.e. the number of photons/sec) only increases the *number* of released electrons and not their kinetic energy. In addition, no time is necessary for the atom to be heated to a critical temperature and therefore the release of the electron is nearly instantaneous upon absorption of the light. Finally, because the photons must be above a certain energy to satisfy the workfunction, a threshold frequency exists below which no photoelectrons are observed. This frequency is measured in units of Hertz (1/second) in honor of the discoverer of the photoelectric effect.

Einstein's Equation 11.3.1 explains the properties of the photoelectric effect quantitatively. A strange implication of this experiment is that light can behave as a kind of massless "particle" now known as a *photon* whose energy $E = h\nu$ can be transferred to an actual particle (an electron), imparting kinetic energy to it, just as in an elastic collision between to massive particles such as billiard balls.

> Robert Millikan initially did not accept Einstein's theory, which he saw as an attack on the wave theory of light, and worked for ten years until 1916, on the photoelectric effect. He even devised techniques for scraping clean the metal surfaces inside the vacuum tube. For all his efforts he found disappointing results: he confirmed Einstein's theory after ten years. In what he writes in his paper, Millikan is still desperately struggling to avoid this conclusion. However, by the time of his Nobel Prize acceptance speech, he has changed his mind rather drastically!

Einstein's simple explanation (Equation 11.3.1) completely accounted for the observed phenomena in Lenard's and Millikan's experiments (Figure 1.3.4) and began an investigation into the field we now call *quantum mechanics*. This new field seeks to provide a quantum explanation for classical mechanics and create a more unified theory of physics and thermodynamics. The study of the photoelectric effect has also lead to the creation of new field of photoelectron spectroscopy. Einstein's theory of the photoelectron presented a completely different way to measure Planck's constant than from black-body radiation.

The Workfunction (Φ)

The **workfunction** is an intrinsic property of the metal. While the workfunctions and ionization energies appear as similar concepts, they are independent. The workfunction of a metal is the minimum amount of energy (E) necessary to remove an electron from the surface of the bulk (*solid*) metal (sometimes referred to as **binding energy**).

$$\mathrm{M(s)} + \Phi \rightarrow \mathrm{M^+(s)} + \mathrm{e^-} \,(\text{free with no kinetic energy})$$

The workfunction is qualitatively similar to ionization energy (IE), which is the amount of energy required to remove an electron from an atom or molecule in the *gaseous* state.

$$\mathrm{M(g)} + \mathrm{IE} \rightarrow \mathrm{M^+(g)} + \mathrm{e^-} \,(\text{free with no kinetic energy})$$

However, these two energies differ in magnitude (Table 1.3.1). For instance, copper has a workfunction of about 4.7 eV, but has a higher ionization energy of 7.7 eV. Generally, the ionization energies for metals are greater than the corresponding workfunctions (i.e., the electrons are less tightly bound in bulk metal).

Table 1.3.1 : Workfunctions and Ionization Energies of Select Elements

Element	Workfunction Φ (eV)	Ionization Energy (eV)
Lithium (Li)	2.93	5.39
Beryllium (Be)	4.98	9.32
Boron (B)	4.45	8.298
Carbon (C)	5.0	11.26
Sodium (Na)	2.36	5.13
Aluminum (Al)	4.20	5.98
Silicon (Si)	4.85	8.15
Potassium (K)	2.3	4.34
Iron (Fe)	4.67	7.87
Cobalt (Co)	4.89	7.88
Copper (Cu)	4.7	7.7

Element	Workfunction Φ (eV)	Ionization Energy (eV)
Gallium (Ga)	4.32	5.99
Germanium (Ge)	5.0	7.89
Arsenic (As)	3.75	9.81
Selenium (Se)	5.9	9.75
Silver (Ag)	4.72	7.57
Tin (Sn)	4.42	7.34
Cesium (Cs)	1.95	3.89
Gold (Au)	5.17	9.22
Mercury (Hg)$_{\text{liquid}}$	4.47	10.43
Bismuth (Bi)	4.34	7.29

✓ Example 1.3.1 : Calcium

a. What is the energy in joules and electron volts of a photon of 420-nm violet light?
b. What is the maximum kinetic energy of electrons ejected from calcium by 420-nm violet light, given that the workfunction for calcium metal is 2.71 eV?

Strategy

To solve part (a), note that the energy of a photon is given by $E = h\nu$. For part (b), once the energy of the photon is calculated, it is a straightforward application of Equation 11.3.1 to find the ejected electron's maximum kinetic energy, since Φ is given.

Solution for (a)

Photon energy is given by

$$E = h\nu$$

Since we are given the wavelength rather than the frequency, we solve the familiar relationship $c = \nu\lambda$ for the frequency, yielding

$$\nu = \frac{c}{\lambda}$$

Combining these two equations gives the useful relationship

$$E = \frac{hc}{\lambda}$$

Now substituting known values yields

$$\begin{aligned} E &= \frac{(6.63 \times 10^{-34}\ J \cdot s)(3.00 \times 10^{8} m/s)}{420 \times 10^{-9}\ m} \\ &= 4.74 \times 10^{-19}\ J \end{aligned}$$

Converting to eV, the energy of the photon is

$$\begin{aligned} E &= (4.74 \times 10^{-19}\ J)\left(\frac{1\ eV}{1.6 \times 10^{-19}\ J}\right) \\ &= 2.96\ eV. \end{aligned}$$

Solution for (b)

Finding the kinetic energy of the ejected electron is now a simple application of Equation 11.3.1. Substituting the photon energy and binding energy yields

$$\begin{aligned} KE_e &= h\nu - \Phi \\ &= 2.96\ eV - 2.71\ eV \\ &= 0.246\ eV. \end{aligned}$$

Discussion

The energy of this 420-nm photon of violet light is a tiny fraction of a joule, and so it is no wonder that a single photon would be difficult for us to sense directly—humans are more attuned to energies on the order of joules. But looking at the energy in electron volts, we can see that this photon has enough energy to affect atoms and molecules. A DNA molecule can be broken with about 1 eV of energy, for example, and typical atomic and molecular energies are on the order of eV, so that the UV photon in this example could have biological effects.

The ejected electron (called a photoelectron) has a rather low energy, and it would not travel far, except in a vacuum. The electron would be stopped by a retarding potential of 0.26 eV. In fact, if the photon wavelength were longer and its energy less than 2.71 eV, then the formula would give a negative kinetic energy, an impossibility. This simply means that the 420-nm photons with their 2.96-eV energy are not much above the frequency threshold. You can show for yourself that the threshold wavelength is 459 nm (blue light). This means that if calcium metal is used in a light meter, the meter will be insensitive to wavelengths longer than those of blue light. Such a light meter would be insensitive to red light, for example.

? Exercise 1.3.1 : Silver

What is the longest-wavelength electromagnetic radiation that can eject a photoelectron from silver? Is this in the visible range?

Answer

Given that the workfunction is 4.72 eV from Table 1.3.1 , then only photons with wavelengths lower than 263 nm will induce photoelectrons (calculated via $E = h\nu$). This is ultraviolet and not in the visible range.

? Exercise 1.3.2

Why is the workfunction of an element generally lower than the ionization energy of that element?

Answer

The workfunction of a metal refers to the minimum energy required to extract an electron from the surface of a (**bulk**) metal by the absorption a photon of light. The workfunction will vary from metal to metal. In contrast, ionization energy is the energy needed to detach electrons from **atoms** and also varies with each particular atom, with the valence electrons require less energy to extract than core electrons (i.e., from lower shells) that are more closely bound to the nuclei. The electrons in the metal lattice there less bound (i.e., free to move within the metal) and removing one of these electrons is much easier than removing an electron from an atom because the metallic bonds of the bulk metal reduces their binding energy. As we will show in subsequent chapters, the more delocalized a particle is, the lower its energy.

Summary

Although Hertz discovered the photoelectron in 1887, it was not until 1905 that a theory was proposed that explained the effect completely. The theory was proposed by Einstein and it made the claim that electromagnetic radiation had to be thought of as a series of particles, called photons, which collide with the electrons on the surface and emit them. This theory ran contrary to the belief that electromagnetic radiation was a wave and thus it was not recognized as correct until 1916 when Robert Millikan experimentally confirmed the theory

The photoelectric effect is the process in which electromagnetic radiation ejects electrons from a material. Einstein proposed photons to be quanta of electromagnetic radiation having energy $E = h\nu$ is the frequency of the radiation. All electromagnetic radiation is composed of photons. As Einstein explained, all characteristics of the photoelectric effect are due to the interaction of individual photons with individual electrons. The maximum kinetic energy KE_e of ejected electrons (photoelectrons) is given by $KE_e = h\nu - \Phi$, where $h\nu$ is the photon energy and Φ is the workfunction (or binding energy) of the electron to the particular material.

Conceptual Questions

1. Is visible light the only type of electromagnetic radiation that can cause the photoelectric effect?
2. Which aspects of the photoelectric effect cannot be explained without photons? Which can be explained without photons? Are the latter inconsistent with the existence of photons?
3. Is the photoelectric effect a direct consequence of the wave character of electromagnetic radiation or of the particle character of electromagnetic radiation? Explain briefly.
4. Insulators (nonmetals) have a higher Φ than metals, and it is more difficult for photons to eject electrons from insulators. Discuss how this relates to the free charges in metals that make them good conductors.
5. If you pick up and shake a piece of metal that has electrons in it free to move as a current, no electrons fall out. Yet if you heat the metal, electrons can be boiled off. Explain both of these facts as they relate to the amount and distribution of energy involved with shaking the object as compared with heating it.

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11.4: Bohr's Theory of the Hydrogen Emission Spectrum

Overview

- To introduce the concept of absorption and emission line spectra and describe the Balmer equation to describe the visible lines of atomic hydrogen.
- Describe Rydberg's theory for the hydrogen spectra.
- Interpret the hydrogen spectrum in terms of the energy states of electrons.

The first person to realize that white light was made up of the colors of the rainbow was Isaac Newton, who in 1666 passed sunlight through a narrow slit, then a prism, to project the colored spectrum on to a wall. This effect had been noticed previously, of course, not least in the sky, but previous attempts to explain it, by Descartes and others, had suggested that the white light became colored when it was refracted, the color depending on the angle of refraction. Newton clarified the situation by using a second prism to reconstitute the white light, making much more plausible the idea that the white light was composed of the separate colors. He then took a monochromatic component from the spectrum generated by one prism and passed it through a second prism, establishing that no further colors were generated. That is, light of a single color did not change color on refraction. He concluded that white light was made up of all the colors of the rainbow, and that on passing through a prism, these different colors were refracted through slightly different angles, thus separating them into the observed spectrum.

Atomic Line Spectrum

The spectrum of *hydrogen*, which turned out to be crucial in providing the first insight into atomic structure over half a century later, was first observed by Anders Angstrom in Uppsala, Sweden, in 1853. His communication was translated into English in 1855. Angstrom, the son of a country minister, was a reserved person, not interested in the social life that centered around the court. Consequently, it was many years before his achievements were recognized, at home or abroad (most of his results were published in Swedish).

Most of what is known about atomic (and molecular) structure and mechanics has been deduced from spectroscopy. Figure 1.4.1 shows two different types of spectra. A continuous spectrum can be produced by an incandescent solid or gas at high pressure (blackbody radiation, for example, is a continuum). An emission spectrum can be produced by a gas at low pressure excited by heat or by collisions with electrons. An absorption spectrum results when light from a continuous source passes through a cooler gas, consisting of a series of dark lines characteristic of the composition of the gas.

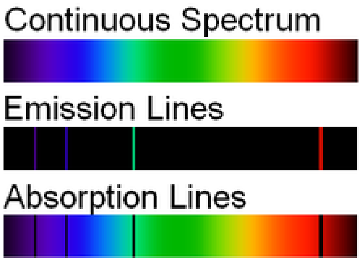


Figure 11.4.1 : Continuous spectrum and two types of line spectra. from Wikipedia.

In 1802, William Wollaston in England had discovered (perhaps by using a thinner slit or a better prism) that in fact the solar spectrum itself had tiny gaps - there were many thin dark lines in the rainbow of colors. These were investigated much more systematically by Joseph von Fraunhofer, beginning in 1814. He increased the dispersion by using more than one prism. He found an "almost countless number" of lines. He labeled the strongest dark lines A, B, C, D, etc. Frauenhofer between 1814 and 1823 discovered nearly 600 dark lines in the solar spectrum viewed at high resolution and designated the principal features with the letters A through K, and weaker lines with other letters (Table 11.4.1). Modern observations of sunlight can detect many thousands of lines. It is now understood that these lines are caused by absorption by the outer layers of the Sun.

Table 11.4.1 : Major Fraunhofer lines, and the elements they are associated with

Designation	Element	Wavelength (nm)
y	O_2	898.765

Designation	Element	Wavelength (nm)
Z	O_2	822.696
A	O_2	759.370
B	O_2	686.719
C	H	656.281
a	O_2	627.661
D_1	Na	589.592
D_2	Na	588.995
D_3 or d	He	587.5618

Fraunhofer Absorption Lines

The Fraunhofer lines are typical spectral absorption lines. These dark lines are produced whenever a cold gas is between a broad spectrum photon source and the detector. In this case, a decrease in the intensity of light in the frequency of the incident photon is seen as the photons are absorbed, then re-emitted in random directions, which are mostly in directions different from the original one. This results in an *absorption line*, since the narrow frequency band of light initially traveling toward the detector, has been turned into heat or re-emitted in other directions.

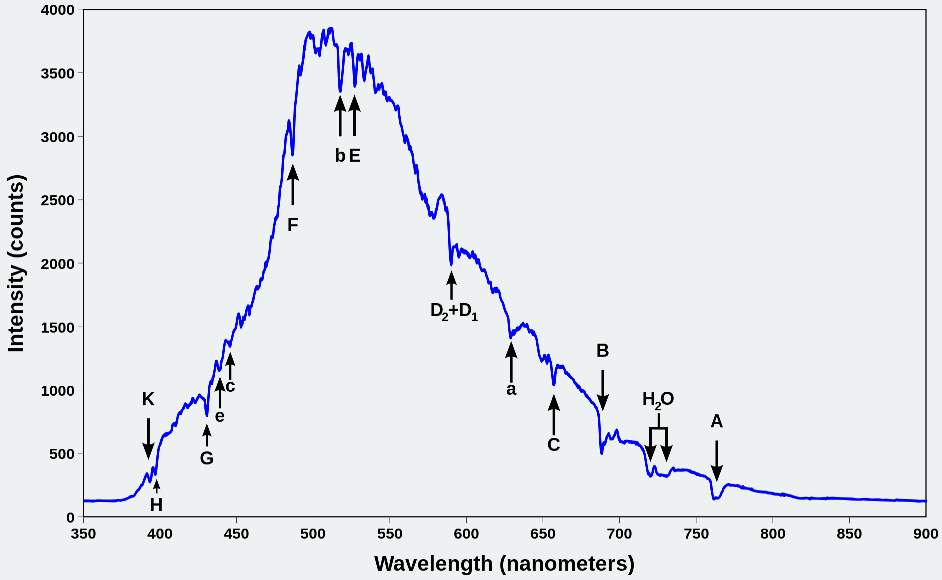


Figure 11.4.2: Spectrum of blue sky. Dips are present at the Fraunhofer line wavelengths. from Wikipedia.

By contrast, if the detector sees photons emitted directly from a glowing gas, then the detector often sees photons emitted in a narrow frequency range by quantum emission processes in atoms in the hot gas, resulting in an *emission line*. In the Sun, Fraunhofer lines are seen from gas in the outer regions of the Sun, which are too cold to directly produce emission lines of the elements they represent.

Gases heated to incandescence were found by Bunsen, Kirkhoff and others to emit light with a series of sharp wavelengths. The emitted light analyzed by a spectrometer (or even a simple prism) appears as a multitude of narrow bands of color. These so called *line spectra* are characteristic of the atomic composition of the gas. The line spectra of several elements are shown in Figure 11.4.3.

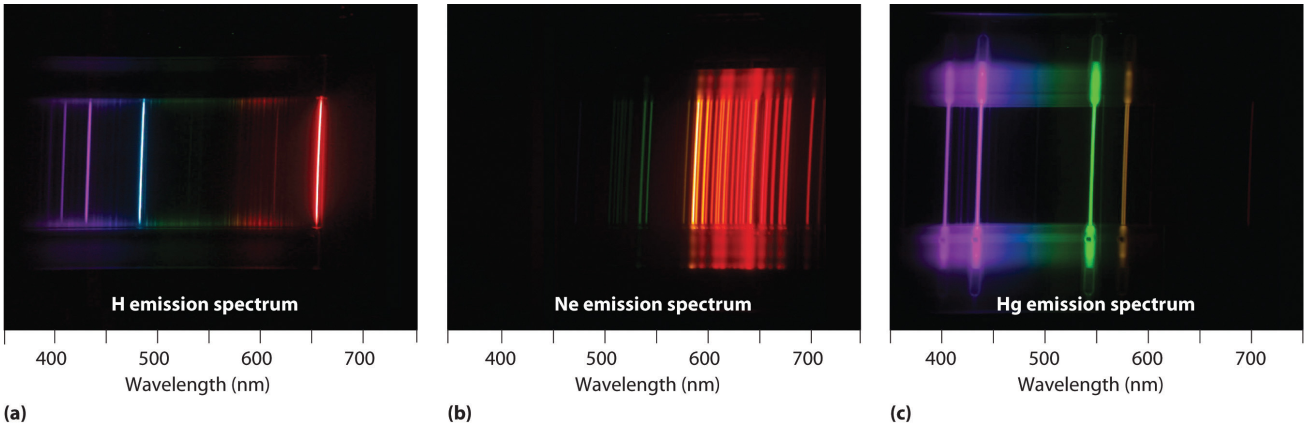


Figure 11.4.3: The Emission Spectra of Elements Compared with Hydrogen. These images show (a) hydrogen gas, which is atomized to hydrogen atoms in the discharge tube; (b) helium; and (c) mercury. The strongest lines in the hydrogen spectrum are in the far UV Lyman series starting at 124 nm and below. The strongest lines in the mercury spectrum are at 181 and 254 nm, also in the UV. These are not shown.

The Balmer Series of Hydrogen

Obviously, if any pattern could be discerned in the spectral lines for a specifc atom (in contract to the mixture that Fraunhofer lines represent), that might be a clue as to the internal structure of the atom. One might be able to build a model. A great deal of effort went into analyzing the spectral data from the 1860's on. The big breakthrough was made by Johann Balmer, a math and Latin teacher at a girls' school in Basel, Switzerland. Balmer had done no physics before, and made his great discovery when he was almost sixty.

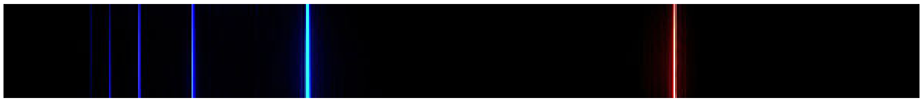


Figure 11.4.4: The visible hydrogen emission spectrum lines in the Balmer series. The red line at the right is the H_α *line and the two leftmost lines are considered to be ultraviolet as they have wavelengths less than 400 nm. from Wikipedia.*

Balmer decided that the most likely atom to show simple spectral patterns was the lightest atom, hydrogen. Angstrom had measured the four visible spectral lines to have wavelengths 656.21, 486.07, 434.01 and 410.12 nm (Figure 11.4.4). Balmer concentrated on just these four numbers, and found they were represented by the formula:

$$\lambda = b\left(\frac{n_2^2}{n_2^2-4}\right) \tag{11.4.1}$$

where

- b = 364.56 nm and
- $n_2 = 3, 4, 5, 6.$

The first four wavelengths of Equation 11.4.1 (with n_2=3,4,5,6) were in excellent agreement with the experimental lines from Angstrom (Table 11.4.2). Balmer predicted that other lines exist in the infrared that correspond to *n* = 7, 8, etc., and in fact some of them had already been observed, unbeknown to Balmer.

Table 11.4.2 : The Balmer Series of Hydrogen Emission Lines

n_2	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
λ	*656*	*486*	*434*	*410*	397	389	383	380
color	*red*	*teal*	*blue*	*indigo*	violet	not visible	not visible	not visible

The n_2 integer in the Balmer series extends theoretically to infinity and the series resents a monotonically increasing energy (and frequency) of the absorption lines with increasing n_2 values. Moreover, the energy difference between successive lines decreased as n_2 increases (Figure 1.4.4). This behavior converges to a highest possible energy as Example 11.4.1 demonstrates. If the lines are plot according to their λ on a linear scale, you will get the appearance of the spectrum in Figure 11.4.4; these lines are called the **Balmer series**.

Balmer's general formula (Equation 11.4.1) can be rewritten in terms of the inverse wavelength typically called the *wavenumber* ($\tilde{\nu}$).

$$\tilde{\nu} = \frac{1}{\lambda} = R_H \left(\frac{1}{4} - \frac{1}{n_2^2} \right) \tag{11.4.2}$$

where

- $n_2 = 3, 4, 5, 6$ and
- R_H is the Rydberg constant (discussed below) and is equal to 109,737 cm^{-1}.

He further conjectured that the 4 could be replaced by 9, 16, 25, … and this also turned out to be true - but these lines, further into the infrared, were not detected until the early twentieth century, along with the ultraviolet lines.

Wavenumbers

The relation between wavelength and frequency for electromagnetic radiation is

$$\lambda \nu = c \tag{11.4.3}$$

In the SI system of units the wavelength, \lambda\) is measured in meters (m) and since wavelengths are usually very small one often uses the nanometer (nm) which is $10^{-9}\ m$. The frequency (ν) in the SI system is measured in reciprocal seconds 1/s − which is called a Hertz (after the discover of the photoelectron effect) and is represented by Hz.

It is common to use the reciprocal of the wavelength in centimeters as a measure of the frequency of radiation. This unit is called a wavenumber and is represented by ($\tilde{\nu}$) and is defined by

$$\tilde{\nu} = \frac{1}{\lambda} = \frac{\nu}{c} \tag{11.4.4}$$

Wavenumbers is a convenient unit in spectroscopy because it is directly proportional to energy.

$$E = \frac{hc}{\lambda} \tag{11.4.5}$$

$$E = hc \times \frac{1}{\lambda} \tag{11.4.6}$$

$$E = hc\tilde{\nu} \tag{11.4.7}$$

$$E \propto \tilde{\nu} \tag{11.4.8}$$

Balmer Series

Calculate the longest and shortest wavelengths (in nm) emitted in the Balmer series of the hydrogen atom emission spectrum.

Solution

From the behavior of the Balmer equation (Equation 11.4.1 and Table 11.4.2), the value of n_2 that gives the longest (i.e., greatest) wavelength (λ) is the smallest value possible of n_2, which is $n_2 = 3$ for this series. This results in

$$\lambda_{longest} = (364.56\ nm) \left(\frac{9}{9-4} \right) \tag{11.4.9}$$

$$\lambda_{longest} = (364.56\ nm)(1.8) = 656.2\ nm \tag{11.4.10}$$

This is also known as the H_α line of atomic hydrogen and is bight red (Figure 1.4.4).

For the shortest wavelength, it should be recognized that the shortest wavelength (greatest energy) is obtained at the limit of greatest (n_2\):

$$\lambda_{shortest} = \lim_{n_2 \to \infty} (364.56\ nm) \left(\frac{n_2^2}{n_2^2 - 4} \right) \tag{11.4.11}$$

This can be solved via L'Hôpital's Rule, or alternatively the limit can be expressed via the equally useful energy expression (Equation 1.4.2) and simply solved:

$$\tilde{\nu}_{greatest} = \lim_{n_2 \to \infty} R_H \left(\frac{1}{4} - \frac{1}{n_2^2} \right) \tag{11.4.12}$$

$$\tilde{\nu}_{greatest} = \lim_{n_2 \to \infty} R_H \left(\frac{1}{4} \right) = 27,434\ cm^{-1} \tag{11.4.13}$$

Since $\frac{1}{\tilde{\nu}} = \lambda$ in units of cm, this converts to 364 nm as the shortest wavelength possible for the Balmer series.

The Balmer series is particularly useful in astronomy because the Balmer lines appear in numerous stellar objects due to the abundance of hydrogen in the universe, and therefore are commonly seen and relatively strong compared to lines from other elements.

The Generalized Rydberg Equation

In an amazing demonstration of mathematical insight, in 1885 Balmer came up with a simple formula for predicting the wavelength of any of the lines in atomic Hydrogen in what we now know as the Balmer series (Equation 11.4.2). Three years later, Rydberg generalized this so that it was possible to determine the wavelengths of any of the lines in the hydrogen emission spectrum. Rydberg suggested that all atomic spectra formed families with this pattern (he was unaware of Balmer's work). It turns out that there are families of spectra following Rydberg's pattern, notably in the alkali metals, sodium, potassium, etc., but not with the precision the hydrogen atom lines fit the Balmer formula, and low values of n_2 predicted wavelengths that deviate considerably.

Rydberg's general equation is as follows:

$$\tilde{\nu} = \frac{1}{\lambda} = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \tag{11.4.14}$$

where

- R_H is the *Rydberg* constant and is equal to 109,737 cm^{-1}.
- n_1 and n_2 are integers (whole numbers) with $n_2 > n_1$.

For the Balmer lines, $n_1 = 2$ and n_2 can be any whole number between 3 and infinity. The various combinations of numbers that can be substituted into this formula allow the calculation the wavelength of any of the lines in the hydrogen emission spectrum; there is close agreement between the wavelengths generated by this formula and those observed in a real spectrum.

Other Series

The results given by Balmer and Rydberg for the spectrum in the visible region of the electromagnetic radiation start with $n_2 = 3$, and $n_1^2 = 2$. Is there a different series with the following formula (e.g., $n_1 = 1$?

$$\frac{1}{\lambda} = R_{\text{H}} \left(\frac{1}{1^2} - \frac{1}{n^2} \right) \tag{11.4.15}$$

The values for n_2 and wavenumber $\tilde{\nu}$ for this series would be:

Table 11.4.3: The Lyman Series of Hydrogen Emission Lines ($n_1 = 1$)

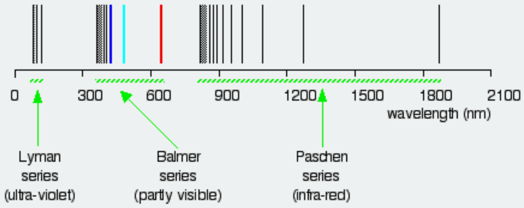
n_2	**2**	**3**	**4**	**5**	**...**
λ (nm)	121	102	97	94	...
$\tilde{\nu}$ (cm-1)	82,2291	97,530	102,864	105,332	...

These lines are in the UV region, and they are not visible, but they are detected by instruments; these lines form a **Lyman series**. The existences of the Lyman series and Balmer's series suggest the existence of more series. For example, the series with $n_2^2 = 3$ and n_1^2 = 4, 5, 6, 7, ... is called **Pashen series**.

Note

The spectral lines are grouped into series according to n_1 values. Lines are named sequentially starting from the longest wavelength/lowest frequency of the series, using Greek letters within each series. For example, the ($n_1 = 1/n_2 = 2$) line is called "Lyman-alpha" (Ly-α), while the ($n_1 = 3/n_2 = 7$) line is called "Paschen-delta" (Pa-δ). The first six series have specific names:

- Lyman series with $n_1 = 1$
- Balmer series with $n_1 = 2$
- Paschen series (or Bohr series) with $n_1 = 3$
- Brackett series with $n_1 = 4$
- Pfund series with $n_1 = 5$
- Humphreys series with $n_1 = 6$



The spectral series of hydrogen based of the Rydberg Equation (on a logarithmic scale).

Example 11.4.2: The Lyman Series

The so-called Lyman series of lines in the emission spectrum of hydrogen corresponds to transitions from various excited states to the *n* = 1 orbit. Calculate the wavelength of the lowest-energy line in the Lyman series to three significant figures. In what region of the electromagnetic spectrum does it occur?

Given: lowest-energy orbit in the Lyman series

Asked for: wavelength of the lowest-energy Lyman line and corresponding region of the spectrum

Strategy:

A. Substitute the appropriate values into Equation 1.5.1 (the Rydberg equation) and solve for λ.
B. Locate the region of the electromagnetic spectrum corresponding to the calculated wavelength.

Solution:

We can use the Rydberg equation to calculate the wavelength:

$$\frac{1}{\lambda} = \Re \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \tag{11.4.16}$$

A For the Lyman series, $n_1 = 1$.

$$\frac{1}{\lambda} = \Re \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) = 1.097 \times m^{-1} \left(\frac{1}{1} - \frac{1}{4} \right) = 8.228 \times 10^6 \ m^{-1} \tag{11.4.17}$$

Spectroscopists often talk about energy and frequency as equivalent. The cm^{-1} unit is particularly convenient. The infrared range is roughly 200 - 5,000 cm^{-1}, the visible from 11,000 to 25.000 cm^{-1} and the UV between 25,000 and 100,000 cm^{-1}. The units of cm^{-1} are called wavenumbers, although people often verbalize it as inverse centimeters. We can convert the answer in part A to cm^{-1}.

$$\tilde{\nu} = \frac{1}{\lambda} = 8.228 \times 10^{6}\ \cancel{m^{-1}} \left(\frac{\cancel{m}}{100\ cm} \right) = 82,280\ cm^{-1} \tag{11.4.18}$$

and

$$\lambda = 1.215 \times 10^{-7}\ m = 122\ nm \tag{11.4.19}$$

This emission line is called Lyman alpha. It is the strongest atomic emission line from the sun and drives the chemistry of the upper atmosphere of all the planets producing ions by stripping electrons from atoms and molecules. It is completely absorbed by oxygen in the upper stratosphere, dissociating O_2 molecules to O atoms which react with other O_2 molecules to form stratospheric ozone

B This wavelength is in the ultraviolet region of the spectrum.

? Exercise 11.4.2: The Pfund Series

The Pfund series of lines in the emission spectrum of hydrogen corresponds to transitions from higher excited states to the \(*n_1* = 5\) orbit. Calculate the wavelength of the *second* line in the Pfund series to three significant figures. In which region of the spectrum does it lie?

Answer: 4.65 × 10^3 nm; infrared

The above discussion presents only a phenomenological description of hydrogen emission lines and fails to provide a probe of the nature of the atom itself. Clearly a continuum model based on classical mechanics is not applicable.

Contributors and Attributions

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11.5: de Broglie's Postulate

Learning Objectives

- To introduce the wave-particle duality of light extends to matter
- To describe how matter (e.g., electrons and protons) can exhibit wavelike properties, e.g., interference and diffraction patterns
- To use algebra to find the de Broglie wavelength or momentum of a particle when either one of these quantities is given

The next real advance in understanding the atom came from an unlikely quarter - a student prince in Paris. Prince Louis de Broglie was a member of an illustrious family, prominent in politics and the military since the 1600's. Louis began his university studies with history, but his elder brother Maurice studied x-rays in his own laboratory, and Louis became interested in physics. After World War I, de Broglie focused his attention on Einstein's two major achievements, the theory of special relativity and the quantization of light waves. He wondered if there could be some connection between them. Perhaps the quantum of radiation really should be thought of as a particle. De Broglie suggested that if waves (photons) could behave as particles, as demonstrated by the photoelectric effect, then the converse, namely that particles could behave as waves, should be true. He associated a wavelength λ to a particle with momentum p using Planck's constant as the constant of proportionality:

$$\lambda=\frac{h}{p} \tag{11.5.1}$$

which is called the **de Broglie wavelength**. The fact that particles can behave as waves but also as particles, depending on which experiment you perform on them, is known as the **wave-particle duality**.

Deriving the de Broglie Wavelength

From the discussion of the photoelectric effect, we have the first part of the particle-wave duality, namely, that electromagnetic waves can behave like particles. These particles are known as *photons*, and they move at the speed of light. Any particle that moves at or near the speed of light has kinetic energy given by Einstein's special theory of relatively. In general, a particle of mass m and momentum p has an energy

$$E=\sqrt{p^2c^2+m^2c^4} \tag{11.5.2}$$

Note that if $p=0$, this reduces to the famous rest-energy expression $E=mc^2$. However, photons are massless particles (technically rest-massless) that always have a finite momentum p. In this case, Equation 11.5.2becomes

$$E=pc.$$

From Planck's hypothesis, one quantum of electromagnetic radiation has energy $E=h\nu$. Thus, equating these two expressions for the kinetic energy of a photon, we have

$$h\nu=\frac{hc}{\lambda}=pc \tag{11.5.3}$$

Solving for the wavelength λ gives Equation 11.5.1:

$$\lambda=\frac{h}{p}=\frac{h}{mv}$$

where v is the velocity of the particle. Hence, de Broglie argued that if particles can behave as waves, then a relationship like this, which pertains particularly to waves, should also apply to particles.

Equation 11.5.1 allows us to associate a wavelength λ to a particle with momentum p. As the momentum increases, the wavelength decreases. In both cases, this means the energy becomes larger. i.e., short wavelengths *and* high momenta correspond to high energies.

> *It is a common feature of quantum mechanics that particles and waves with short wavelengths correspond to high energies and vice versa.*

Having decided that the photon might well be a particle with a rest mass, even if very small, it dawned on de Broglie that in other respects it might not be too different from other particles, especially the very light electron. In particular, maybe the electron also had an associated wave. The obvious objection was that if the electron was wavelike, why had no diffraction or interference effects been observed? But there was an answer. If de Broglie's relation between momentum and wavelength also held for electrons, the wavelength was sufficiently short that these effects would be easy to miss. As de Broglie himself pointed out, the wave nature of light is not very evident in everyday life. As the next section will demonstrate, the validity of de Broglie’s proposal was confirmed by electron diffraction experiments of G.P. Thomson in 1926 and of C. Davisson and L. H. Germer in 1927. In these experiments it was found that electrons were scattered from atoms in a crystal and that these scattered electrons produced an interference pattern. These diffraction patterns are characteristic of wave-like behavior and are exhibited by both electrons (i.e., matter) and electromagnetic radiation (i.e., light).

Example 1.6.1 : Electron Waves

Calculate the de Broglie wavelength for an electron with a kinetic energy of 1000 eV.

Solution

To calculate the de Broglie wavelength (Equation 11.5.1), the momentum of the particle must be established and requires knowledge of both the mass and velocity of the particle. The mass of an electron is $9.109383 \times 10^{-28}\ g$ and the velocity is obtained from the given kinetic energy of 1000 eV:

$$\begin{aligned} KE &= \frac{mv^2}{2} \\ &= \frac{p^2}{2m} = 1000\ eV \end{aligned}$$

Solve for momentum

$$p = \sqrt{2mKE}$$

convert to SI units

$$p = \sqrt{(1000\ \ e\cancel{V}) \left(\frac{1.6 \times 10^{-19}\ J}{1\ \ e\cancel{V}} \right) (2)(9.109383 \times 10^{-31}\ kg)}$$

expanding definition of joule into base SI units and cancel

$$\begin{aligned} p &= \sqrt{(3.1 \times 10^{-16}\ kg \cdot m^2/s^2)(9.109383 \times 10^{-31}\ kg)} \\ &= \sqrt{2.9 \times 10^{-40}\ kg^2\ m^2/s^2} \\ &= 1.7 \times 10^{-23} kg \cdot m/s \end{aligned}$$

Now substitute the momentum into the equation for de Broglie's wavelength (Equation 11.5.1) with Planck's constant ($h = 6.626069 \times 10^{-34}\ J \cdot s$). After expanding units in Plank's constant

$$\begin{aligned} \lambda &= \frac{h}{p} \\ &= \frac{6.626069 \times 10^{-34}\ kg \cdot m^2/s}{1.7 \times 10^{-23} kg \cdot m/s} \\ &= 3.87 \times 10^{-11}\ m \\ &= 38.9\ pm \end{aligned}$$

? Exercise 1.6.1 : Baseball Waves

Calculate the de Broglie wavelength for a fast ball thrown at 100 miles per hour and weighing 4 ounces. Comment on whether the wave properties of baseballs could be experimentally observed.

Answer

Following the unit conversions below, a 4 oz baseball has a mass of 0.11 kg. The velocity of a fast ball thrown at 100 miles per hour in m/s is 44.7 m/s.

$$m = (4 \ \cancel{oz}) \left(\dfrac{0.0283 \ kg}{1 \ \cancel{oz}} \right) = 0.11 kg$$

$$v = \left(\dfrac{100 \ \cancel{mi}}{\cancel{hr}} \right) \left(\dfrac{1609.34 \ m}{\cancel{mi}} \right) \left(\dfrac{1 \ \cancel{hr}}{3600 \ s} \right) = 44.7 \ m/s$$

The de Broglie wavelength of this fast ball is:

$$\lambda = \dfrac{h}{mv} = \dfrac{6.626069 \times 10^{-34} \ kg \cdot m^2/s}{(0.11 \ kg)(44.7 \ m/s)} = 1.3 \times 10^{-34} m$$

? Exercise 1.6.2 : Electrons vs. Protons

If an electron and a proton have the same velocity, which would have the longer de Broglie wavelength?

a. The electron
b. The proton
c. They would have the same wavelength

Answer

Equation 11.5.1shows that the de Broglie wavelength of a particle's matter wave is inversely proportional to its momentum (mass times velocity). Therefore the smaller mass particle will have a smaller momentum and longer wavelength. The electron is the lightest and will have the longest wavelength.

This was the prince's Ph.D. thesis, presented in 1924. His thesis advisor was somewhat taken aback, and was not sure if this was sound work. He asked de Broglie for an extra copy of the thesis, which he sent to Einstein. Einstein wrote shortly afterwards: *"I believe it is a first feeble ray of light on this worst of our physics enigmas*" and the prince got his Ph.D.

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11.6: The Heisenberg Uncertainty Principle

Learning Objectives

- To understand that sometime you cannot know everything about a quantum system as demonstrated by the Heisenberg uncertainly principle.

In classical physics, studying the behavior of a physical system is often a simple task due to the fact that several physical qualities can be measured simultaneously. However, this possibility is absent in the quantum world. In 1927 the German physicist Werner Heisenberg described such limitations as the Heisenberg Uncertainty Principle, or simply the Uncertainty Principle, stating that it is not possible to measure both the momentum and position of a particle simultaneously.

The Heisenberg Uncertainty Principle is a fundamental theory in quantum mechanics that defines why a scientist cannot measure multiple quantum variables simultaneously. Until the dawn of quantum mechanics, it was held as a fact that all variables of an object could be known to exact precision simultaneously for a given moment. Newtonian physics placed no limits on how better procedures and techniques could reduce measurement uncertainty so that it was conceivable that with proper care and accuracy all information could be defined. Heisenberg made the bold proposition that there is a lower limit to this precision making our knowledge of a particle inherently uncertain.

Probability

Matter and photons are waves, implying they are spread out over some distance. What is the position of a particle, such as an electron? Is it at the center of the wave? The answer lies in how you measure the position of an electron. Experiments show that you will find the electron at some definite location, unlike a wave. But if you set up exactly the same situation and measure it again, you will find the electron in a different location, often far outside any experimental uncertainty in your measurement. Repeated measurements will display a statistical distribution of locations that appears wavelike (Figure 1.9.1).

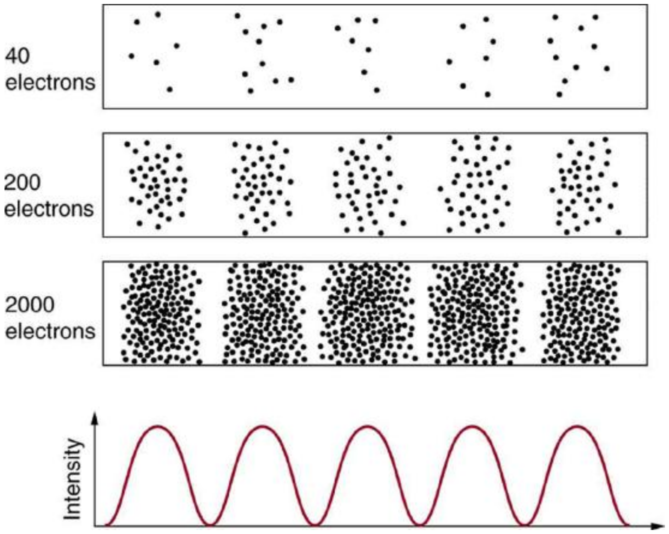

Figure 1.9.1 : The building up of the diffraction pattern of electrons scattered from a crystal surface. Each electron arrives at a definite location, which cannot be precisely predicted. The overall distribution shown at the bottom can be predicted as the diffraction of waves having the de Broglie wavelength of the electrons (CC BY 4.0; OpenStax).

After de Broglie proposed the wave nature of matter, many physicists, including Schrödinger and Heisenberg, explored the consequences. The idea quickly emerged that, *because of its wave character, a particle's trajectory and destination cannot be precisely predicted for each particle individually*. However, each particle goes to a definite place (Figure 1.9.1). After compiling enough data, you get a distribution related to the particle's wavelength and diffraction pattern. There is a certain *probability* of finding the particle at a given location, and the overall pattern is called a **probability distribution**. Those who developed quantum mechanics devised equations that predicted the probability distribution in various circumstances.

It is somewhat disquieting to think that you cannot predict exactly where an individual particle will go, or even follow it to its destination. Let us explore what happens if we try to follow a particle. Consider the double-slit patterns obtained for electrons and photons in Figure 1.9.2 . The interferrence patterns build up statistically as individual particles fall on the detector. This can be observed for photons or electrons—for now, let us concentrate on electrons. You might imagine that the electrons are interfering with one another as any waves do. To test this, you can lower the intensity until there is never more than one electron between the slits and the screen. The same interference pattern builds up!

This implies that a particle's probability distribution spans both slits, and the particles actually interfere with themselves. Does this also mean that the electron goes through both slits? An electron is a basic unit of matter that is not divisible. But it is a fair question, and so we should look to see if the electron traverses one slit or the other, or both. One possibility is to have coils around the slits that detect charges moving through them. What is observed is that an electron always goes through one slit or the other; it does not split to go through both.

But there is a catch. If you determine that the electron went through one of the slits, you no longer get a double slit pattern—instead, you get single slit interference. There is no escape by using another method of determining which slit the electron went through. Knowing the particle went through one slit forces a single-slit pattern. If you do not observe which slit the electron goes through, you obtain a double-slit pattern. How does knowing which slit the electron passed through change the pattern? The answer is fundamentally important—*measurement affects the system being observed*. Information can be lost, and in some cases it is impossible to measure two physical quantities simultaneously to exact precision. For example, you can measure the position of a moving electron by scattering light or other electrons from it. Those probes have momentum themselves, and by scattering from the electron, they change its momentum *in a manner that loses information*. There is a limit to absolute knowledge, even in principle.

Heisenberg's Uncertainty Principle

It is mathematically possible to express the uncertainty that, Heisenberg concluded, always exists if one attempts to measure the momentum and position of particles. First, we must define the variable "x" as the position of the particle, and define "p" as the momentum of the particle. The momentum of a photon of light is known to simply be its frequency, expressed by the ratio h/λ, where h represents Planck's constant and λ represents the wavelength of the photon. The position of a photon of light is simply its wavelength (λ). To represent finite change in quantities, the Greek uppercase letter delta, or Δ, is placed in front of the quantity. Therefore,

$$\Delta p = \frac{h}{\lambda} \tag{11.6.1}$$

$$\Delta x = \lambda \tag{11.6.2}$$

By substituting Δx for λ into Equation 11.6.1, we derive

$$\Delta p = \frac{h}{\Delta x} \tag{11.6.3}$$

or,

$$\underbrace{\Delta p \Delta x = h}_{\text{early form of uncertainty principle}} \tag{11.6.4}$$

A Common Trend in Quantum Systems

Equation 11.6.4 can be derived by assuming the particle of interest is behaving as a particle, and not as a wave. Simply let $\Delta p = mv$, and $\Delta x = h/(mv)$ (from De Broglie's expression for the wavelength of a particle). Substituting in Δp for mv in the second equation leads to Equation 11.6.4.

Equation 11.6.4 was further refined by Heisenberg and his colleague Niels Bohr, and was eventually rewritten as

$$\Delta p_x \Delta x \geq \frac{h}{4\pi} = \frac{\hbar}{2} \tag{11.6.5}$$

with $\hbar = \frac{h}{2\pi} = 1.0545718 \times 10^{-34}\ m^2 \cdot kg/s$.

Equation 11.6.5 reveals that the more accurately a particle's position is known (the smaller Δx is), the less accurately the momentum of the particle in the x direction (Δp_x) is known. Mathematically, this occurs because the smaller Δx becomes, the larger Δp_x must become in order to satisfy the inequality. However, the more accurately momentum is known the less accurately position is known (Figure 1.9.2).

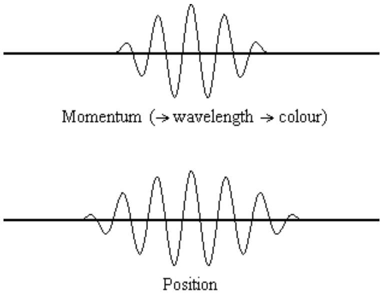

Figure 1.9.2 : The animation shows the relevant spreads in the uncertainty for position and momentum of light/photons (light wave's corresponding photon particle). From the result of de Broglie, we know that for a particle with known momentum, p will have a precise value for its de Broglie wavelength can be determined (and hence a specific color of the light).

What is the Proper Definition of Uncertainty?

Equation 11.6.5 relates the uncertainty of momentum and position. An immediate questions that arise is if Δx represents the full range of possible x values or if it is half (e.g., $\langle x \rangle \pm \Delta x$). Δx is the standard deviation and is a statistic measure of the spread of x values. The use of half the possible range is more accurate estimate of Δx. As we will demonstrated later, once we construct a wavefunction to describe the system, then both x and Δx can be explicitly derived. However for now, Equation 11.6.5 will work.

For example: If a problem argues a particle is trapped in a box of length, L, then the uncertainly of it position is $\pm L/2$. So the value of Δx used in Equation 11.6.5 should be $L/2$, not L.

Example 1.9.1

An electron is confined to the size of a magnesium atom with a 150 pm radius. What is the **minimum** uncertainty in its velocity?

Solution

The uncertainty principle (Equation 11.6.5):

$$\Delta p \Delta x \geq \frac{\hbar}{2}$$

can be written

$$\Delta p \geq \frac{\hbar}{2 \Delta x}$$

and substituting $\Delta p = m \Delta v$ since the mass is not uncertain.

$$\Delta v \geq \frac{\hbar}{2\ m\ \Delta x}$$

the relevant parameters are

- mass of electron $m = m_e = 9.109383 \times 10^{-31}\ kg$
- uncertainty in position: $\Delta x = 150 \times 10^{-12} m$

$$\begin{aligned} \Delta v &\geq \frac{1.0545718 \times 10^{-34}\ \cancel{kg} m^{\cancel{2}}/s}{(2)\ (9.109383 \times 10^{-31}\ \ \cancel{kg})\ (150 \times 10^{-12}\ \ \cancel{m})} \\ &= 3.9 \times 10^5\ m/s \end{aligned}$$

Exercise 1.9.1

What is the maximum uncertainty of velocity the electron described in Example 1.9.1 ?

Answer

Infinity. There is no limit in the maximum uncertainty, just the minimum uncertainty.

Understanding the Uncertainty Principle through Wave Packets and the Slit Experiment

It is hard for most people to accept the uncertainty principle, because in classical physics the velocity and position of an object can be calculated with certainty and accuracy. However, in quantum mechanics, the wave-particle duality of electrons does not allow us to accurately calculate both the momentum and position because the wave is not in one exact location but is spread out over space. A "wave packet" can be used to demonstrate how either the momentum or position of a particle can be precisely calculated, but not both of them simultaneously. An accumulation of waves of varying wavelengths can be combined to create an average wavelength through an interference pattern: this average wavelength is called the "wave packet". The more waves that are combined in the "wave packet", the more precise the position of the particle becomes and the more uncertain the momentum becomes because more wavelengths of varying momenta are added. Conversely, if we want a more precise momentum, we would add less wavelengths to the "wave packet" and then the position would become more uncertain. Therefore, there is no way to find both the position and momentum of a particle simultaneously.

Several scientists have debated the Uncertainty Principle, including Einstein. Einstein created a slit experiment to try and disprove the Uncertainty Principle. He had light passing through a slit, which causes an uncertainty of momentum because the light behaves like a particle and a wave as it passes through the slit. Therefore, the momentum is unknown, but the initial position of the particle is known. Here is a video that demonstrates particles of light passing through a slit and as the slit becomes smaller, the final possible array of directions of the particles becomes wider. As the position of the particle becomes more precise when the slit is narrowed, the direction, or therefore the momentum, of the particle becomes less known as seen by a wider horizontal distribution of the light.

✓ Example 1.9.2

The speed of a 1.0 g projectile is known to within $10^{-6}\ m/s$.

a. Calculate the *minimum* uncertainty in its position.
b. What is the *maximum* uncertainty of its position?

Solution a

From Equation 11.6.5, the $\Delta p_x = m\Delta v_x$ with $m = 1.0\ g$. Solving for Δx to get

$$
\begin{aligned}
\Delta x &= \frac{\hbar}{2m\Delta v} \\
&= \frac{1.0545718 \times 10^{-34}\ m^2 \cdot kg/s}{(2)(0.001\ kg)(10^{-6}\ m/s)} \\
&= 5.3 \times 10^{-26}\ m
\end{aligned}
$$

This negligible for all intents and purpose as expected for any macroscopic object.

Solution b

Unlimited (or the size of the universe). The Heisenberg uncertainty principles does not quantify the maximum uncertainty.

? Exercise 1.9.2

Estimate the minimum uncertainty in the speed of an electron confined to a hydrogen atom within a diameter of $1 \times 10^{-10} m$?

Answer

We need to quantify the uncertainty of the electron in position. We can estimate that as $\pm 5 \times 10^{-10} m$. Hence, substituting the relavant numbers into Equation 11.6.5and solving for Δv we get

$$\Delta v = 1.15 \times 10^{6}\ km/s$$

Notice that the uncertainty is significantly greater for the electron in a hydrogen atom than in the magnesium atom (Example 1.9.1) as expected since the magnesium atom is appreciably bigger.

Heisenberg's Uncertainty Principle not only helped shape the new school of thought known today as quantum mechanics, but it also helped discredit older theories. Most importantly, the Heisenberg Uncertainty Principle made it obvious that there was a fundamental error in the Bohr model of the atom. Since the position and momentum of a particle cannot be known simultaneously, Bohr's theory that the electron traveled in a circular path of a fixed radius orbiting the nucleus was obsolete. Furthermore, Heisenberg's uncertainty principle, when combined with other revolutionary theories in quantum mechanics, helped shape wave mechanics and the current scientific understanding of the atom.

Humor: Heisenberg and the Police

- Heisenberg get pulled over for speeding by the police. The officer asks him "Do you know how fast you were going?"
- Heisenberg replies, "No, but we know exactly where we are!"
- The officer looks at him confused and says "you were going 108 miles per hour!"
- Heisenberg throws his arms up and cries, "Great! Now we're lost!"

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11.7: The Schrödinger Wave Equation

Beginning in the early 20th century, physicists began to acknowledge that matter--much like electromagnetic radiation--possessed wave-like behaviors. While electromagnetic radiation were well understood to obey Maxwell's Equations, matter obeyed no known equations.

Introduction

In 1926, the Austrian physicist Erwin Schrödinger formulated what came to be known as the (time-dependent) Schrödinger Equation:

$$i\hbar\frac{\partial}{\partial t}\Psi(x,t)=\frac{-\hbar}{2m}\nabla^2\Psi(x,t)+V(x)\Psi(x,t) \tag{11.7.1}$$

Equation 11.7.1 effectively describes matter as a wave that fluctuates with both displacement and time. Since the imaginary portion of the equation dictates its time dependence, it is sufficed to say that for most purposes it can be treated as time-independent. The result is seen in Equation 11.7.2:

$$\frac{-\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2}+V(x)\psi(x)=E\psi(x) \tag{11.7.2}$$

Although this time-independent Schrödinger Equation can be useful to describe a matter wave in free space, we are most interested in waves when confined to a small region, such as an electron confined in a small region around the nucleus of an atom. Several different models have been developed that provide a means by which to study a matter-wave when confined to a small region: the particle in a box (infinite well), finite well, and the Hydrogen atom. We will discuss each of these in order to develop a greater understanding for how a wave behaves when it is in a bound state.

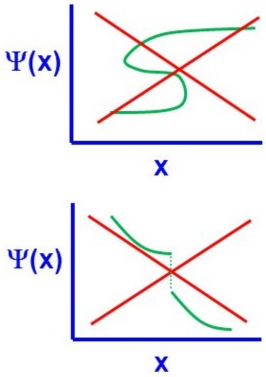

Figure 11.7.1 : Two unacceptable wavefunctions. (left) This is not a single-valued function and (right) this is a non-continuous function

There are four general aspects that are applicable to an acceptable wavefunction

1. An acceptable wavefunction will be the solution of the Schrödinger equation (either Equations 11.7.1 or 11.7.2).
2. An acceptable wavefunction must be normalizable so will approaches zero as position approaches infinity.
3. An acceptable wavefunction must be a continuous function of position.
4. An acceptable wavefunction will have a continuous slope (Figure 11.7.1).

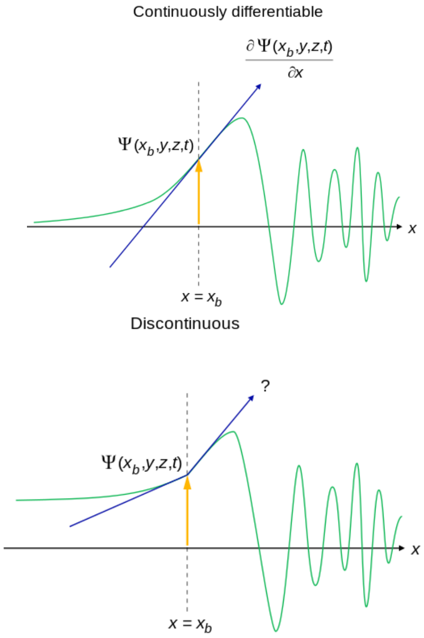

Figure 11.7.2 : Wavefunction continuity in space

Interpretation of the Wavefunction

Since wavefunctions can in general be complex functions, the physical significance cannot be found from the function itself because the $\sqrt{-1}$ is not a property of the physical world. Rather, the physical significance is found in the product of the wavefunction and its complex conjugate, i.e. the absolute square of the wavefunction, which also is called the square of the modulus.

$$\psi^*(r,t)\psi(r,t) = |\psi(r,t)|^2 \tag{11.7.3}$$

where r is a vector (x, y, z) specifying a point in three-dimensional space. The square is used, rather than the modulus itself, just like the intensity of a light wave depends on the square of the electric field. At one time it was thought that for an electron described by the wavefunction $\psi(r)$, the quantity $e\psi^*(ri)\psi(r_i)d\tau$ was the amount of charge to be found in the volume $d\tau$ located at r_i. However, Max Born found this interpretation to be inconsistent with the results of experiments.

The Born interpretation, which generally is accepted today, is that $\psi^*(r_i)\psi(r_i)\,d\tau$ is the probability that the electron is in the volume dτ located at r_i. The Born interpretation therefore calls the wavefunction the probability amplitude, the absolute square of the wavefunction is called the probability density, and the probability density times a volume element in three-dimensional space ($d\tau$) is the probability. The idea that we can understand the world of atoms and molecules only in terms of probabilities is disturbing to some, who are seeking more satisfying descriptions through ongoing research.

Normalization of the Wavefunction

A probability is a real number between 0 and 1. An outcome of a measurement which has a probability 0 is an impossible outcome, whereas an outcome which has a probability 1 is a certain outcome. The probability of a measurement of x yielding a result between $-\infty$ and $+\infty$ is

$$P_{x\in-\infty:\infty}(t) = \int_{-\infty}^{\infty} |\psi(x,t)|^2 dx. \tag{11.7.4}$$

However, a measurement of x *must* yield a value between $-\infty$ and $+\infty$, since the particle has to be located somewhere. It follows that $P_{x\in-\infty:\infty}(t) = 1$, or

$$\int_{-\infty}^{\infty} |\psi(x,t)|^2 dx = 1, \tag{11.7.5}$$

which is generally known as the *normalization condition* for the wavefunction.

Example 11.7.1: Normalizing a Gaussian wavefunction

Normalize the wavefunction of a Gaussian wave packet, centered on $x = x_o$, and of characteristic width σ: i.e.,

$$\psi(x) = \psi_0 \mathrm{e}^{-(x-x_0)^2/(4\sigma^2)}. \tag{11.7.6}$$

Solution

To determine the normalization constant ψ_0, we simply substitute Equation 11.7.6 into Equation 11.7.5, to obtain

$$|\psi_0|^2 \int_{-\infty}^{\infty} \mathrm{e}^{-(x-x_0)^2/(2\sigma^2)} dx = 1. \tag{11.7.7}$$

Changing the variable of integration to $y = (x - x_0)/(\sqrt{2}\sigma)$, we get

$$|\psi_0|^2 \sqrt{2}\sigma \int_{-\infty}^{\infty} \mathrm{e}^{-y^2} dy = 1. \tag{11.7.8}$$

However,

$$\int_{-\infty}^{\infty} \mathrm{e}^{-y^2} dy = \sqrt{\pi}, \tag{11.7.9}$$

which implies that

$$|\psi_0|^2 = \frac{1}{(2\pi\sigma^2)^{1/2}}. \tag{11.7.10}$$

Hence, a general **normalized** Gaussian wavefunction takes the form

$$\psi(x) = \frac{e^{\mathrm{i}\phi}}{(2\pi\sigma^2)^{1/4}} e^{-(x-x_0)^2/(4\sigma^2)} \tag{11.7.11}$$

where ϕ is an arbitrary real phase-angle.

Contributors and Attributions

- David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski ("Quantum States of Atoms and Molecules")

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11.8: Particle in a One-Dimensional Box

A particle in a 1-dimensional box is a fundamental quantum mechanical approximation describing the translational motion of a single particle confined inside an infinitely deep well from which it *cannot* escape.

Introduction

The particle in a box problem is a common application of a quantum mechanical model to a simplified system consisting of a particle moving horizontally within an infinitely deep well from which it cannot escape. The solutions to the problem give possible values of E and ψ that the particle can possess. E represents allowed energy values and $\psi(x)$ is a wavefunction, which when squared gives us the probability of locating the particle at a certain position within the box at a given energy level.

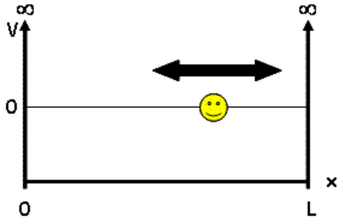
recipe for Quantum Mechanics

To solve the problem for a particle in a 1-dimensional box, we must follow our *Big, Big recipe for Quantum Mechanics*:

1. Define the Potential Energy, V
2. Solve the Schrödinger Equation
3. Solve for the wavefunctions
4. Solve for the allowed energies

Step 1: Define the Potential Energy V

The potential energy is *0 inside the box* (V=0 for 0<x<L) and *goes to infinity at the walls of the box* (V=∞ for x<0 or x>L). We assume the walls have infinite potential energy to ensure that the particle has zero probability of being at the walls or outside the box. Doing so significantly simplifies our later mathematical calculations as we employ these **boundary conditions** when solving the Schrödinger Equation.



Step 2: Solve the Schrödinger Equation

The time-independent Schrödinger equation for a particle of mass m moving in one direction with energy E is

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2}+V(x)\psi(x)=E\psi(x) \tag{11.8.1}$$

with

- $\hbar$ is the reduced Planck constant where $\hbar=\frac{h}{2\pi}$
- m is the mass of the particle
- $\psi(x)$ is the stationary time-independent wavefunction
- $V(x)$ is the potential energy as a function of position
- E is the energy, a real number

This equation can be modified for a particle of mass m free to move parallel to the x-axis with zero potential energy (V = 0 everywhere) resulting in the quantum mechanical description of free motion in one dimension:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2}=E\psi(x) \tag{11.8.2}$$

This equation has been well studied and gives a general solution of:

$$\psi(x)=A\sin(kx)+B\cos(kx) \tag{11.8.3}$$

where A, B, and k are constants.

Step 3: Define the Wavefunction

The solution to the Schrödinger equation we found above is the general solution for a 1-dimensional system. We now need to apply our **boundary conditions** to find the solution to our particular system. According to our boundary conditions, the probability of finding the particle at $x = 0$ or $x = L$ is zero. When $x = 0$, then $\sin(0) = 0$ and $\cos(0) = 1$; therefore, B *must equal 0* to fulfill this boundary condition giving:

$$\psi(x) = A\sin(kx) \tag{11.8.4}$$

We can now solve for our constants (A and k) systematically to define the wavefunction.

Solving for k
Differentiate the wavefunction with respect to x:

$$\frac{d\psi}{dx} = kA\cos(kx) \tag{11.8.5}$$

Differentiate the wavefunction algain with respect to x:

$$\frac{d^2\psi}{dx^2} = -k^2 A\sin(kx) \tag{11.8.6}$$

Since $\psi(x) = A\sin(kx)$, then

$$\frac{d^2\psi}{dx^2} = -k^2\psi \tag{11.8.7}$$

If we then solve for k by comparing with the Schrödinger equation above, we find:

$$k = \left(\frac{8\pi^2 mE}{h^2}\right)^{1/2} \tag{11.8.8}$$

Now we plug k into our wavefunction (Equation 11.8.4):

$$\psi = A\sin\left(\frac{8\pi^2 mE}{h^2}\right)^{1/2} x \tag{11.8.9}$$

Solving for A
To determine A, we have to apply the boundary conditions again. Recall that the *probability of finding a particle at* $x = 0$ *or* $x = L$ *is zero.*

When x = L:

$$0 = A\sin\left(\frac{8\pi^2 mE}{h^2}\right)^{1/2} L \tag{11.8.10}$$

This is only true when

$$\left(\frac{8\pi^2 mE}{h^2}\right)^{1/2} L = n\pi \tag{11.8.11}$$

where $n = 1, 2, 3, \ldots$

Plugging this back in gives us:

$$\psi = A\sin\frac{n\pi}{L}x \tag{11.8.12}$$

To determine A, recall that the total probability of finding the particle inside the box is 1, meaning there is no probability of it being outside the box. When we find the probability and set it equal to 1, we are *normalizing* the wavefunction.

$$\int_0^L \psi^2 dx = 1 \tag{11.8.13}$$

For our system, the normalization looks like:

$$A^2 \int_0^L \sin^2\left(\frac{n\pi}{L}\right) x\, dx = 1 \tag{11.8.14}$$

Using the solution for this integral from an integral table, we find our normalization constant, A:

$$A = \sqrt{\frac{2}{L}} \tag{11.8.15}$$

Which results in the normalized wavefunctions for a particle in a 1-dimensional box:

$$\psi_n = \sqrt{\frac{2}{L}} \sin \frac{n\pi}{L} x \tag{11.8.16}$$

where $n = 1, 2, 3, \ldots$

Step 4: Determine the Allowed Energies

Solving for the energy of each ψ requires substituting Equation 11.8.16 into Equation 11.8.2 to get the allowed energies for a particle in a box:

$$E_n = \frac{n^2 h^2}{8mL^2} \tag{11.8.17}$$

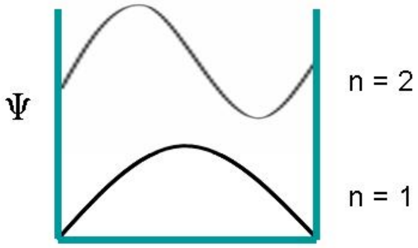
Equation 11.8.17 is a very important result and tells us that:

1. The energy of a particle is quantized.
2. The lowest possible energy of a particle is **NOT** zero. This is called the **zero-point energy** and means the particle can never be at rest because it always has some kinetic energy.

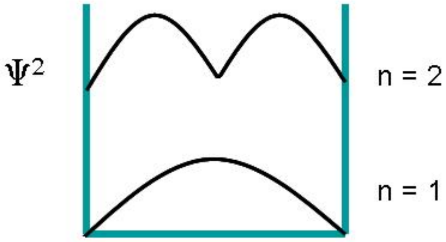
This is also consistent with the Heisenberg Uncertainty Principle: if the particle had zero energy, we would know where it was in both space and time.

What does all this mean?

The wavefunction for a particle in a box at the $n = 1$ and $n = 2$ energy levels look like this:



The probability of finding a particle a certain spot in the box is determined by squaring ψ. The probability distribution for a particle in a box at the $n = 1$ and $n = 2$ energy levels looks like this:



Notice that the number of **nodes** (places where the particle has zero probability of being located) increases with increasing energy n. Also note that as the energy of the particle becomes greater, the quantum mechanical model breaks down as the energy levels get closer together and overlap, forming a continuum. This continuum means the particle is free and can have any energy value. At such high energies, the classical mechanical model is applied as the particle behaves more like a continuous wave. Therefore, the particle in a box problem is an example of Wave-Particle Duality.

✓ Example 11.8.1

What is the ΔE between the $n=4$ and $n=5$ states for an F_2 molecule trapped within in a one-dimension well of length 3.0 cm? At what value of n does the energy of the molecule reach ¼k_BT at 450 K, and what is the separation between this energy level and the one immediately above it?

Solution

Since this is a one-dimensional particle in a box problem, the particle has only kinetic energy (V = 0), so the permitted energies are:

$$E_n = \frac{n^2h^2}{8mL^2}$$

with $n = 1, 2, \ldots$

The energy difference between $n=4$ and $n=5$ is then

$$\Delta E = E_5 - E_4 = \frac{5^2h^2}{8mL^2} - \frac{4^2h^2}{8mL^2}$$

Using Equation 11.8.17 with the mass of F_2 (37.93 amu = $6.3 \times 10^{-26}\ kg$) and the length of the box ($L = 3 \times 3.0 \times 10^{-2}\ \text{m}^2$:

$$\Delta E = \frac{9h^2}{8mL^2} = \frac{9(6.626\times10^{-34}\ \text{kg}\cdot\text{m}^2\cdot\text{s}^{-1})^2}{8(6.30938414\times10^{-26}\ \text{kg})(3.0\times10^{-2}\ \text{m}^2)^2}$$

$$\Delta E = 8.70 \times 10^{-39}\ J$$

The n value for which the energy reaches $\frac{1}{4}k_BT$:

$$\frac{n^2h^2}{8mL^2} = \frac{1}{4}k_BT$$

$$n = 1.79\times10^9$$

The separation between $n+1$ and n:

$$\Delta E = E_{n+1} - E_n = \frac{(n+1)^2h^2 - (n)^2h^2}{8mL^2}$$

$$\Delta E = \frac{(2n+1)h^2}{8mL^2}$$

$$\Delta E = 3.47\times10^{-30}\ J$$

Important Facts to Learn from the Particle in the Box

- The energy of a particle is quantized. This means it can only take on discreet energy values.
- The lowest possible energy for a particle is **NOT** zero (even at 0 K). This means the particle *always* has some kinetic energy.
- The square of the wavefunction is related to the probability of finding the particle in a specific position for a given energy level.
- The probability changes with increasing energy of the particle and depends on the position in the box you are attempting to define the energy for
- In classical physics, the probability of finding the particle is independent of the energy and the same at all points in the box

Helpful Links

- Provides a live quantum mechanical simulation of the particle in a box model and allows you to visualize the solutions to the Schrödinger Equation: www.falstad.com/qm1d/

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1. Chang, Raymond. *Physical Chemistry for the Biosciences*. Sansalito, CA: University Science, 2005.

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11.9: Quantum-Mechanical Tunneling

Tunneling is a quantum mechanical phenomenon when a particle is able to penetrate through a potential energy barrier that is higher in energy than the particle's kinetic energy. This amazing property of microscopic particles play important roles in explaining several physical phenomena including radioactive decay. Additionally, the principle of tunneling leads to the development of Scanning Tunneling Microscope (STM) which had a profound impact on chemical, biological and material science research.

Violating Classical Mechanics

Consider a ball rolling from one valley to another over a hill (Figure $11.9.1$). If the ball has enough energy (E) to overcome the potential energy (V) at the top of the barrier between each valley, then it can roll from one valley to the other. This is the classical picture and is controlled by the simple Law of Conservation of Energy approach taught in beginning physics courses. However, If the ball does not have enough kinetic energy ($E < V$), to overcome the barrier it will never roll from one valley to the other. In contrast, when quantum effects are taken into effect, the ball can "tunnel" through the barrier to the other valley, even if its kinetic energy is less than the potential energy of the barrier to the top of one of the hills.

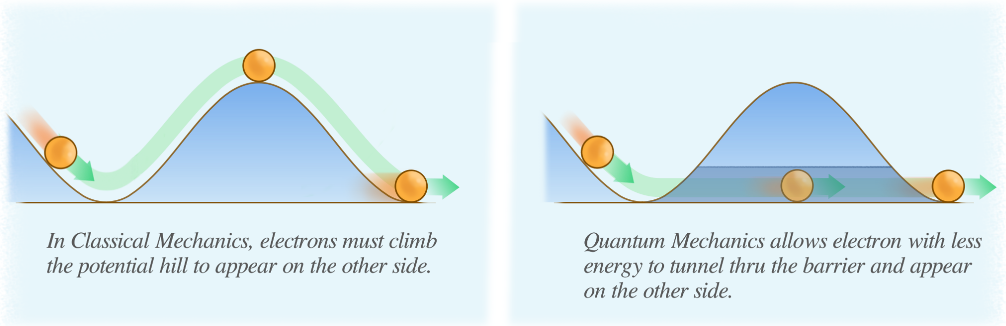

Figure 11.9.1: Contrasting classical (over the barrier) motion vs. quantum (through the barrier) motion. (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

The Heisenberg Uncertainty Principle in Action

The reason for the difference between classical and quantum motion comes from wave-particle nature of matter. One interpretation of this duality involves the Heisenberg uncertainty principle, which defines a limit on how precisely the position and the momentum of a particle can be known at the same time. This implies that there are no solutions with a probability of exactly zero (or one), though a solution may approach infinity if, for example, the calculation for its position was taken as a probability of 1, the other, i.e. its speed, would have to be infinity. Hence, the probability of a given particle's existence on the opposite side of an intervening barrier is non-zero, and such particles will appear on the 'other' (a semantically difficult word in this instance) side with a relative frequency proportional to this probability.

Microscopic particles such as protons, or electrons would behave differently as a consequence of wave-particle duality. Consider a particle with energy E that is confined in a box which has a barrier of height V. Classically, the box will prevent these particles from escaping due to the insufficiency in kinetic energy of these particles to get over the barrier. However, if the thickness of the barrier is thin, the particles have some probability of penetrating through the barrier **without** sufficient energy and appear on the other side of the box (Figure $11.9.2$).

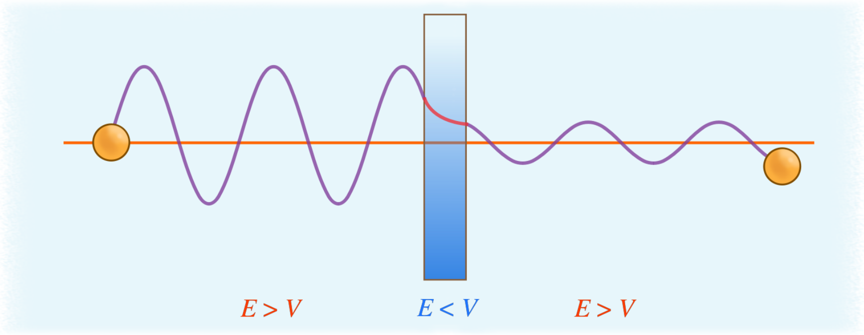

Figure 11.9.2: Quantum tunneling through a barrier. The energy of the tunneled particle is the same but the amplitude is decreased. (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

When it reaches a barrier it cannot overcome, a particle's wave function changes from sinusoidal to exponentially diminishing in form. The solution for the Schrödinger equation in such a medium (Figure $11.9.2$; blue region) is:

$$\psi = Ne^{-\beta x} \tag{11.9.1}$$

where

- N is a normalization constant and
- $\beta = \sqrt{\dfrac{2m(V-E)}{\hbar^2}}$

For a quantum particle to *appreciably* tunnel through a barrier three conditions must be met (Figure $11.9.2$):

1. The height of the barrier must be **finite** and the thickness of the barrier should be **thin**.
2. The potential energy of the barrier exceeds the kinetic energy of the particle ($E < V$).
3. The particle has wave properties because the wavefunction is able to penetrate through the barrier. This suggests that quantum tunneling only apply to microscopic objects such protons or electrons and does not apply to macroscopic objects.

If these conditions are met, there would be some probability of finding the particles on the other side of the barrier. Beginning as a sinusoidal wave, a particle begins tunneling through the barrier and goes into exponential decay until it exits the barrier and gets transmitted out the other side as a final sinusoidal wave with a smaller amplitude. The act of tunneling decreases the wave amplitude due the reflection of the incident wave when it comes into the contact with the barrier but does not affect the wave equation.

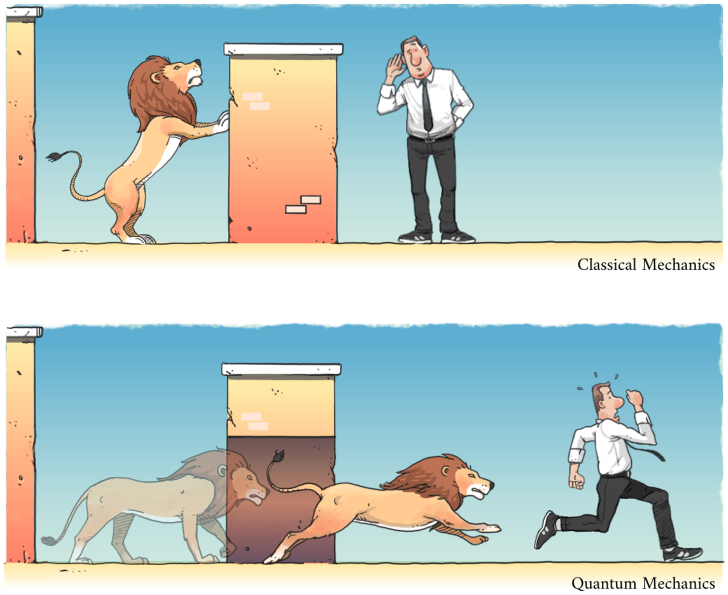

Figure 11.9.3: Quantum tunnelling of alion through a barrier is a quantum effect with no classical analog. (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

The probability, P, of a particle tunneling through the potential energy barrier is derived from the Schrödinger Equation and is described as,

$$P = \exp\left(\frac{-4a\pi}{h}\sqrt{2m(V-E)}\right) \tag{11.9.2}$$

with $E < V$

where

- V is the potential barrier,
- E is the kinetic energy possessed by the particle, and
- a is the thickness of the barrier.
- m is mass of the particle
- h is Planks Constant ($6.6260 \times 10^{-34} m^2 kg/s$)

Therefore, the probability of an object tunneling through a barrier decreases with the object's increasing mass and with the increasing gap between the energy of the object and the energy of the barrier. And although the wave function never quite reaches 0 (as can be determined from the functionality), this explains how tunneling is frequent on nanoscale, but negligible at the macroscopic level. Equation 11.9.2 argues that the probability of tunneling decreases exponentially with the square root of the particles mass (particles with a small mass can effectively tunnel through barriers more easily than those with larger mass) and the thickness of the barrier (a)

✓ Example 11.9.1

An electron having total kinetic energy E of 4.50 eV approaches a rectangular energy barrier with $V = 5.00\,eV$ and $L = 950\,pm$. Classically, the electron cannot pass through the barrier because $E < V$. Calculate probability of tunneling of this electron through the barrier.

Solution

This is a straightforward application of Equation 11.9.2.

$$P = \exp\left(\frac{-4a\pi}{h}\sqrt{2m(V-E)}\right)$$

The electronvolt (eV) is a unit of energy that is equal to approximately $1.6 \times 10^{-19}\ J$, which is the conversion used below.

The mass of an electron is $9.10 \times 10^{-31}\ kg$

$$P = \exp\left[\left(-\frac{(4)(950 \times 10^{-12}\ m)(\pi)}{6.6260 \times 10^{-34} m^2 kg/s}\right)\sqrt{(2)(9.10 \times 10^{-31}\ kg)(5.00 - 4.50\ \ \cancel{eV})(1.60 \times 10^{-19} J/\ \cancel{eV})}\right]$$

$$= \exp^{-6.88} = 1.03 \times 10^{-3}$$

There is a ~0.1% probability of the electrons tunneling though the barrier.

Alpha Decay Radioactivity

Protons and neutrons in a nucleus have kinetic energy, but it is about 8 MeV less than that needed to get out from attractive nuclear potential (Figure $11.9.4$). Hence, they are bound by an average of 8 MeV per nucleon. The slope of the hill outside the bowl is analogous to the repulsive Coulomb potential for a nucleus, such as for an α particle outside a positive nucleus. In α decay, two protons and two neutrons spontaneously break away as a ^{4}He unit. Yet the protons and neutrons do not have enough kinetic energy to classically get over the rim.

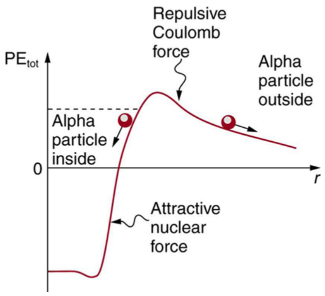

Figure 11.9.4: Nucleons within an atomic nucleus are bound or trapped by the attractive nuclear force, as shown in this simplified potential energy curve. An particle outside the range of the nuclear force feels the repulsive Coulomb force. The α particle inside the nucleus does not have enough kinetic energy to get over the rim, yet it does manage to get out by quantum mechanical tunneling. (CC BY; OpenStax)

The α article tunnels through a region of space it is forbidden to be in, and it comes out of the side of the nucleus. Like an electron making a transition between orbits around an atom, it travels from one point to another without ever having been in between (Figure $11.9.5$). The wave function of a quantum mechanical particle varies smoothly, going from within an atomic nucleus (on one side of a potential energy barrier) to outside the nucleus (on the other side of the potential energy barrier). Inside the barrier, the wave function does not become zero but decreases exponentially, and we do not observe the particle inside the barrier. The probability of finding a particle is related to the square of its wave function, and so there is a small probability of finding the particle outside the barrier, which implies that the particle can tunnel through the barrier.

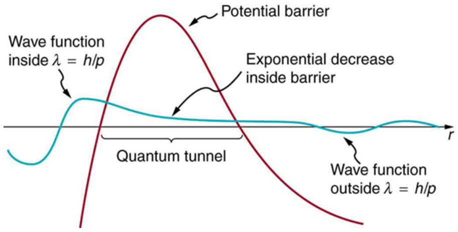

Figure 11.9.5: The wave function representing a quantum mechanical particle must vary smoothly, going from within the nucleus (to the left of the barrier) to outside the nucleus (to the right of the barrier). Inside the barrier, the wave function does not abruptly become zero; rather, it decreases exponentially. Outside the barrier, the wave function is small but finite, and there it smoothly becomes sinusoidal. Owing to the fact that there is a small probability of finding the particle outside the barrier, the particle can tunnel through the barrier. (CC BY; OpenStax)

Scanning Tunneling Microscopy (STM)

A metal tip usually made out of tungsten is placed between a very small distance above a conducting or semiconducting surface. This distance acts as a potential barrier for tunneling. The space between the tip and the surface normally is vacuum. When electrons tunnel from the metal tip to the surface, a current is created and monitored by a computer (Figure $11.9.6$). The current depends on the distance between the tip and the surface, which is controlled by a piezoelectric cylinder. If there is a strong current, the tip will move away from the surface. The increase of the potential barrier will decrease the probability of tunneling and decrease the current. If the current becomes too weak, the tip moves closer to the surface. The potential barrier will be reduced and the current will increase. The variations in the current as the tip moves over the sample are reconstructed by the computer to produce topological image of the scanned surface.

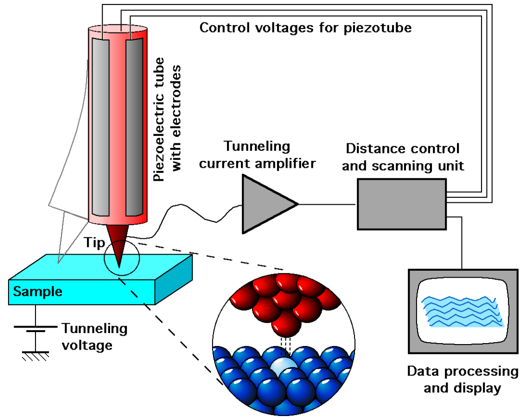

Figure 11.9.6: Schematic diagram of a scanning tunneling microscope. (CC BY-SA 2.0 Austria; Michael Schmid via Wikipedia).

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1. Chang, Raymond. *Physical Chemistry for the Biosciences*. Sansalito, CA: University Science, 2005. Print.
2. Engel, Thomas. Quantum Chemistry and Spectroscopy.Upper Saddle River, NJ. Pearson, 2006. Print.

Contributors and Attributions

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11.10: The Schrödinger Wave Equation for the Hydrogen Atom

The hydrogen atom, consisting of an electron and a proton, is a two-particle system, and the internal motion of two particles around their center of mass is equivalent to the motion of a single particle with a reduced mass. This reduced particle is located at r, where r is the vector specifying the position of the electron relative to the position of the proton. The length of r is the distance between the proton and the electron, and the direction of r and the direction of r is given by the orientation of the vector pointing from the proton to the electron. Since the proton is much more massive than the electron, we will assume throughout this chapter that the reduced mass equals the electron mass and the proton is located at the center of mass.

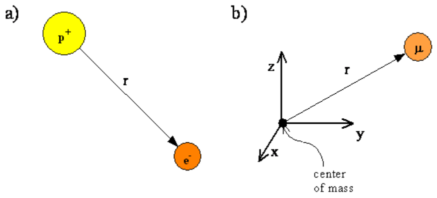


Figure 11.10.1: a) The proton (p^+) and electron (e^-) of the hydrogen atom. b) Equivalent reduced particle with reduced mass μ at distance r from center of mass.

Since the internal motion of any two-particle system can be represented by the motion of a single particle with a reduced mass, the description of the hydrogen atom has much in common with the description of a diatomic molecule discussed previously. The Schrödinger Equation for the hydrogen atom

$$\hat{H}(r,\theta,\varphi)\psi(r,\theta,\varphi)=E\psi(r,\theta,\varphi) \tag{11.10.1}$$

employs the same kinetic energy operator, $\hat{T}$, written in spherical coordinates. For the hydrogen atom, however, the distance, r, between the two particles can vary, unlike the diatomic molecule where the bond length was fixed, and the rigid rotor model was used. The hydrogen atom Hamiltonian also contains a potential energy term, $\hat{V}$, to describe the attraction between the proton and the electron. This term is the Coulomb potential energy,

$$\hat{V}(r)=-\frac{e^2}{4\pi\epsilon_0 r} \tag{11.10.2}$$

where r is the distance between the electron and the proton. The Coulomb potential energy depends inversely on the distance between the electron and the nucleus and does not depend on any angles. Such a potential is called a central potential.

It is convenient to switch from Cartesian coordinates x, y, z to spherical coordinates in terms of a radius r, as well as angles ϕ, which is measured from the positive x axis in the xy plane and may be between 0 and 2π, and θ, which is measured from the positive z axis towards the xy plane and may be between 0 and π.

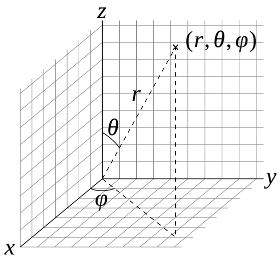


Figure 11.10.2: Spherical Coordinates

The time-indepdent Schrödinger equation (in spherical coordinates) for a electron around a positively charged nucleus is then

$$\left\{-\frac{\hbar^2}{2\mu r^2}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]-\frac{e^2}{4\pi\epsilon_0 r}\right\}\psi(r,\theta,\varphi)=E\psi(r,\theta,\varphi) \tag{11.10.3}$$

Since the angular momentum operator does not involve the radial variable, r, we can separate variables in Equation 11.10.3 by using a **product wavefunction**. We know that the eigenfunctions of the angular momentum operator are the Spherical Harmonic functions (Table M4), $Y(\theta,\varphi)$, so a good choice for a product function is

$$\psi(r,\theta,\varphi)=R(r)Y(\theta,\varphi) \tag{11.10.4}$$

The Spherical Harmonic $Y(\theta,\varphi)$ functions provide information about where the electron is around the proton, and the radial function $R(r)$ describes how far the electron is away from the proton. A solution for both $R(r)$ and $Y(\theta,\varphi)$ with E_n that depends on only one quantum number n, although others are required for the proper description of the wavefunction:

$$E_n=-\frac{m_e e^4}{8\epsilon_0^2 h^2 n^2} \tag{11.10.5}$$

with $n = 1, 2, 3 . . . \infty$

The hydrogen atom wavefunctions, $\psi(r, \theta, \phi)$, are called atomic orbitals. An atomic orbital is a function that describes one electron in an atom. The wavefunction with n = 1, l l = 0 is called the 1s orbital, and an electron that is described by this function is said to be “in” the ls orbital, i.e. have a 1s orbital state. The constraints on n, l l), and m_l that are imposed during the solution of the hydrogen atom Schrödinger equation explain why there is a single 1s orbital, why there are three 2p orbitals, five 3d orbitals, etc. We will see when we consider multi-electron atoms, these constraints explain the features of the Periodic Table. In other words, the Periodic Table is a manifestation of the Schrödinger model and the physical constraints imposed to obtain the solutions to the Schrödinger equation for the hydrogen atom.

The Three Quantum Numbers

Schrödinger’s approach requires three quantum numbers (n, l, and m_l) to specify a wavefunction for the electron. The quantum numbers provide information about the spatial distribution of an electron. Although n can be any positive integer (NOT zero), only certain values of l and m_l are allowed for a given value of \(n).

The principal quantum number (n): One of three quantum numbers that tells the average relative distance of an electron from the nucleus. indicates the energy of the electron and the average distance of an electron from the nucleus

$$n = 1,\ 2,\ 3,\ 4,\ .\ .\ . \tag{11.10.6}$$

Asn increases for a given atom, so does the average distance of an electron from the nucleus. A negatively charged electron that is, on average, closer to the positively charged nucleus is attracted to the nucleus more strongly than an electron that is farther out in space. This means that electrons with higher values of n are easier to remove from an atom. All wave functions that have the same value of n are said to constitute a principal shell. All the wave functions that have the same value of n because those electrons have similar average distances from the nucleus. because those electrons have similar average distances from the nucleus. As you will see, the principal quantum number n corresponds to the n used by Bohr to describe electron orbits and by Rydberg to describe atomic energy levels.

The Azimuthal Quantum Number: The second quantum number is often called the azimuthal quantum number (l). One of three quantum numbers that describes the shape of the region of space occupied by an electron.. The value of l describes the shape of the region of space occupied by the electron. The allowed values of l depend on the value of n and can range from 0 to n − 1:

$$l = 0,\ 1, ., 2,\ 3,\ .\ .\ (n-1) \tag{11.10.7}$$

For example, if n = 1, l can be only 0; if n = 2, l can be 0 or 1; and so forth. For a given atom, all wave functions that have the same values of both n and l form a subshell. A group of wave functions that have the same values of n and l. The regions of space occupied by electrons in the same subshell usually have the same shape, but they are oriented differently in space.

The Magnetic Quantum Number: The third quantum number is the magnetic quantum number (m_l). One of three quantum numbers that describes the orientation of the region of space occupied by an electron with respect to an applied magnetic field.. The value of m_l describes the orientation of the region in space occupied by an electron with respect to an applied magnetic field. The allowed values of m_l depend on the value of l: m_l can range from −l to l in integral steps:

$$m = -l,\ -l+1,\ .\ .\ .0,\ \ .\ .\ .l-1, l \tag{11.10.8}$$

For example, if $l = 0$, ml can be only 0; if l = 1, m_l can be −1, 0, or +1; and if l = 2, m_l can be −2, −1, 0, +1, or +2.

Each wave function with an allowed combination of n, l, and ml values describes an atomic orbital A wave function with an allowed combination of n, l and ml quantum numbers., a particular spatial distribution for an electron. For a given set of quantum numbers, each principal shell has a fixed number of subshells, and each subshell has a fixed number of orbitals.

✓ Example 11.10.1: Number of subshells

How many subshells and orbitals are contained within the principal shell with n = 4?

Given: value of n

Asked for: number of subshells and orbitals in the principal shell

Strategy:

A Given n = 4, calculate the allowed values of l. From these allowed values, count the number of subshells.

B For each allowed value of l, calculate the allowed values of ml. The sum of the number of orbitals in each subshell is the number of orbitals in the principal shell.

Solution

A We know that l can have all integral values from 0 to n − 1. If n = 4, then l can equal 0, 1, 2, or 3. Because the shell has four values of l, it has four subshells, each of which will contain a different number of orbitals, depending on the allowed values of ml.

B For l = 0, ml can be only 0, and thus the l = 0 subshell has only one orbital. For l = 1, ml can be 0 or ±1; thus the l = 1 subshell has three orbitals. For l = 2, ml can be 0, ±1, or ±2, so there are five orbitals in the l = 2 subshell. The last allowed value of l is l = 3, for which ml can be

0, ±1, ±2, or ±3, resulting in seven orbitals in the l = 3 subshell. The total number of orbitals in the n = 4 principal shell is the sum of the number of orbitals in each subshell and is equal to n2:

$$\underset{(l=0)}{1} + \underset{(l=1)}{3} + \underset{(l=2)}{5} + \underset{(l=3)}{7} = 16 \text{ orbitals} = (4 \text{ principal shells})^2$$

? Exercise 11.10.1

How many subshells and orbitals are in the principal shell with *n* = 3?

Answer: three subshells; nine orbitals

Rather than specifying all the values of *n* and *l* every time we refer to a subshell or an orbital, chemists use an abbreviated system with lowercase letters to denote the value of *l* for a particular subshell or orbital:

l =	0	1	2	3
Designation	*s*	*p*	*d*	*f*

The principal quantum number is named first, followed by the letter *s*, *p*, *d*, or *f* as appropriate. These orbital designations are derived from corresponding spectroscopic characteristics of lines involving them: *s*harp, *p*rinciple, *d*iffuse, and *f*undamental. A 1*s* orbital has *n* = 1 and *l* = 0; a 2*p* subshell has *n* = 2 and *l* = 1 (and has three 2*p* orbitals, corresponding to m_l = −1, 0, and +1); a 3*d* subshell has *n* = 3 and *l* = 2 (and has five 3*d* orbitals, corresponding to m_l = −2, −1, 0, +1, and +2); and so forth.

We can summarize the relationships between the quantum numbers and the number of subshells and orbitals as follows (Table $11.10.1$):

- Each principal shell has *n* subshells. For *n* = 1, only a single subshell is possible (1*s*); for *n* = 2, there are two subshells (2*s* and 2*p*); for *n* = 3, there are three subshells (3*s*, 3*p*, and 3*d*); and so forth. Every shell has an *ns* subshell, any shell with *n* ≥ 2 also has an *np* subshell, and any shell with *n* ≥ 3 also has an *nd* subshell. Because a 2*d* subshell would require both *n* = 2 and *l* = 2, which is not an allowed value of *l* for *n* = 2, a 2*d* subshell does not exist.
- Each subshell has 2*l* + 1 orbitals. This means that all *ns* subshells contain a single *s* orbital, all *np* subshells contain three *p* orbitals, all *nd* subshells contain five *d* orbitals, and all *nf* subshells contain seven *f* orbitals.

Note

Each principal shell has *n* subshells, and each subshell has 2*l* + 1 orbitals.

Table 11.10.1: Allowed values of n, *l*, and m_l through n = 4

n	*l*	Subshell Designation	m_l	Number of Orbitals in Subshell	Number of Orbitals in Shell
1	0	1*s*	0	1	1
2	0	2*s*	0	1	4
	1	2*p*	−1, 0, 1	3	
3	0	3*s*	0	1	9
	1	3*p*	−1, 0, 1	3	
	2	3*d*	−2, −1, 0, 1, 2	5	
4	0	4*s*	0	1	16
	1	4*p*	−1, 0, 1	3	
	2	4*d*	−2, −1, 0, 1, 2	5	
	3	4*f*	−3, −2, −1, 0, 1, 2, 3	7	

The Radial Component

The first six radial functions are provided in Table $11.10.2$ Note that the functions in the table exhibit a dependence on Z, the atomic number of the nucleus. Other one electron systems have electronic states analogous to those for the hydrogen atom, and inclusion of the charge on the nucleus allows the same wavefunctions to be used for all one-electron systems. For hydrogen, $Z = 1$ and for helium, $Z = 2$.

Table 11.10.2: Hydrogen-like atomic wavefunctions for n values $1, 2, 3$: Z is the atomic number of the nucleus, and $\rho = \dfrac{Zr}{a_0}$, where a_0 is the Bohr radius and r is the radial variable.

n	ℓ	m	**Radial Component**
$n=1$	$\ell=0$	$m=0$	$\psi_{100} = \dfrac{1}{\sqrt{\pi}}\left(\dfrac{Z}{a_0}\right)^{\frac{3}{2}} e^{-\rho}$
$n=2$	$\ell=0$	$m=0$	$\psi_{200} = \dfrac{1}{\sqrt{32\pi}}\left(\dfrac{Z}{a_0}\right)^{\frac{3}{2}} (2-\rho)e^{\dfrac{-\rho}{2}}$
	$\ell=1$	$m=0$	$\psi_{210} = \dfrac{1}{\sqrt{32\pi}}\left(\dfrac{Z}{a_0}\right)^{\frac{3}{2}} \rho e^{-\rho/2}\cos(\theta)$
	$\ell=1$	$m=\pm1$	$\psi_{21\pm1} = \dfrac{1}{\sqrt{64\pi}}\left(\dfrac{Z}{a_0}\right)^{\dfrac{3}{2}} \rho e^{-\rho/2}\sin(\theta)$
$n=3$	$\ell=0$	$m=0$	$\psi_{300} = \dfrac{1}{81\sqrt{3\pi}}\left(\dfrac{Z}{a_0}\right)^{\frac{3}{2}} (27-18\rho+2$
	$\ell=1$	$m=0$	$\psi_{310} = \dfrac{1}{81}\sqrt{\dfrac{2}{\pi}}\left(\dfrac{Z}{a_0}\right)^{\dfrac{3}{2}} (6r-\rho^2)e^{-\rho/}$
	$\ell=1$	$m=\pm1$	$\psi_{31\pm1} = \dfrac{1}{81\sqrt{\pi}}\left(\dfrac{Z}{a_0}\right)^{\frac{3}{2}} (6\rho-\rho^2)e^{-r/}$
	$\ell=2$	$m=0$	$\psi_{320} = \dfrac{1}{81\sqrt{6\pi}}\left(\dfrac{Z}{a_0}\right)^{\frac{3}{2}} \rho^2 e^{-\rho/3}(3cos^2$
	$\ell=2$	$m=\pm1$	$\psi_{32\pm1} = \dfrac{1}{81\sqrt{\pi}}\left(\dfrac{Z}{a_0}\right)^{\frac{3}{2}} \rho^2 e^{-\rho/3}\sin(\theta$
	$\ell=2$	$m=\pm2$	$\psi_{32\pm2} = \dfrac{1}{162\sqrt{\pi}}\left(\dfrac{Z}{a_0}\right)^{\frac{3}{2}} \rho^2 e^{-\rho/3}\sin^2($

Visualizing the variation of an electronic wavefunction with r,θ, and ϕ is important because the absolute square of the wavefunction depicts the charge distribution (electron probability density) in an atom or molecule. The charge distribution is central to chemistry because it is related to chemical reactivity. For example, an electron deficient part of one molecule is attracted to an electron rich region of another molecule, and such interactions play a major role in chemical interactions ranging from substitution and addition reactions to protein folding and the interaction of substrates with enzymes.

Methods for separately examining the radial portions of atomic orbitals provide useful information about the distribution of charge density within the orbitals. Graphs of the radial functions, R(r), for the 1s, 2s, and 2p orbitals plotted in Figure 11.10.2left). The quantity $R(r)^* R(r)$ gives the radial probability density; i.e., the probability density for the electron to be at a point located the distance r from the proton. Radial probability densities for three types of atomic orbitals are plotted in Figure 11.10.2(right).

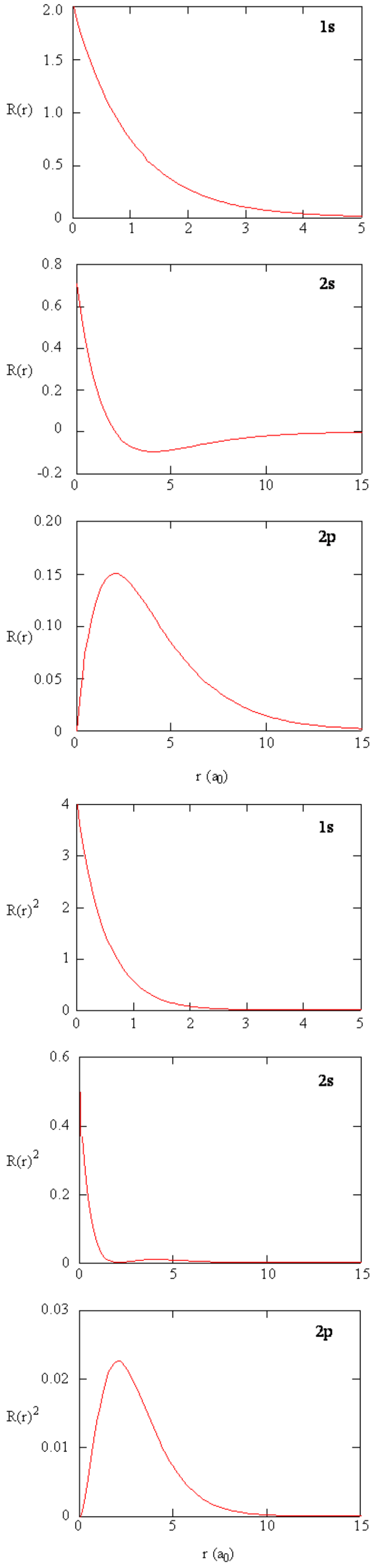
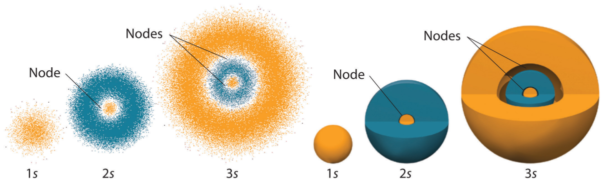


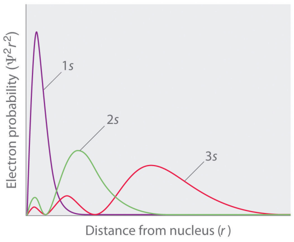
Figure 11.10.2: (left) Radial **function**, R(r), for the 1s, 2s, and 2p orbitals. (right) Radial probability **densities** for the 1s, 2s, and 2p orbitals.

For the hydrogen atom, the peak in the radial probability plot occurs at r = 0.529 Å (52.9 pm), which is exactly the radius calculated by Bohr for the n = 1 orbit. Thus the *most probable radius* obtained from quantum mechanics is identical to the radius calculated by classical mechanics. In Bohr's model, however, the electron was assumed to be at this distance 100% of the time, whereas in the Schrödinger model, it is at this distance only some of the time. The difference between the two models is attributable to the wavelike behavior of the electron and the Heisenberg uncertainty principle.

Figure 11.10.3 compares the electron probability densities for the hydrogen 1*s*, 2*s*, and 3*s* orbitals. Note that all three are spherically symmetrical. For the 2*s* and 3*s* orbitals, however (and for all other *s* orbitals as well), the electron probability density does not fall off smoothly with increasing *r*. Instead, a series of minima and maxima are observed in the radial probability plots (part (c) in Figure 11.10.3). The minima correspond to spherical nodes (regions of zero electron probability), which alternate with spherical regions of nonzero electron probability.



(a) Electron probability **(b) Contour probability**



(c) Radial probability

Figure 11.10.3: Probability Densities for the 1 s, 2 s, and 3*s* Orbitals of the Hydrogen Atom. (a) The electron probability density in any plane that contains the nucleus is shown. Note the presence of circular regions, or nodes, where the probability density is zero. (b) Contour surfaces enclose 90% of the electron probability, which illustrates the different sizes of the 1*s*, 2*s*, and 3*s* orbitals. The cutaway drawings give partial views of the internal spherical nodes. The orange color corresponds to regions of space where the phase of the wave function is positive, and the blue color corresponds to regions of space where the phase of the wave function is negative. (c) In these plots of electron probability as a function of distance from the nucleus (*r*) in all directions (radial probability), the most probable radius increases as*n* increases, but the 2*s* and 3*s* orbitals have regions of significant electron probability at small values of *r*.

The Angular Component

The angular component of the wavefunction $Y(\theta,\phi)$ in Equation 11.10.4 does much to give an orbital its distinctive shape. $Y(\theta,\phi)$ is typically normalized so the the integral of $Y^2(\theta,\phi)$ over the unit sphere is equal to one. In this case, $Y^2(\theta,\phi)$ serves as a probability function. The probability function can be interpreted as the probability that the electron will be found on the ray emitting from the origin that is at angles (θ,ϕ) from the axes. The probability function can also be interpreted as the probability distribution of the electron being at position (θ,ϕ) on a sphere of radius *r*, given that it is *r* distance from the nucleus. $Y_{l,m_l}(\theta,\phi)$ are also the wavefunction solutions to Schrödinger's equation for a rigid rotor consisting of rotating bodies, for example a diatomic molecule. These are called Spherical Harmonic functions (Table M4).

s Orbitals (l=0)

Three things happen to *s* orbitals as *n* increases (Figure 6.6.2):

1. They become larger, extending farther from the nucleus.
2. They contain more nodes. This is similar to a standing wave that has regions of significant amplitude separated by nodes, points with zero amplitude.
3. For a given atom, the *s* orbitals also become higher in energy as *n* increases because of their increased distance from the nucleus.

Orbitals are generally drawn as three-dimensional surfaces that enclose 90% of the electron density. Although such drawings show the relative sizes of the orbitals, they do not normally show the spherical nodes in the 2*s* and 3*s* orbitals because the spherical nodes lie inside the 90% surface. Fortunately, the positions of the spherical nodes are not important for chemical bonding.

p Orbitals (l=1)

Only *s* orbitals are spherically symmetrical. As the value of *l* increases, the number of orbitals in a given subshell increases, and the shapes of the orbitals become more complex. Because the 2*p* subshell has *l* = 1, with three values of m_l (−1, 0, and +1), there are three 2*p* orbitals).

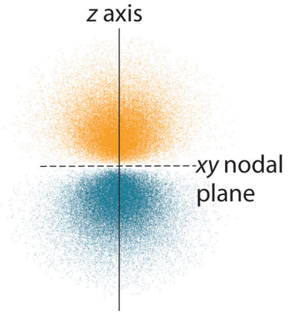


Figure 6.6.2, the colors correspond to regions of space where the phase of the wave function is positive (orange) and negative (blue).

The electron probability distribution for one of the hydrogen 2*p* orbitals is shown in Figure 11.10.4 Because this orbital has two lobes of electron density arranged along the *z* axis, with an electron density of zero in the *xy* plane (i.e., the *xy* plane is a nodal plane), it is a $2p_z$ orbital. As shown in Figure 11.10.5, the other two 2*p* orbitals have identical shapes, but they lie along the *x* axis ($2p_x$) and *y* axis ($2p_y$), respectively. Note that each *p* orbital has just one nodal plane. In each case, the phase of the wave function for each of the 2*p* orbitals is positive for the lobe that points along the positive axis and negative for the lobe that points along the negative axis. It is important to emphasize that these signs correspond to the *phase* of the wave that describes the electron motion, *not* to positive or negative charges.

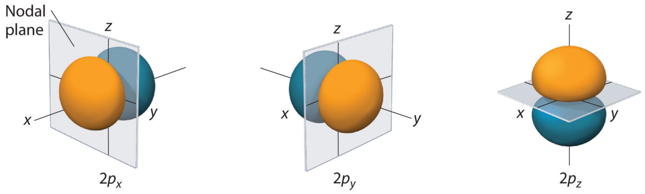


Figure 11.10.5: The Three Equivalent 2 p Orbitals of the Hydrogen Atom

The surfaces shown enclose 90% of the total electron probability for the $2p_x$, $2p_y$, and $2p_z$ orbitals. Each orbital is oriented along the axis indicated by the subscript and a nodal plane that is perpendicular to that axis bisects each 2*p* orbital. The phase of the wave function is positive (orange) in the region of space where *x*, *y*, or *z* is positive and negative (blue) where *x*, *y*, or *z* is negative. Just as with the *s* orbitals, the size and complexity of the *p* orbitals for any atom increase as the principal quantum number *n* increases. The shapes of the 90% probability surfaces of the 3*p*, 4*p*, and higher-energy *p* orbitals are, however, essentially the same as those shown in Figure Figure 11.10.5

d Orbitals (l=2)

Subshells with *l* = 2 have five *d* orbitals; the first principal shell to have a *d* subshell corresponds to *n* = 3. The five *d* orbitals have m_l values of −2, −1, 0, +1, and +2 (Figure 11.10.6).

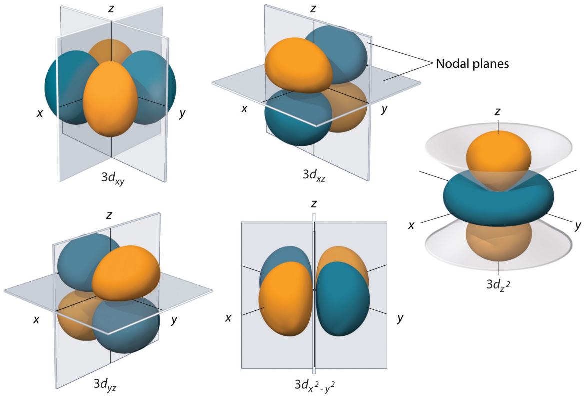


Figure 11.10.6: The Five Equivalent 3d Orbitals of the Hydrogen Atom. The surfaces shown enclose 90% of the total electron probability for the five hydrogen 3d orbitals. Four of the five 3d orbitals consist of four lobes arranged in a plane that is intersected by two perpendicular nodal planes. These four orbitals have the same shape but different orientations. The fifth 3d orbital, $3d_{z^2}$, has a distinct shape even though it is mathematically equivalent to the others. The phase of the wave function for the different lobes is indicated by color: orange for positive and blue for negative.

The hydrogen 3d orbitals have more complex shapes than the 2p orbitals. All five 3d orbitals contain two nodal surfaces, as compared to one for each p orbital and zero for each s orbital. In three of the d orbitals, the lobes of electron density are oriented between the x and y, x and z, and y and z planes; these orbitals are referred to as the $3d_{xy}$, \)3d_{xz}_, and \)3d_{yz}\) orbitals, respectively. A fourth d orbital has lobes lying along the x and y axes; this is the 3dx2−y2 orbital. The fifth 3d orbital, called the $3d_{z^2}$ orbital, has a unique shape: it looks like a $2p_z$ orbital combined with an additional doughnut of electron probability lying in the xy plane. Despite its peculiar shape, the $3d_{z^2}$ orbital is mathematically equivalent to the other four and has the same energy. In contrast to p orbitals, the phase of the wave function for d orbitals is the same for opposite pairs of lobes. As shown in Figure 11.10.6, the phase of the wave function is positive for the two lobes of the dz^2 orbital that lie along the z axis, whereas the phase of the wave function is negative for the doughnut of electron density in the xy plane. Like the s and p orbitals, as n increases, the size of the d orbitals increases, but the overall shapes remain similar to those depicted in Figure 6.6.5.

f Orbitals (l=3)

Principal shells with $n = 4$ can have subshells with $l = 3$ and m_l values of −3, −2, −1, 0, +1, +2, and +3. These subshells consist of seven *f* orbitals. Each *f* orbital has three nodal surfaces, so their shapes are complex (not shown).

Energies

The constraint that n be greater than or equal to $l+1$ also turns out to quantize the energy, producing the same quantized expression for hydrogen atom energy levels that was obtained from the Bohr model of the hydrogen atom.

$$E = -\frac{Z^2}{n^2} Rhc \tag{11.10.9}$$

or

$$E_n = -\frac{Z^2 \mu e^4}{8\epsilon_0^2 h^2 n^2} \tag{11.10.10}$$

The relative energies of the atomic orbitals with $n \leq 4$ for a hydrogen atom are plotted in Figure 11.10.7; note that the orbital energies depend on *only* the principal quantum number *n*. Consequently, the energies of the 2*s* and 2*p* orbitals of hydrogen are the same; the energies of the 3*s*, 3*p*, and 3*d* orbitals are the same; and so forth. The orbital energies obtained for hydrogen using quantum mechanics are exactly the same as the allowed energies calculated by Bohr. In contrast to Bohr's model, however, which allowed only one orbit for each energy level, quantum mechanics predicts that there are *4* orbitals with different electron density distributions in the $n = 2$ principal shell (one 2*s* and three 2*p* orbitals), *9* in the $n = 3$ principal shell, and *16* in the $n = 4$ principal shell.

Note

For a single electron system, the energy of that electron is a function of only the principal quantum number (Equation 11.10.9).

The different values of *l* and m_l for the individual orbitals within a given principal shell are not important for understanding the emission or absorption spectra of the hydrogen atom under most conditions, but they do explain the splittings of the main lines that are observed when hydrogen atoms are placed in a magnetic field. As we have just seen, however, quantum mechanics also predicts that in the hydrogen atom, all orbitals with the same value of *n* (e.g., the three 2*p* orbitals) are degenerate, meaning that they have the same energy. Figure 11.10.7shows that the energy levels become closer and closer together as the value of *n* increases, as expected because of the $1/n^2$ dependence of orbital energies.

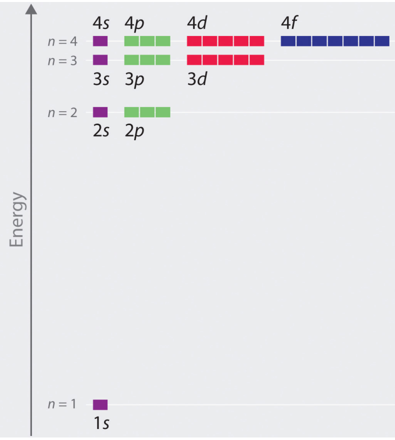


Figure 11.10.7: Orbital Energy Level Diagram for the Hydrogen Atom. Each box corresponds to one orbital. Note that the difference in energy between orbitals decreases rapidly with increasing values of n.

In general, both energy and radius decrease as the nuclear charge increases. Thus the most stable orbitals (those with the lowest energy) are those closest to the nucleus. For example, in the ground state of the hydrogen atom, the single electron is in the 1s orbital, whereas in the first excited state, the atom has absorbed energy and the electron has been promoted to one of the n = 2 orbitals. In ions with only a single electron, the energy of a given orbital depends on only n, and all subshells within a principal shell, such as the px, py, and pz orbitals, are degenerate.

Note: Bohr vs. Schrödinger

It is interesting to compare the results obtained by solving the Schrödinger equation with Bohr’s model of the hydrogen atom. There are several ways in which the Schrödinger model and Bohr model differ.

1. First, and perhaps most strikingly, the Schrödinger model does not produce well-defined orbits for the electron. The wavefunctions only give us the probability for the electron to be at various directions and distances from the proton.
2. Second, the quantization of angular momentum is different from that proposed by Bohr. Bohr proposed that the angular momentum is quantized in integer units of $\hbar$, while the Schrödinger model leads to an angular momentum of $(l(l+1)\hbar^2)^{\frac{1}{2}}$.
3. Third, the quantum numbers appear naturally during solution of the Schrödinger equation while Bohr had to postulate the existence of quantized energy states. Although more complex, the Schrödinger model leads to a better correspondence between theory and experiment over a range of applications that was not possible for the Bohr model.

Electron Spin: The Fourth Quantum Number

The quantum numbers n, l, m are not sufficient to fully characterize the physical state of the electrons in an atom. In 1926, Otto Stern and Walther Gerlach carried out an experiment that could not be explained in terms of the three quantum numbers n, l, m and showed that there is, in fact, another quantum-mechanical degree of freedom that needs to be included in the theory. The experiment is illustrated in the Figure 11.10.8 A beam of atoms (e.g. hydrogen or silver atoms) is sent through a spatially inhomogeneous magnetic field with a definite field gradient toward one of the poles. It is observed that the beam splits into two beams as it passes through the field region.

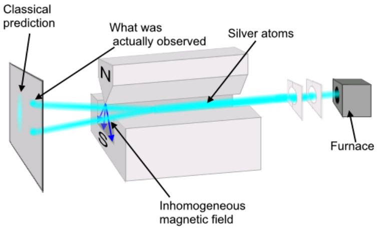


Figure 11.10.8: The Stern-Gerlach apparatus. from Wikipedia

The fact that the beam splits into 2 beams suggests that the electrons in the atoms have a degree of freedom capable of coupling to the magnetic field. That is, an electron has an *intrinsic magnetic moment* M arising from a degree of freedom that has no classical analog. The magnetic moment must take on only 2 values according to the Stern-Gerlach experiment. The intrinsic property that gives rise to the magnetic moment must have some analog to a *spin*, S; unlike position and momentum, which have clear classical analogs, spin does not. The implication of the Stern-Gerlach experiment is that we need to include a fourth quantum number, m_s in our description of the physical state of the electron. That is, in addition to give its principle, angular, and magnetic quantum numbers, we also need to say if it is a spin-up electron or a spin-down electron.

Note: Spin is a Quantum Phenomenon

Unlike position and momentum, which have clear classical analogs, spin does not.

George Uhlenbeck (1900–1988) and Samuel Goudsmit (1902–1978), proposed that the splittings were caused by an electron spinning about its axis, much as Earth spins about its axis. When an electrically charged object spins, it produces a magnetic moment parallel to the axis of rotation, making it behave like a magnet. Although the electron cannot be viewed solely as a particle, spinning or otherwise, it is indisputable that it does have a magnetic moment. This magnetic moment is called electron spin.

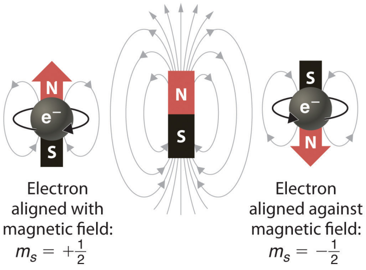


Figure 11.10.9: Electron Spin. In a magnetic field, an electron has two possible orientations with different energies, one with spin up, aligned with the magnetic field, and one with spin down, aligned against it. All other orientations are forbidden.

In an external magnetic field, the electron has two possible orientations (Figure 11.10.9). These are described by a fourth quantum number (m_s), which for any electron can have only two possible values, designated +½ (up) and −½ (down) to indicate that the two orientations are opposites; the subscript *s* is for spin. An electron behaves like a magnet that has one of two possible orientations, aligned either with the magnetic field or against it. The implications of electron spin for chemistry were recognized almost immediately by an Austrian physicist, Wolfgang Pauli (1900–1958; Nobel Prize in Physics, 1945), who determined that each orbital can contain no more than two electrons whoe developed the Pauli exclusion principle.

Note: Pauli Exclusion Principle

No two electrons in an atom can have the same values of all four quantum numbers (n, l, m_l, m_s).

By giving the values of n, l, and m_l, we also specify a particular orbital (e.g., 1*s* with $n = 1$, $l = 0$, $m_l = 0$). Because m_s has only two possible values (+½ or −½), two electrons, *and only two electrons*, can occupy any given orbital, one with spin up and one with spin down. With this information, we can proceed to construct the entire periodic table, which was originally based on the physical and chemical properties of the known elements.

✓ Example 11.10.2

List all the allowed combinations of the four quantum numbers (n, l, m_l, m_s) for electrons in a 2*p* orbital and predict the maximum number of electrons the 2*p* subshell can accommodate.

Given: orbital

Asked for: allowed quantum numbers and maximum number of electrons in orbital

Strategy:

A. List the quantum numbers (n, l, m_l) that correspond to an n = 2*p* orbital. List all allowed combinations of (n, l, m_l).
B. Build on these combinations to list all the allowed combinations of (n, l, m_l, m_s).
C. Add together the number of combinations to predict the maximum number of electrons the 2*p* subshell can accommodate.

Solution:

A For a 2*p* orbital, we know that $n = 2$, $l = n - 1 = 1$, and $m_l = -l, (-l + 1), \ldots, (l - 1), l$. There are only three possible combinations of (n, l, m_l): (2, 1, 1), (2, 1, 0), and (2, 1, −1).

B Because m_s is independent of the other quantum numbers and can have values of only +½ and −½, there are six possible combinations of (n, l, m_l, m_s): (2, 1, 1, +½), (2, 1, 1, −½), (2, 1, 0, +½), (2, 1, 0, −½), (2, 1, −1, +½), and (2, 1, −1, −½).

C Hence the 2*p* subshell, which consists of three 2*p* orbitals ($2p_x$, $2p_y$, and $2p_z$), can contain a total of six electrons, two in each orbital.

? Exercise 11.10.2

List all the allowed combinations of the four quantum numbers (n, l, m_l, m_s) for a 6*s* orbital, and predict the total number of electrons it can contain.

Answer: (6, 0, 0, +½), (6, 0, 0, −½); two electrons

Contributors and Attributions

- David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski ("Quantum States of Atoms and Molecules")

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11.11: Many-Electron Atoms and the Periodic Table

Quantum mechanics can account for the periodic structure of the elements, by any measure a major conceptual accomplishment for any theory. Although accurate computations become increasingly more challenging as the number of electrons increases, the general patterns of atomic behavior can be predicted with remarkable accuracy.

Figure $11.11.1$ shows a schematic representation of a helium atom with two electrons whose coordinates are given by the vectors r_1 and r_2. The electrons are separated by a distance $r_{12} = |r_1 - r_2|$. The origin of the coordinate system is fixed at the nucleus. As with the hydrogen atom, the nuclei for multi-electron atoms are so much heavier than an electron that the nucleus is assumed to be the center of mass. Fixing the origin of the coordinate system at the nucleus allows us to exclude translational motion of the center of mass from our quantum mechanical treatment.

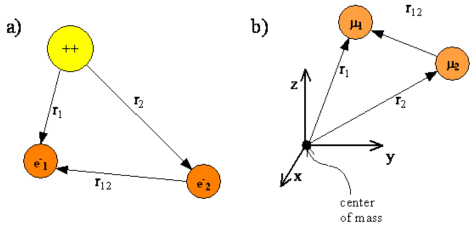


Figure $11.11.1$ **:** a) The nucleus (++) and electrons (e-) of the helium atom. b) Equivalent reduced particles with the center of mass (approximately located at the nucleus) at the origin of the coordinate system. Note that μ_1 and $\mu_2 \approx m_e$.

The Schrödinger equation operator for the hydrogen atom serves as a reference point for writing the Schrödinger equation for atoms with more than one electron. Start with the same general form we used for the hydrogen atom Hamiltonian

$$(\hat{T} + \hat{V})\psi = E\psi \tag{11.11.1}$$

Include a kinetic energy term for each electron and a potential energy term for the attraction of each negatively charged electron for the positively charged nucleus and a potential energy term for the mutual repulsion of each pair of negatively charged electrons. The He atom Schrödinger equation is

$$\left(-\frac{\hbar^2}{2m_e}(\nabla_1^2 + \nabla_2^2) + V(r_1) + V(r_2) + V(r_{12}) \right) \psi = E\psi \tag{11.11.2}$$

where

$$V(r_1) = -\frac{2e^2}{4\pi\epsilon_0 r_1} \tag{11.11.3}$$

$$V(r_2) = -\frac{2e^2}{4\pi\epsilon_0 r_2} \tag{11.11.4}$$

$$V(r_{12}) = +\frac{e^2}{4\pi\epsilon_0 r_{12}} \tag{11.11.5}$$

Equation $11.11.2$ can be extended to any atom or ion by including terms for the additional electrons and replacing the He nuclear charge +2 with a general charge Z; e.g.

$$V(r_1) = -\frac{Ze^2}{4\pi\epsilon_0 r_1} \tag{11.11.6}$$

Equation $11.11.2$ then becomes

$$\left(-\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 + \sum_i V(r_i) + \sum_{i \neq j} V(r_{ij}) \right) \psi = E\psi \tag{11.11.7}$$

Given what we have learned from the previous quantum mechanical systems we've studied, we predict that exact solutions to the multi-electron Schrödinger equation would consist of a family of multi-electron wavefunctions, each with an associated energy eigenvalue. These wavefunctions and energies would describe the ground and excited states of the multi-electron atom, just as the hydrogen wavefunctions and their associated energies describe the ground and excited states of the hydrogen atom. We would predict quantum numbers to be involved, as well.

The fact that electrons interact through their electron-electron repulsion means that an exact wavefunction for a multi-electron system would be a single function that depends **simultaneously** upon the coordinates of all the electrons; i.e., a multi-electron wavefunction:

$$\Psi(r_1, r_2, \cdots r_i) \tag{11.11.8}$$

Unfortunately, the electron-electron repulsion terms make it impossible to find an exact solution to the Schrödinger equation for many-electron atoms. The most basic ansatz to the exact solutions involve writing a multi-electron wavefunction as a **simple product of single-**electron wavefunctions

$$\psi(r_1, r_2, \cdots, r_i) = \varphi_1(r_1)\varphi_2(r_2)\cdots\varphi_i(r_i) \tag{11.11.9}$$

Obtaining the energy of the atom in the state described by that wavefunction as the **sum** of the energies of the one-electron components.

By writing the multi-electron wavefunction as a product of single-electron functions in Equation 11.11.9, we conceptually transform a multi-electron atom into a collection of individual electrons located in individual orbitals whose spatial characteristics and energies can be separately identified. For atoms these single-electron wavefunctions are called atomic orbitals. For molecules, as we will see in the next chapter, they are called molecular orbitals. While a great deal can be learned from such an analysis, it is important to keep in mind that such a discrete, compartmentalized picture of the electrons is an approximation, albeit a powerful one.

Electron Configurations

The specific arrangement of electrons in orbitals of an atom determines many of the chemical properties of that atom and is formulated via the *Aufbau* principle, which means "building-up" in German. Aufbau principles determine the order in which atomic orbitals are filled as the atomic number is increased. For the hydrogen atom, the order of increasing orbital energy is given by 1*s* < 2*s* = 2*p* < 3*s* = 3*p* = 3*d*, etc. The dependence of energy on *n* alone leads to extensive degeneracy, which is however removed for orbitals in many-electron atoms. Thus 2*s* lies below 2*p*, as already observed in helium. Similarly, 3*s*, 3*p* and 3*d* increase energy in that order, and so on. The 4*s* is lowered sufficiently that it becomes comparable to 3*d*. The general ordering of atomic orbitals is summarized in the following scheme:

$$\begin{gathered} 1s < 2s < 2p < 3s < 3p < 4s \sim 3d < 4p < 5s \sim 4d \\ < 5p < 6s \sim 5d \sim 4f < 6p < 7s \sim 6d \sim 5f \end{gathered} \tag{11.11.10}$$

and illustrated in Figure 11.11.2 This provides enough orbitals to fill the ground states of all the atoms in the periodic table. For orbitals designated as comparable in energy, e.g., 4*s* $\sim$ 3*d*, the actual order depends which other orbitals are occupied. The energy of atomic orbitals increases as the principal quantum number, n, increases. In any atom with two or more electrons, the repulsion between the electrons makes energies of subshells with different values of *l* differ so that the energy of the orbitals increases within a shell in the order *s* < *p* < *d* < *f*. Figure 11.11.2 depicts how these two trends in increasing energy relate. The 1*s* orbital at the bottom of the diagram is the orbital with electrons of lowest energy. The energy increases as we move up to the 2*s* and then 2*p*, 3*s*, and 3*p* orbitals, showing that the increasing *n* value has more influence on energy than the increasing *l* value for small atoms. However, this pattern does not hold for larger atoms. The 3*d* orbital is higher in energy than the 4*s* orbital. Such overlaps continue to occur frequently as we move up the chart.

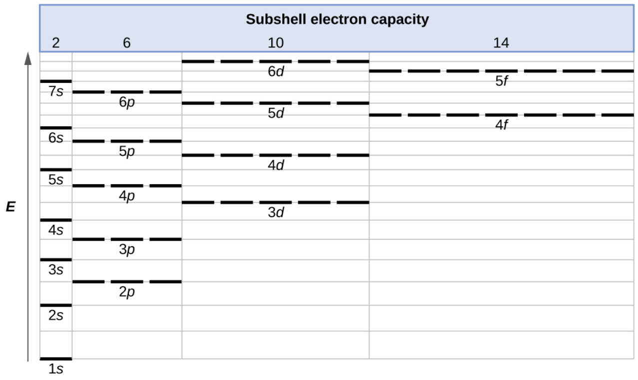


Figure 11.11.2: Generalized energy-level diagram for atomic orbitals in an atom with two or more electrons (not to scale).

Electrons in successive atoms on the periodic table tend to fill low-energy orbitals first. The arrangement of electrons in the orbitals of an atom is called the electron configuration of the atom. We describe an electron configuration with a symbol that contains three pieces of information (Figure 11.11.3):

1. The number of the principal quantum shell, *n*,
2. The letter that designates the orbital type (the subshell, *l*), and
3. A superscript number that designates the number of electrons in that particular subshell.

For example, the notation $2p^4$ (read "two–p–four") indicates four electrons in a *p* subshell (*l* = 1) with a principal quantum number (*n*) of 2. The notation $3d^8$ (read "three–d–eight") indicates eight electrons in the *d* subshell (i.e., *l* = 2) of the principal shell for which *n* = 3.

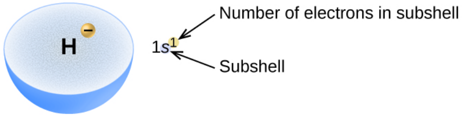


Figure 11.11.3: The diagram of an electron configuration specifies the subshell (n and l value, with letter symbol) and superscript number of electrons.

To determine the electron configuration for any particular atom, we can "build" the structures in the order of atomic numbers. Beginning with hydrogen, and continuing across the periods of the periodic table, we add one proton at a time to the nucleus and one electron to the proper subshell until we have described the electron configurations of all the elements. This procedure is called the Aufbau principle, from the German word *Aufbau* ("to build up"). Each added electron occupies the subshell of lowest energy available (in the order shown in Figure 11.11.4), subject to the limitations imposed by the allowed quantum numbers according to the Pauli exclusion principle. Electrons enter higher-energy subshells only after lower-energy subshells have been filled to capacity. Figure 11.11.3illustrates the traditional way to remember the filling order for atomic orbitals.

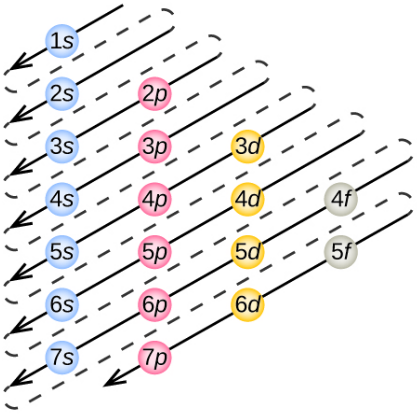
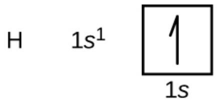


Figure 11.11.4: The arrow leads through each subshell in the appropriate filling order for electron configurations. This chart is straightforward to construct. Simply make a column for all the s orbitals with each n shell on a separate row. Repeat for p, d, and f. Be sure to only include orbitals allowed by the quantum numbers (no 1p or 2d, and so forth). Finally, draw diagonal lines from top to bottom as shown.

We will now construct the ground-state electron configuration and orbital diagram for a selection of atoms in the first and second periods of the periodic table. Orbital diagrams are pictorial representations of the electron configuration, showing the individual orbitals and the pairing arrangement of electrons. We start with a single hydrogen atom (atomic number 1), which consists of one proton and one electron. Referring to either Figure 11.11.4, we would expect to find the electron in the 1*s* orbital. By convention, the $m_s = +\frac{1}{2}$ value is usually filled first. The electron configuration and the orbital diagram are:

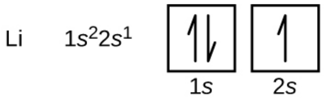


Following hydrogen is the noble gas helium, which has an atomic number of 2. The helium atom contains two protons and two electrons. The first electron has the same four quantum numbers as the hydrogen atom electron (*n* = 1, *l* = 0, m_l = 0, $m_s = +\frac{1}{2}$). The second electron also goes into the 1*s* orbital and fills that orbital. The second electron has the same *n*, *l*, and m_l quantum numbers, but must have the opposite spin quantum number, $m_s = -\frac{1}{2}$. This is in accord with the Pauli exclusion principle: No two electrons in the same atom can have the same set of four quantum numbers. For orbital diagrams, this means two arrows go in each box (representing two electrons in each orbital) and the arrows must point in opposite directions (representing paired spins). The electron configuration and orbital diagram of helium are:

In this figure, the element symbol H e is followed by the electron configuration, "1 s superscript 2." An orbital diagram is provided that consists of a single square. The square is labeled below as "1 s." It contains a pair of half arrows: one pointing up and the other down.

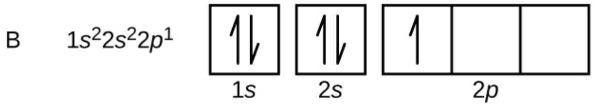
The *n* = 1 shell is completely filled in a helium atom.

The next atom is the alkali metal lithium with an atomic number of 3. The first two electrons in lithium fill the 1*s* orbital and have the same sets of four quantum numbers as the two electrons in helium. The remaining electron must occupy the orbital of next lowest energy, the 2*s* orbital (Figure 11.11.4). Thus, the electron configuration and orbital diagram of lithium are:



An atom of the alkaline earth metal beryllium, with an atomic number of 4, contains four protons in the nucleus and four electrons surrounding the nucleus. The fourth electron fills the remaining space in the 2*s* orbital.

An atom of boron (atomic number 5) contains five electrons. The *n* = 1 shell is filled with two electrons and three electrons will occupy the *n* = 2 shell. Because any *s* subshell can contain only two electrons, the fifth electron must occupy the next energy level, which will be a 2*p* orbital. There are three degenerate 2*p* orbitals (m_l = −1, 0, +1) and the electron can occupy any one of these *p* orbitals. When drawing orbital diagrams, we include empty boxes to depict any empty orbitals in the same subshell that we are filling.



Carbon (atomic number 6) has six electrons. Four of them fill the 1*s* and 2*s* orbitals. The remaining two electrons occupy the 2*p* subshell. We now have a choice of filling one of the 2*p* orbitals and pairing the electrons or of leaving the electrons unpaired in two different, but degenerate, *p* orbitals. The orbitals are filled as described by Hund's rule: the lowest-energy configuration for an atom with electrons within a set of degenerate orbitals is that having the maximum number of unpaired electrons. Thus, the two electrons in the carbon 2*p* orbitals have identical *n*, *l*, and m_s quantum numbers and differ in their m_l quantum number (in accord with the Pauli exclusion principle). The electron configuration and orbital diagram for carbon are:

In this figure, the element symbol C is followed by the electron configuration, "1 s superscript 2 2 s superscript 2 2 p superscript 2." The orbital diagram consists of two individual squares followed by 3 connected squares in a single row. The first blue square is labeled below as, "1 s." The second is similarly labeled, "2 s." The connected squares are labeled below as, "2 p." All squares not connected to each other contain a pair of half arrows: one pointing up and the other down. The first two squares in the group of 3 each contain a single upward pointing arrow.

Nitrogen (atomic number 7) fills the 1*s* and 2*s* subshells and has one electron in each of the three 2*p* orbitals, in accordance with Hund's rule. These three electrons have unpaired spins. Oxygen (atomic number 8) has a pair of electrons in any one of the 2*p* orbitals (the electrons have opposite spins) and a single electron in each of the other two. Fluorine (atomic number 9) has only one 2*p* orbital containing an unpaired electron. All of the electrons in the noble gas neon (atomic number 10) are paired, and all of the orbitals in the $n = 1$ and the $n = 2$ shells are filled. The electron configurations and orbital diagrams of these four elements are:

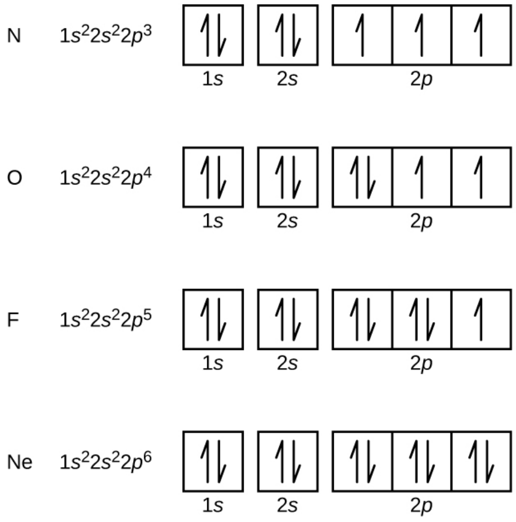


Figure 11.11.5). Since the core electron shells correspond to noble gas electron configurations, we can abbreviate electron configurations by writing the noble gas that matches the core electron configuration, along with the valence electrons in a condensed format. For our sodium example, the symbol [Ne] represents core electrons, ($1\ s^2 2s^2 2p^6$) and our abbreviated or condensed configuration is $[Ne]3s^1$.

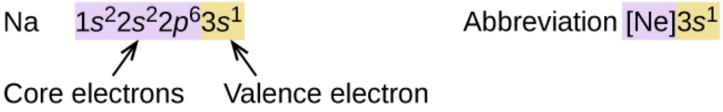


Figure 11.11.5: A core-abbreviated electron configuration (right) replaces the core electrons with the noble gas symbol whose configuration matches the core electron configuration of the other element.

Similarly, the abbreviated configuration of lithium can be represented as $[He]2s^1$, where [He] represents the configuration of the helium atom, which is identical to that of the filled inner shell of lithium. Writing the configurations in this way emphasizes the similarity of the configurations of lithium and sodium. Both atoms, which are in the alkali metal family, have only one electron in a valence *s* subshell outside a filled set of inner shells.

$$\begin{gathered}\mathrm{Li:[He]}\,2s^1\\ \mathrm{Na:[Ne]}\,3s^1\end{gathered} \tag{11.11.11}$$

The alkaline earth metal magnesium (atomic number 12), with its 12 electrons in a $[Ne]3s^2$ configuration, is analogous to its family member beryllium, $[He]2s^2$. Both atoms have a filled *s* subshell outside their filled inner shells. Aluminum (atomic number 13), with 13 electrons and the electron configuration $[Ne]3s^2 3p^1$, is analogous to its family member boron, $[He]2s^2 2p^1$.

The electron configurations of silicon (14 electrons), phosphorus (15 electrons), sulfur (16 electrons), chlorine (17 electrons), and argon (18 electrons) are analogous in the electron configurations of their outer shells to their corresponding family members carbon, nitrogen, oxygen, fluorine, and neon, respectively, except that the principal quantum number of the outer shell of the heavier elements has increased by one to $n = 3$. Figure

Beginning with the transition metal scandium (atomic number 21), additional electrons are added successively to the 3*d* subshell. This subshell is filled to its capacity with 10 electrons (remember that for $l = 2$ [*d* orbitals], there are $2l + 1 = 5$ values of m_l, meaning that there are five *d* orbitals that have a combined capacity of 10 electrons). The 4*p* subshell fills next. Note that for three series of elements, scandium (Sc) through copper (Cu), yttrium (Y) through silver (Ag), and lutetium (Lu) through gold (Au), a total of 10 *d* electrons are successively added to the $(n - 1)$ shell next to the *n* shell to bring that $(n - 1)$ shell from 8 to 18 electrons. For two series, lanthanum (La) through lutetium (Lu) and actinium (Ac) through lawrencium (Lr), 14 *f* electrons ($l = 3$, $2l + 1 = 7$

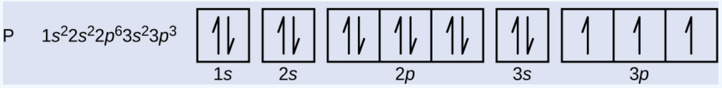
m_l values; thus, seven orbitals with a combined capacity of 14 electrons) are successively added to the (n – 2) shell to bring that shell from 18 electrons to a total of 32 electrons.

Example 11.11.1

Quantum Numbers and Electron Configurations What is the electron configuration and orbital diagram for a phosphorus atom? What are the four quantum numbers for the last electron added?

Solution

The atomic number of phosphorus is 15. Thus, a phosphorus atom contains 15 electrons. The order of filling of the energy levels is 1*s*, 2*s*, 2*p*, 3*s*, 3*p*, 4*s*, . . . The 15 electrons of the phosphorus atom will fill up to the 3*p* orbital, which will contain three electrons:



The last electron added is a 3*p* electron. Therefore, n = 3 and, for a *p*-type orbital, l = 1. The m_l value could be –1, 0, or +1. The three *p* orbitals are degenerate, so any of these m_l values is correct. For unpaired electrons, convention assigns the value of $+\frac{1}{2}$ for the spin quantum number; thus, $m_s = +\frac{1}{2}$.

Exercise 11.11.1

Identify the atoms from the electron configurations given:

a. [Ar]$4s^23d^5$
b. [Kr]$5s^24d^{10}5p^6$

Answer

(a) Mn (b) Xe

Effective Charge, Shielding and Penetration

For an atom or an ion with only a single electron, we can calculate the potential energy by considering only the electrostatic attraction between the positively charged nucleus and the negatively charged electron. When more than one electron is present, however, the total energy of the atom or the ion depends not only on attractive electron-nucleus interactions but also on repulsive electron-electron interactions. When there are two electrons, the repulsive interactions depend on the positions of *both* electrons at a given instant, but because we cannot specify the exact positions of the electrons, it is impossible to exactly calculate the repulsive interactions. Consequently, we must use approximate methods to deal with the effect of electron-electron repulsions on orbital energies.

If an electron is far from the nucleus (i.e., if the distance r between the nucleus and the electron is large), then at any given moment, most of the other electrons will be *between* that electron and the nucleus. Hence the electrons will cancel a portion of the positive charge of the nucleus and thereby decrease the attractive interaction between it and the electron farther away. As a result, the electron farther away experiences an effective nuclear charge (Z_{eff}) that is *less* than the actual nuclear charge Z (Figure 11.11.6). This effect is called electron shielding.

As the distance between an electron and the nucleus approaches infinity, Z_{eff} approaches a value of 1 because all the other ($Z - 1$) electrons in the neutral atom are, on the average, between it and the nucleus. If, on the other hand, an electron is very close to the nucleus, then at any given moment most of the other electrons are farther from the nucleus and do not shield the nuclear charge. At $r \approx 0$, the positive charge experienced by an electron is approximately the full nuclear charge, or $Z_{eff} \approx Z$. At intermediate values of r, the effective nuclear charge is somewhere between 1 and Z: $1 \le Z_{eff} \le Z$. Thus the actual Z_{eff} experienced by an electron in a given orbital depends not only on the spatial distribution of the electron in that orbital but also on the distribution of all the other electrons present. This leads to large differences in Z_{eff} for different elements, as shown in Figure 2.5.1 for the elements of the first three rows of the periodic table. Notice that only for hydrogen does $Z_{eff} = Z$, and only for helium are Z_{eff} and Z comparable in magnitude.

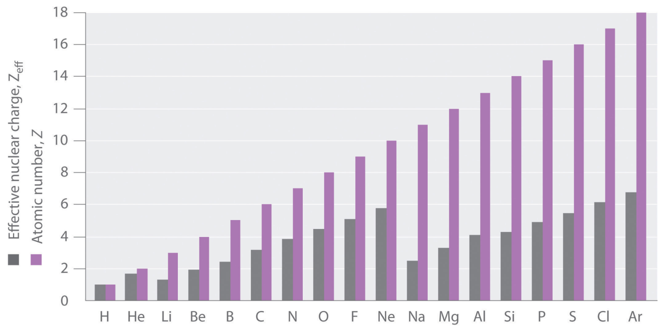


Figure 11.11.6: Relationship between the Effective Nuclear Charge Z_{eff} and the Atomic Number Z for the Outer Electrons of the Elements of the First Three Rows of the Periodic Table. Except for hydrogen, Z_{eff} is *always* less than Z, and Z_{eff} increases from left to right as you go across a row.

Because of the effects of shielding and the different radial distributions of orbitals with the same value of *n* but different values of *l*, the different subshells are not degenerate in a multielectron atom. For a given value of *n*, the *ns* orbital is always lower in energy than the *np* orbitals, which are lower in energy than the *nd* orbitals, and so forth. As a result, some subshells with higher principal quantum numbers are actually lower in energy than subshells with a lower value of *n*; for example, the 4*s* orbital is lower in energy than the 3*d* orbitals for most atoms.

Note

Except for the single electron containing hydrogen atom, in every other element Z_{eff} is always less than Z.

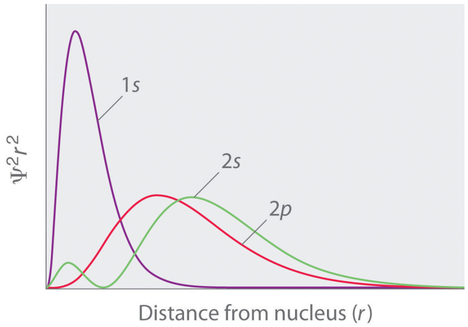


Figure 11.11.7: Orbital Penetration. A comparison of the radial probability distribution of the 2 s and 2*p* orbitals for various states of the hydrogen atom shows that the 2*s* orbital penetrates inside the 1*s* orbital more than the 2*p* orbital does. Consequently, when an electron is in the small inner lobe of the 2*s* orbital, it experiences a relatively large value of Z_{eff}, which causes the energy of the 2*s* orbital to be lower than the energy of the 2*p* orbital.

Ionization Energy

Ionization energy is the energy required to remove an electron from a neutral atom in its gaseous phase. Conceptually, ionization energy is the opposite of electronegativity. The lower this energy is, the more readily the atom becomes a cation. Therefore, the higher this energy is, the more unlikely it is the atom becomes a cation. Generally, elements on the right side of the periodic table have a higher ionization energy because their valence shell is nearly filled. Elements on the left side of the periodic table have low ionization energies because of their willingness to lose electrons and become cations. Thus, ionization energy increases from left to right on the periodic table.

Another factor that affects ionization energy is *electron shielding*. Electron shielding describes the ability of an atom's inner electrons to shield its positively-charged nucleus from its valence electrons. When moving to the right of a period, the number of electrons increases and the strength of shielding increases. As a result, it is easier for valence shell electrons to ionize, and thus the ionization energy decreases down a group. Electron shielding is also known as *screening*.

Note

- The ionization energy of the elements within a period generally increases from left to right. This is due to valence shell stability.
- The ionization energy of the elements within a group generally decreases from top to bottom. This is due to electron shielding.
- The noble gases possess very high ionization energies because of their full valence shells as indicated in the graph. Note that helium has the highest ionization energy of all the elements.

Some elements have several ionization energies; these varying energies are referred to as the first ionization energy, the second ionization energy, third ionization energy, etc. The first ionization energy is the energy requiredto remove the outermost, or highest, energy electron, the second ionization energy is the energy required to remove any subsequent high-energy electron from a gaseous cation, etc. Below are the chemical equations describing the first and second ionization energies:

First Ionization Energy:

$$X_{(g)} \rightarrow X^+_{(g)} + e^- \tag{11.11.12}$$

Second Ionization Energy:

$$X^+_{(g)} \rightarrow X^{2+}_{(g)} + e^- \tag{11.11.13}$$

Generally, any subsequent ionization energies (2nd, 3rd, etc.) follow the same periodic trend as the first ionization energy.

Ionization energies decrease as atomic radii increase. This observation is affected by n (the principal quantum number) and Z_{eff} (based on the atomic number and shows how many protons are seen in the atom) on the ionization energy (I). The relationship is given by the following equation:

$$I = \frac{R_H Z^2_{eff}}{n^2} \tag{11.11.14}$$

- Across a period, Z_{eff} *increases* and n (principal quantum number) *remains the same*, so the ionization energy *increases*.
- Down a group, n *increases* and Z_{eff} *increases slightly;* the ionization energy *decreases*.

Figure 11.11.8: Periodic trends in ionization energy.

The periodic structure of the elements is evident for many physical and chemical properties, including chemical valence, atomic radius, electronegativity, melting point, density, and hardness. The classic prototype for periodic behavior is the variation of the first ionization energy with atomic number, which is plotted in Figure 11.11.8

Electron Affinity

The electron affinity (EA) of an element E is defined as minus the internal energy change associated with the gain of an electron by a gaseous atom, at 0 K :

$$E_{(g)} + e^- \rightarrow E^-_{(g)} \tag{11.11.15}$$

Unlike ionization energies, which are always positive for a neutral atom because energy is required to remove an electron, electron affinities can be positive (energy is released when an electron is added), negative (energy must be added to the system to produce an anion), or zero (the process is energetically neutral).

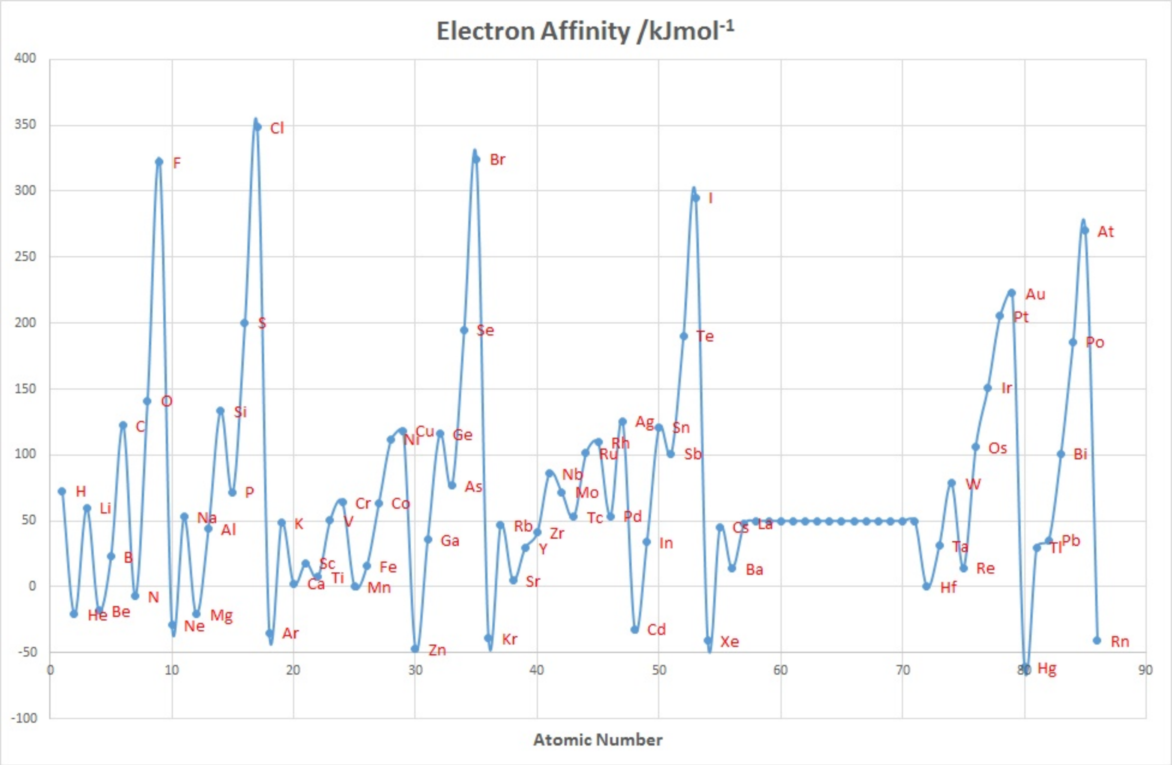


***Figure 11.11.9**: Periodic trends in electron affinities.*

The periodic trends of electron affinity (Figure 11.11.9) shows that chlorine has the most positive electron affinity of any element, which means that more energy is released when an electron is added to a gaseous chlorine atom than to an atom of any other element, EA= 348.6 kJmol^{-1} and the Group 17 elements have the largest values overall. The addition of a second electron to an element is expected to be much less favored since there will be repulsion between the negatively charged electron and the overall negatively charged anion. For example, for O the values are:

$$O_{(g)} + e^{\rightarrow} O^{-}_{(g)} \quad EA = +141\ kJmol^{-1} \tag{11.11.16}$$

$$O^{-}_{(g)} + e^{-} \rightarrow O^{2-})(g) \quad EA = -798\ kJmol^{-1} \tag{11.11.17}$$

David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski ("Quantum States of Atoms and Molecules")

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11.E: Quantum Mechanics and Atomic Structure (Exercises)

11.1: The Wave Theory of Light

Q11.1

What is the wavelength associated with a photon of a light with the energy is $3.6 \times 10^{-19}\ J$?

S11.1

$$E = hv = \frac{hc}{\lambda}$$

$$3.6 \times 10^{-19}\ J = \frac{(6.626 \times 10^{-34}\ J\ s)(3 \times 10^{8}\ ms^{-1})}{\lambda}$$

$$\lambda = 0.55 \times 10^{-7}\ m = 550\ nm$$

Q11.2

Calculate the energy of a photon of a light with the frequency is $6.5 \times 10^{-14}\ s^{-1}$?

S11.2

$$E = hv$$

$$E = (6.626 \times 10^{-34} J\ s)(6.5 \times 10^{-14} s^{-1})$$

$$E = 4.3 \times 10^{-19}\ J$$

Q11.3a

What are the wavelength of the light emitted by atomic hydrogen when the electron move from $n = 5$ to $n = 3$ orbit in the Bohr model?

S11.3a

Bohr model:

$$\frac{1}{\lambda} = R_H \left(\frac{1}{n_a^2} - \frac{1}{n_b^2} \right)$$

$$\frac{1}{\lambda} = (1.09678 \times 10^{-2} nm^{-1}) \left(\frac{1}{9} - \frac{1}{25} \right)$$

$$\lambda = 1,282\ nm$$

Q11.3b

Calculate the different energy between $n = 3$ and $n = 4$ of atomic hydrogen based on Bohr orbits

S11.3b

$$\Delta E = -hcR_H \left(\frac{1}{3^2} - \frac{1}{4^2} \right)$$

$$\Delta E = -6.626 \times 10^{-34} J.s)(2.9979 \times 10^{8}\ m/s)(109,737\ cm^{-1}) \left(\frac{1}{3^2} - \frac{1}{4^2} \right))$$

$$\Delta E = 1.8 \times 10^{-21}\ J$$

Q11.4

Calculate the wavenumber of the wavelength of the light emitted from the $n = 8$ to $n = 6$ transition.

S11.4

This is a simple application of the Rydberg equation

$$\tilde{\nu} R_H \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

with $n_i = 6$ and $n_f = 8$.

$$\tilde{\nu} = 109,737 cm^{-1} \left(\frac{1}{6^2} - \frac{1}{8^2} \right) = 1333.61\ cm^{-1}$$

Q11.5

Calculate the wavelength associated with a 42 g baseball with speed of 80 m/s.

S11.5

$$\lambda = \frac{h}{p} = \frac{h}{mv}$$

$$\lambda = \frac{6.626 \times 10^{34} Js}{(0.042\ kg)(80 m/s)} = 1.97 \times 10^{-34}\ m$$

This is a very small wavelength as expected since a ball behaves rather classically (i.e., non-quantum).

Q11.6

Calculate the energy of a 530-nm photon.

S11.6

$$p = \frac{E}{c}$$

$$\lambda = \frac{h}{p}$$

$$\lambda = \frac{hc}{E}$$

$$E = \frac{hc}{\lambda} = \frac{(6.626 \times 1 -^{-34})(3 \times 10^8)}{530 \times 10^{-9}} = 3.75 \times 10^{-9}\ J$$

11.3: The Photoelectric Effect

Q11.7

Describe Planck's three experimental observations that explain the photoelectric effect.

S11.7

"When light of a certain frequency shines on a clean metal surface, electrons are ejectedd from the metal. Experimentally, it is found that:

1. The number of electrons ejected is proportional to the intensity of light
2. The kinetic energy of the ejected electrons is proportional to the frequency of the ejected light
3. No electrons can be ejected if the frequency of the light is lower than a certain value, called the threshold frequency (nu_o).

Q11.8a

What is the difference between classical and quantum mechanics? Provide the equation relating the energy of emitted radiation to frequency.

S11.8a

Classical mechanics predicts that the radiant energy produced by oscillating objects is continuous. Quantum mechanics predicts that their energy can be viewed as existing in discrete levels. The equation is

$$E = h\nu$$

. Energy is emitted in discrete multiples of $h\nu$, where h = Planck's constant.

Q11.8b

Do you expect the *first* ionization of an atom to be an endothermic process or an exothermic process?

S11.8b

It will be endothermic because energy is needed to ionize the atom.

11.2: Planck's Quantum Theory

Q11.9a

Calculate the wavelength of light with an energy of $5.22 \times 10^{-19}\ J$.

S11.9a

Rearrange the equation

$$E = \frac{hc}{\lambda}$$

so that the unknown value is the wavelength of light

$$\lambda = \frac{hc}{E}$$

$$\lambda = \frac{(6.626 \times 10^{-34} Js)(3.0 \times 10^{8} m/s)}{5.22 \times 10^{-19} J} = 3.81 \times 10^{-7} m = 381 nm$$

Q11.9b

You realize after class that you forgot to write down the final wavelength of your proton. You do, however, remember that the potential difference was 114 V. From this information, figure out the final wavelength:

S11.9b

$\frac{1}{2} mv^2 = eV$

$e = 1.6x10^{-19} C$ This is the charge of the electron
m=9.11x10^{-31}kg
$v = \sqrt{\frac{2eV}{m}}$
$\sqrt{\frac{2(1.6 \cdot 10^{-19})(114)}{1.67 \cdot 10^{-31}}}$
=2.0x10^{9}m/s
$\lambda = \frac{h}{mv}$
$\lambda = \frac{6.626 \cdot 10^{-34}}{(9.11 \cdot 10^{-31})(2 \cdot 10^{9})}$
$\lambda = 3.64 \cdot 10^{-13} m$

Q11.10a

given the uncertainty for position of an electron circling an atom is 0.5A^{0}. Find uncertainty in its velocity?

S11.10a

$$\Delta p \geq h/ 4\pi\Delta x = 6.626 \text{ x } 10^{-34} \text{ Js}/ 4\pi(0.5 \text{ x } 10^{-10}\text{m}) = 1.311.05 \text{ x } 10^{-24}\text{kg m s}^{-1}$$

$$\Delta \text{ v}= \Delta p/ \text{ m} \geq 1.3 \text{ x } 10^{-24} \text{ kg m s}^{-1}/ 9.109 \text{ x } 10^{-31} \text{ kg} = 1 \text{ x } 10^{6} \text{ m s}^{-1}$$

Q11.10

If the uncertainty of measuring the position of an electron is 2.0 Å, what is the uncertainty of simultaneously measuring its velocity? *Hint: What formula deals with uncertainty of measurements?*

11.5: de Broglie's Postulate

11.6: The Heisenberg Uncertainty Principle

11.7: The Schrödinger Wave Equation

Q11.11

A typical mass for a horse is 510 kg, and a typical galloping speed is 22 kilometers per hour. Use these values to answer the following questions.

a. What is the momentum of a galloping horse? What is its wavelength?
b. If a galloping horse's velocity and position are simultaneously measured, and the velocity is measured to within ± 1.0%, what is the uncertainty of its position?
c. Suppose Planck's constant was actually 0.01 J s. How would that change your answers to (a) and (b)? Which values would be unchanged?

Hints:

- *de Broglie's postulate deals with the wave-like properties of particles.*
- *Heisenberg's uncertainty principle deals with uncertainty of simultaneous measurements.*

S11.11

(a)

1. Use the relationship between velocity and momentum to find the momentum.

$$p = mv$$

$$p = 510\ kg \times 22\ \frac{km}{hr} \times \frac{1000\ m}{km} \times \frac{hr}{3600\ s}$$

$$p = 3.1 \times 10^{3}\ \frac{kg\, m}{s}$$

2. Find the de Broglie wavelength.

$$\lambda = \frac{h}{p}$$

$$\lambda = \frac{6.626 \times 10^{-34}\ J\ s}{3.1 \times 10^{3}\ \frac{kg\, m}{s}} \times \frac{\frac{kg\, m^{2}}{s^{2}}}{J}$$

$$\lambda = 2.1 \times 10^{-37}\ m$$

(b)

1. Find the uncertainty of momentum from the uncertainty of velocity.

$$\Delta p = m \Delta v$$

$$\Delta v = 0.01 \times v$$

$$\Delta p = 510\ kg \times 0.01 \times 22\ \frac{km}{hr} \times \frac{1000\ m}{km} \times \frac{hr}{3600\ s}$$

$$\Delta p = 31\, \frac{kg\, m}{s}$$

2. Use Heisenberg's uncertainty principle to find the uncertainty of position.

$$\Delta x \Delta p \geq \frac{h}{4\pi}$$

$$\Delta x \geq \frac{h}{4\pi \Delta p}$$

$$\Delta x \geq \frac{6.626\times 10^{-34}\ J\,s}{4\pi\times 3.1\times 10^{3}\,\frac{kg\,m}{s}}\times\frac{\frac{kg\,m^{2}}{s^{2}}}{J}$$

$$\Delta x \geq 1.7\times 10^{-36}\ m$$

(c)

The calculations that involve Planck's constant (h) will change. This much larger value will make the wave-like properties of the horse more important; its wavelength and uncertainty of position will increase dramatically:

$$\lambda' = \frac{h'}{p} = \frac{0.010\ J\,s}{3.1\times 10^{3}\ \frac{kg\,m}{s}\times\frac{\frac{kg\,m^{2}}{s^{2}}}{J}}$$

$$\lambda' = 3.2\times 10^{-6}\ m = 3200\ nm$$

$$\Delta x' \geq \frac{h'}{4\pi\Delta p} = \frac{0.010\ J\,s}{4\pi\times 3.1\times 10^{3}\,\frac{kg\,m}{s}}\times\frac{\frac{kg\,m^{2}}{s^{2}}}{J}$$

$$\Delta x' \geq 2.6\times 10^{-5} m = 26\ \mu m$$

The momentum would not change.

Q11.12a

how fast must a person weighing 42 kg move through a door 0.5 m wide in order to be diffracted?

S11.12a

$$p = h/\lambda = 6.626 \text{ x } 10^{-34}\ \text{J s}/\ 0.5$$

$$= 3.313 \text{ x } 10^{-34}\ \text{kg m s}^{-1}$$

$$V = p/m = 3.313 \text{ x } 10^{-34} / 42\ \text{kg} = 7.88 \text{ x } 10^{-36}\ \text{ms}^{-1}$$

Q11.12b

When a particle passes through a slit, diffraction occurs if the particle's wavelength is on the same order of magnitude as the width of the slit. At approximately what velocity would a 1670 kg car have to move through the Lincoln Tunnel (6.6 m width) for diffraction to occur? *Hint: How can you find the wavelength of the car?*

S11.12b

1. Use de Broglie's equation to relate velocity to wavelength; solve for velocity.

$$\lambda = \frac{h}{mv}$$

$$v = \frac{h}{m\lambda}$$

2. Set the wavelength equal to the tunnel width and solve.

$$v = \frac{6.626\times 10^{-34}\ J\,s}{1670\ kg\times 6.6\ m}\times\frac{\frac{kg\,m^{2}}{s^{2}}}{J}$$

Answer: the car would have to be driving *very* slowly.

$$v = 6.0\times 10^{-38}\ m/s$$

Q11.13a

The Paschen emission spectrum is the collection of spectral lines emitted by H atoms, where the final state is n = 3. What are the shortest and longest wavelengths (in nm) of Paschen spectral lines? *Hints: The minimum value for* n_i *is 4, the maximum value for* n_i *is infinity and the Rydberg formula describes the emission spectra of hydrogen*

Q11.13b

Spectral lines of Lyman and Balmer series do not overlap. Verify this statement.

S11.13b

A photon has a specific energy according to the energy between the excited and ground state.

E = (1/nf2 - 1/ni2), A = hv

The lyman series is when nf is the ground state or nf =1 and Balmer series is when nf =2

nf = 1 the value , ni from 2 to infinity with the values between 1 and ½. For the balmer series ni is from 3 to infinity the range between 1/4 and 5/36. Thus, these intervals don not overlap --> the energies do not overlap --> the lines in the series cant overlap

Q11.14

Assume the Rydberg constant for He^+ is $9.72x10^{-18}$nm, calculate the wavelength of He^+ ions from n=3 to n=2.

S11.14

$$\frac{1}{\lambda} = R_H \left| \frac{1}{n_i^2} - \frac{1}{n_f^2} \right|$$

$$\frac{1}{\lambda} = 9.72 \times 10^{-18} \left| \frac{1}{3^2} - \frac{1}{2^2} \right|$$

$$\lambda = 7.41 \times 10^{17} nm$$

Q11.15

Derive from the following equation to solve for wavelength.

$$\Delta E = hcR_H (\frac{1}{n_i^2} - \frac{1}{n_f^2})$$

S11.15

$$\Delta E = R_H \left| \frac{1}{n_i^2} - \frac{1}{n_f^2} \right|$$

$$\frac{v}{c} = \Delta E = R_H \left| \frac{1}{n_i^2} - \frac{1}{n_f^2} \right|$$

$$\frac{1}{\lambda} = \frac{v}{c} = \Delta E = R_H \left| \frac{1}{n_i^2} - \frac{1}{n_f^2} \right|$$

$$\lambda = \frac{1}{R_H \left| \frac{1}{n_i^2} - \frac{1}{n_f^2} \right|}$$

Q11.16

Photosynthesis occurs when light excites the electrons in the chloroplasts of leaves. If you flash a light of 500 nm at the plant and assuming your flashlight emits $4.5x10^{20}$ numbers of photons, how much energy in joules was that one flash?

Q11.50

What is an antiatom? How is it different from a regular hydrogen? What will happen if these two collided with one another?

S11.50

An antiatom is a hydrogen atom with reversed electrical charges compared to that of a hydrogen atom. The proton is called an antiproton and it bears a negative charge rather than a positive charge. The electron, or antielectron, has a positive charge rather than a negative charge. As a result, an antiatom and regular hydrogen would obliterate one another should they collide. Subsequent energy would then be released.

Q11.51

A scientist determined the kinetic energy released electrons of cesium metal through a photoelectric experiment. Determine h and the \work function for cesium graphically from the following results:

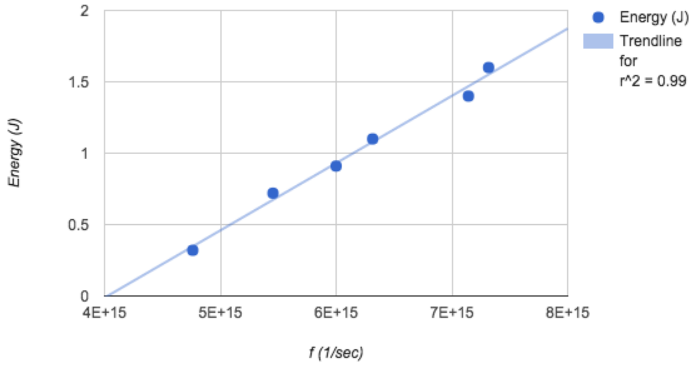
λ/nm	410	420	475	500	550	630
V/volt	1.6	1.4	1.1	0.91	0.72	0.37

S11.51

First, convert wavelength to frequency and volt to energy in J.

f (1/sec)	**Energy (J)**
7.31707×10^{15}	1.6
7.14286×10^{15}	1.4
6.3157×10^{15}	1.1
6×10^{15}	0.91
5.45455×10^{15}	0.72
4.7619×10^{15}	0.32

Then graph the values and determine the linear equation.



The linear equation is

$$y = 4.7 \times 10^{-16} f - 1.89$$

Use the equation below:

hf-ϕ=E$_k$ (max kinetic energy)

h=slope

ϕ= y-intercept

h= 4.7 X 10^{-16}

ϕ= 1.89

Q11.52

Calculate the de Broglie wavelength of a Cl_2 molecule at 300 K.

S11.52

$$v_{rms} = \sqrt{\frac{3RT}{M}}$$

=((3)(8.314)(300)/(70.8X10^{-3} kg) = 325 m/s

$$\lambda = \frac{h}{mv_{rms}}$$

=(6.626X10^{-34} J*s)/[(70.8 amu)(1.66X10^{-27} kg/amu)(325 m/s)] = 1.73 X 10^{-11} m

Q11.53

Consider a balloon with a diameter of $2.5 \times 10^{-5}\ m$. What is the uncertainty of the velocity of an oxygen molecule that is trapped inside.

S11.53

Use the direct application of the uncertainty principle:

$$\Delta x \Delta p \geq \frac{h}{4\pi}$$

Let's consider the molecule has an uncertainly that is $\pm radius$ of the balloon.

$$\Delta x = 1.3 \times 10^{-5}\ m$$

The uncertainty of the momentum of the molecule can be estimated via the uncertainty principle.

$$\Delta p = \frac{h}{4\pi \Delta x} = \frac{(6.626 \times 10^{-34} J * s)}{(4\pi)(1.3 \times 10^{-5}\ m)} = 4.05 \times 10^{-30} kg\, m\, s^{-1}$$

This can be converted to uncertainty in velocity via

$$p = mv$$

or

$$\Delta p = m_e \Delta v$$

with the electron mass m_e equal to $9.109 \times 10^{-31}\ kg$. since the mass of the molecule is **not** uncertain.

$$\Delta v = \frac{\Delta p}{m_e} = \frac{4.05 \times 10^{-30}}{9.109 \times 10^{-31}\ kg} = 4.5\ m/s$$

11.8: Particle in a One-Dimensional Box

Q11.55

What conditions must be satisfied for the Schrodinger's equation for ψ to be an acceptable wavefunction. What are some examples of unacceptable wave functions?

Q11.56

The equation for calculating the energies of the electron in a hydrogen atom or a hydrogenlike ion is given by En = -(2.18 x10^-18 J)Z^2(1/n^2), where Z is the atomic number of the element. One way to modify this equation for many-electron atoms is to replace Z with (Z- [sigma]), where [sigma] is a positive dimensionless quantity called the shielding constant. Consider the lithium atom as an example. The physical significance of sigma that it represents the extent of shielding that the two 1s electrons exert on each other.

Thus the quantity (Z - [sigma]) is appropriated called the "effective nuclear change." Use the first ionization energy of lithium to calculate the value of [sigma].

Q11.57

Calculate the wavelength and frequency of an emitted gamma particle that has energy of 3.11 x 10^12 J mol^-1.

11.9: Quantum-Mechanical Tunneling

11.10: The Schrödinger Wave Equation for the Hydrogen Atom

11.11: Many-Electron Atoms and the Periodic Table

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CHAPTER OVERVIEW

12: The Chemical Bond

Chemical bond refers to the forces holding atoms together to form molecules and solids. This force is of an electric nature, and the attraction between electrons of one atom to the nucleus of another atom contributes to what is known as **chemical bonds**. A chemical bond is a lasting attraction between atoms that enables the formation of chemical compounds and may result from the electrostatic force of attraction between atoms with opposite charges, or through the sharing of electrons as in the covalent bonds. The strength of chemical bonds varies considerably.

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12.1: Lewis Structures

Chemical bond refers to the forces holding atoms together to form molecules and solids. This force is of an electric nature, and the attraction between electrons of one atom to the nucleus of another atom contributes to what is known as **chemical bonds**. Various theories regarding chemical bonds have been proposed over the past 300 years, during which our interpretation of the world has also changed. Some old concepts such as Lewis dot structure and valency are still rather useful in our understanding of the chemical properties of atoms and molecules, and new concepts involving quantum mechanics of chemical bonding interpret modern observations very well. You learn new concepts such as bond length, bond energy, bond order, covalent bond, ionic bond, polar and non-polar bond etc. These concepts help you understand the material world at the molecular level.

Of the three primary theories of bonding discussed in this class (Lewis Theory, Valance Bond Theory and Molecular orbital theory), Lewis theory does not take full advantage of the quantum mechanical concepts discussed previously. Key to this theory is the Lewis Structure, which is a very simplified representation of the electrons in a molecule and is use to show how the electrons are arranged around individual atoms in a molecule. Between 1916 and 1919, Gilbert Newton Lewis, Walther Kossel, and Irving Langmuir formulated a theory to explain chemical bonding. This theory is now called **Lewis Theory** and it is based on the following five principles:

1. **Valence electrons**, or the electrons in the outermost electron shell, have an essential role in chemical bonding.
2. **Ionic bonds** are formed between atoms when electrons are transferred from one atom to another. Ionic bond is a bond between nonmetals and metals .
3. **Covalent bonds** are formed between atoms when pairs of electrons are shared between atoms. A covalent bond is between two nonmetals.
4. Electrons are transferred/shared so that each atom may reach a more stable electron configuration, i.e., the noble gas configuration which contains 8 valence electrons; this is called **octet rule**.
5. Although many different Lewis structures can be constructed, those that are most stable have the lowest formal charge on the atoms.

Writing out Lewis structures can be at times, tricky and somewhat difficult. Moreover, a compound can have multiple Lewis Structures that contribute to the shape of the overall compound, so one Lewis structure of a compound may not necessarily be exactly what the compound looks like. If you need a refresher on how to constructing Lewis Structures consult the following Modules: Writing Lewis Structures, Lewis Structures I and Lewis Structures II.

In Lewis Structures, valence electrons are represented as dots and only outer-shell electrons are considered (e.g., the valence electrons and not the core electrons). Single (covalent) bonds are made up of two shared electrons and are represented by two dots between the bonded atoms or a single line. Double bonds and triple bonds are represented as two and three lines/(pairs of electrons), respectively. Lone pairs on the outer rims of an atom are represented as two dots. This is because they are the ones involved in chemical reactions. For the 2nd and 3rd periods elements, the number of valence electrons range from 1 to 8. Lewis dot structure for them are as indicated:

$$\dot{\mathrm{Li}} \quad \underset{\cdot}{\dot{\mathrm{Be}}} \quad \cdot\dot{\mathrm{B}}\cdot \quad \cdot\underset{\cdot}{\dot{\mathrm{C}}}\cdot \quad \cdot\underset{\cdot}{\dot{\mathrm{N}}}: \quad :\underset{\cdot}{\dot{\mathrm{O}}}: \quad :\underset{\cdot}{\ddot{\mathrm{F}}}: \quad :\underset{\cdot\cdot}{\ddot{\mathrm{Ne}}}: \tag{12.1.1}$$

Lewis made the valence electron visible with dots. Other examples include the following molecules:

$$\mathrm{H}:\mathrm{H} \qquad \mathrm{H}:\underset{\cdot\cdot}{\ddot{\mathrm{O}}}:\mathrm{H} \qquad \mathrm{H}:\underset{\cdot\cdot}{\ddot{\mathrm{F}}}: \qquad \begin{matrix} & \mathrm{H} & \\ \mathrm{H}: & \underset{\cdot\cdot}{\ddot{\mathrm{N}}} & :\mathrm{H} \end{matrix} \qquad \begin{matrix} & \mathrm{H} & \\ \mathrm{H}: & \underset{\cdot\cdot}{\ddot{\mathrm{C}}} & :\mathrm{H} \\ & \mathrm{H} & \end{matrix} \qquad :\mathrm{N}:::\mathrm{N}: \qquad :\ddot{\mathrm{O}}::\ddot{\mathrm{O}}: \qquad :\ddot{\mathrm{F}}:\ddot{\mathrm{F}}: \qquad :\ddot{\mathrm{O}}::\mathrm{C}::\ddot{\mathrm{O}}:$$

Note

Lewis structure does NOT attempt to explain the geometry of molecules, how the bonds form, or how the electrons are shared between the atoms. It is the simplest and most limited theory on electronic structure.

Principle 1: Valence Electrons

The electrons of an atom can divided into two categories: valence and core electrons. Valence electrons are those occupying the outermost shell or highest energy level of an atom while core electrons are those occupying the innermost shell or lowest energy level. This difference greatly influences the role of the two types of electrons in a chemical reaction. Generally, valence electrons can participate in the formation of chemical bonding, but core electrons cannot. While core electrons are not involved in bonding, they do have an influence on the chemical reactivity of an atom.

The electron configuration of the oxygen atoms is

$$O:\ 1s^2 2s^2 2p^4 \tag{12.1.2}$$

As discussed before, this configuration may be shorted

$$O:\ [He]2s^2 2p^4 \tag{12.1.3}$$

where the $[He]$ stands for the configuration of helium ($1s^2 2s^2$). The $1s$ electrons in oxygen (Equation 12.1.2) do not participate in bonding, i.e., chemistry, and are called **core electrons**. The other electrons (i.e., the $2s^2 2p^4$ part) are call **valence electrons** and are responsible for the making and breaking of chemical bonds.

The configuration of calcium with 20 electrons can be written

$$Ca:\ [Ar]4s^2 \tag{12.1.4}$$

where the $[Ar]$ stands for the configuration of argon ($1s^2 2s^2 2p^6 3s^2 3p^6$). Electronic configurations that are the same as noble gases are very stable since they have a full octet (except helium with a full 1s orbital). The electrons in the argon-like closed shell of Equation 12.1.4 are the core electrons and the two electrons in the 4s orbital are valence electrons.

✓ Example 12.1.1: Cobalt

What are the core and valence electrons in cobalt?

Solution

Start by writing the electron configuration of cobalt (i.e., 27 electrons):

$$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^7$$

However, argon has the electronic structure $1s^2 2s^2 2p^6 3s^2 3p^6$, so we can write the configuration of cobalt as

$$[Ar]4s^2 3d^7$$

The two electrons in the $4s$ orbital and the seven electrons in the 3d are the valence electrons: all others are core electrons.

Principle 2: Ionic Bonding

In ionic bonding, electrons are transferred from one atom to another resulting in the formation of positive and negative ions. The electrostatic attractions between the positive and negative ions hold the compound together. The predicted overall energy of the ionic bonding process, which includes the ionization energy of the metal and electron affinity of the nonmetal, is usually positive, indicating that the reaction is endothermic and unfavorable. However, this reaction is highly favorable because of their electrostatic attraction.

The energy of the electrostatic attraction (E), a measure of the force's strength, is inversely proportional to the internuclear distance between the charged particles (r):

$$E = k\frac{Q_1 Q_2}{r} \tag{12.1.5}$$

where each ion's charge is represented by the symbol Q. The proportionality constant k is equal to 2.31 × 10^{-28} J·m.

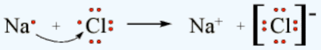
✓ Example 12.1.2: Ionic Bonding in NaCl

For example, in the reaction of Na (sodium) and Cl (chlorine), each Cl atom takes one electron from a Na atom. Therefore each Na becomes a Na^+ cation and each Cl atom becomes a Cl^- anion. Due to their opposite charges, they attract each other to form an ionic lattice. The formula (ratio of positive to negative ions) in the lattice is **NaCl**.

$$2Na_{(s)} + Cl_{2(g)} \rightarrow 2NaCl_{(s)}$$

Sodium has one valence electron and chlorine has seven valence electrons; the two elements react such that the chlorine atom takes the valence electron from the sodium atom leaving the chlorine atom with one extra electron and thus negatively charged and the Sodium atom without an electron and thus positively charged. The two atoms then become ions and because of their opposite charges the ions are held together in an ionic bond (Equation 12.1.5).

The chlorine has a high affinity for electrons, and the sodium has a low ionization potential. Thus the chlorine gains an electron from the sodium atom. The Lewis Structure of this reaction is (here we will consider one chlorine atom, rather than Cl_2) is:

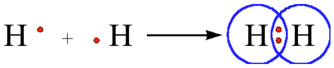


The arrow indicates the transfer of the electron from sodium to chlorine to form the Na^+ metal ion and the Cl^- chloride ion

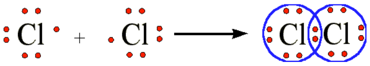
Principle 3: Covalent Bonding

Covalent bonding occurs when pairs of electrons are shared by atoms. Atoms will covalently bond with other atoms in order to gain more stability, which is gained by forming a full electron shell. By sharing their outer most (valence) electrons, atoms can fill up their outer electron shell and gain stability. Nonmetals will readily form covalent bonds with other nonmetals in order to obtain stability, and can form anywhere between one to three covalent bonds with other nonmetals depending on how many valence electrons they posses. Although it is said that atoms share electrons when they form covalent bonds, they do not usually share the electrons equally.

The diatomic hydrogen molecule (H_2) is the simplest model of a covalent bond, and is represented in Lewis structures as:

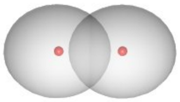


The ***shared pair*** of electrons provides ***each*** hydrogen atom with two electrons in its valence shell (the 1*s*) orbital. In a sense, it has the electron configuration of the noble gas helium. When two chlorine atoms covalently bond to form Cl_2Cl_2, the following sharing of electrons occurs:



Each chlorine atom shared the bonding pair of electrons and achieves the electron configuration of the noble gas argon. In Lewis structures the bonding pair of electrons is usually displayed as a line, and the unshared electrons as dots:

The shared electrons are not located in a fixed position between the nuclei. In the case of the H_2H_2 compound, the electron density is concentrated between the two nuclei:



The two atoms are bound into the H_2H_2 molecule mainly due to the attraction of the positively charged nuclei for the negatively charged electron cloud located between them.

✓ Example 12.1.3: The Chlorate Ion

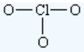
Draw the Lewis Structure for the chlorate ion (ClO_3^-).

Solution

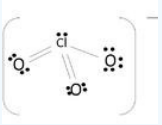
First, lets find the how many valence electrons chlorate has:

$$ClO_3^- : 7\ e^-(\text{from Cl}) + 3(6)\ e^-(\text{from 3 O atoms}) + 1\ (\text{from the total charge of -1}) = 26$$

There are 26 valence electrons. Next lets draw the basic framework of the molecule:



The molecule uses covalent bonds to hold together the atoms to the central Chlorine. The remaining electrons become non-bonding electrons. Since 6 electrons were used for the bonds, the 20 others become those un-bonding electrons to complete the octet:



The oxygen atom's shells fill up with 18 electrons, and the other 2 complete Chlorine's octet

Example 12.1.4: Formaldehyde

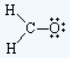
Constructing the Lewis Structure of the formaldehyde (H_2CO) molecule.

Solution

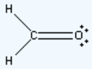
First find number of valence electrons:

H_2CO: 2(1) e^- (from the H atoms) + 4 e^- (from the C atom) + 6 e^- (from the O atom)

There are 12 valence electrons. Next draw out the framework of the molecule:



To satisfy the octet of Carbon, one of the pairs of electrons on Oxygen must be moved to create a double bond with Carbon. Therefore our Lewis Structure would look as it does below:



The Hydrogen atoms are each filled up with their two electrons and both the Carbon and the Oxygen atoms' octets are filled.

Principle 4: The Octet Rule

The **octet rule** is a chemical **rule** of thumb that reflects observation that atoms of main-group elements tend to combine in such a way that each atom has eight electrons in its valence shell, giving it the same electronic configuration as a noble gas. The **Octet Rule** requires all atoms in a molecule to have 8 valence electrons--either by sharing, losing or gaining electrons--to become stable. For covalent bonds, atoms to share their electrons with each other to satisfy the octet rule. It requires eight electrons because that is the amount of electrons needed to fill a *s*- and *p*- orbital (electron configuration); also known as a noble gas configuration. Although it is important to remember the "magic number" is 8, but there are many octet rule exceptions.

Octet Rule

A stable arrangement is attended when the atom is surrounded by eight electrons. This octet can be made up by own electrons and some electrons which are donated (e.g, ionic bonding) or shared (covalent bonding). An atom continues to form bonds until an octet of electrons is reached.

For the first rows in the periodic table, the magic number 8 can easily be explained from quantum mechanics of the multiple electron atoms discussed previously. In particular, electrons possess four quantum numbers (usually n, l, m_l, and m_s), which are restricted as such:

$$n = 1, 2, 3, \ldots \tag{12.1.6}$$

$$l = 0, 1, 2, \ldots, n-1 \tag{12.1.7}$$

$$m_l = -l, -l+1, \ldots, 0, \ldots, l-1, l \tag{12.1.8}$$

$$m_s = -\frac{1}{2}, \frac{1}{2} \tag{12.1.9}$$

where

- n is the principal quantum number (dealing with energy states),
- l is the orbital quantum number (dealing with subshells),
- m_l is the orbital magnetic quantum number (direction of l) and
- m_s is the spin quantum number (direction of spin).

By the Pauli's Exclusion Principle all of these numbers cannot be the same for any two electrons in an atom. So in the $n = 2$ shell you can have two possible values for l, one possible value for m_l when $l = 0$, three possible values for m_l when $l = 1$, and two possible values for m_s. This sums to a total of eight possible value vectors:

$$(1+3) \cdot 2 = 8 \tag{12.1.10}$$

In the $n = 3$ shell, the Octet rule also holds for $l < 2$, which gives you sort of the same combinatorics all over again.

Since the quantum numbers cannot be the same for any electrons in an atom, adding an extra electron to an atom with eight electrons in its outermost shell forces the electron to occupy an orbital with a higher principal quantum number (n). Since the binding energy of the electron increases with n, this is energetically unfavorable to binding with an atom that has more space in its outermost shell. For example, for the nonmetals (and the 's' block metals) to achieve an octet, the number of valence electrons is equal to the group number (Table $12.1.1$).

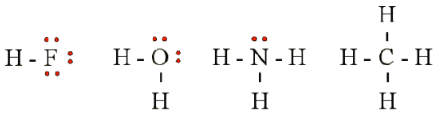
Table 12.1.1: Select electronic properties of p-block elements of the 2nd row.

Element	Group	Valence electrons	Number of Covalent Bonds needed to form valence octet
F	17	7	1
O	16	6	2
N	15	5	3
C	14	4	4

Note: The 18 Electron Rule

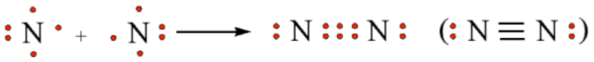
The octet rule is not a law and it only works for a handful of elements, mainly the second-row p-block ones; there are many exceptions. Transition metals compounds often have 18 electrons on the metal atom because eighteen is the number of electrons in the nearest noble gas configuration in transition metals, which includes s + p + d electrons. The second and third row of transition metals have f electrons, too, but we usually simplify and don't worry about those electrons for electron counting purposes; we treat them like core electrons, not valence electrons.

Lewis theory successfully describe the covalent interactions between various nonmetal elements. Examples of hydride compounds of the elements in Table 12.2.1 (covalent compounds with hydrogen):



The sharing of a pair of electrons represents a single covalent bond, usually just referred to as a ***single bond***. However, in many molecules atoms attain complete octets by sharing more than one pair of electrons between them.

- Two electron pairs shared a ***double bond***
- Three electron pairs shared a ***triple bond***



Because each nitrogen contains five valence electrons, they need to share three pairs to each achieve a valence octet. The strong nitrogen triple bond makes the molecule fairly inert. Moreover, the N - N bond distance in N_2 is 1.10 Å, which is appreciably shorter than the average N-N single bonds (14.7Å).

Principle 5: Formal Charges

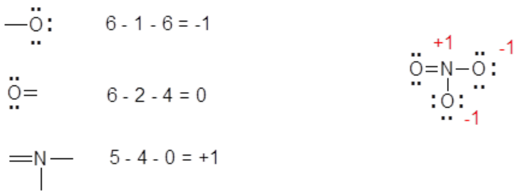
It is sometimes possible to write more than one Lewis structure for a substance that does not violate the octet rule, as we saw for CH_2O, but not every Lewis structure may be equally reasonable. In these situations, we can choose the most stable Lewis structure by considering the formal charge on the atoms, which is the difference between the number of valence electrons in the free atom and the number assigned to it in the Lewis electron structure. The formal charge is a way of computing the charge distribution within a Lewis structure; the sum of the formal charges on the atoms within a molecule or an ion must equal the overall charge on the molecule or ion. A formal charge does *not* represent a true charge on an atom in a covalent bond but is simply used to predict the most likely structure when a compound has more than one valid Lewis structure. To calculate formal charges, we assign electrons in the molecule to individual atoms according to these rules:

- Nonbonding electrons are assigned to the atom on which they are located.
- Bonding electrons are divided equally between the bonded atoms.

For each atom, we then compute a formal charge:

$$\text{formal charge} = \underset{(free\ atom)}{valence\ e^-} - \underset{(atom\ in\ Lewis\ structure)}{\left(nonbonding\ e^- + \frac{bonding\ e^-}{2}\right)} \tag{12.1.11}$$

The most favorable Lewis Structure has the smallest formal charge for the atoms, and negative formal charges tend to come from more electronegative atoms. An **example** of determining formal charge can be seen below with the nitrate ion, NO_3^-:



- The double bonded O atom has *6 electrons*: 4 non-bonding and 2 bonding (one electron for each bond). Since O should have 6 electrons, the *formal charge is 0*.
- The two singly bonded O atoms each have *7 electrons*: 6 non-bonding and 1 bonding electron. Since O should have 6 electrons, and there is one extra electron, those O atoms each have *formal charges of -1*.
- The N atom has 4 electrons: 4 bonding and 0 non-bonding electrons. Since N should have 5 electrons and there are only 4 electrons for this N, the N atom has a *formal charge of +1*.
- The charges add up to the overall charge of the ion. 0 + (-1) + (-1) + 1 = -1. Thus, these charges are correct, as the overall charge of nitrate is -1.

In general you want the fewest number of formal charges possible, i.e. formal charges of 0 for as many of the atoms in a structure as possible. Also the formal charges should match the electronegativity of the atom, that is negative charges should be on the more electronegative atoms and positive charges on the least electronegative atoms if possible. Charges of -1 and +1 on adjacent atoms can usually be removed by using a lone pair of electrons from the -1 atom to form a double (or triple) bond to the atom with the +1 charge.

Summary

Lewis Structures are visual representations of the bonds between atoms and illustrate the lone pairs of electrons in molecules. They can also be called Lewis dot diagrams and are used as a simple way to show the configuration of atoms within a molecule. Electrons are shown as "dots" or for bonding electrons as a line between the two atoms. The goal is to obtain the "best" electron configuration, *i.e.* the octet rule and formal charges need to be satisfied. Lewis structures can also be useful in predicting molecular geometry in conjunction with hybrid orbitals. A compound may have multiple resonance forms that are also all correct Lewis structures. This section will discuss the rules for writing out Lewis structures correctly.

Contributors and Attributions

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- Andreas Hagen (via StackExchange)

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12.2: Valence Bond Theory

Valence bond (VB) theory is one of two basic theories, along with molecular orbital (MO) theory, that were developed to use the methods of quantum mechanics to explain chemical bonding. It focuses on how the atomic orbitals of the dissociated atoms combine to give individual chemical bonds when a molecule is formed. In contrast, molecular orbital theory, which will be discussed elsewhere, predict wavefunctions that cover the entire molecule.

The simplest case to consider is the hydrogen molecule, H_2. When we say that the two hydrogen nuclei share their electrons to form a covalent bond, what we mean in VB theory terms is that the two spherical 1*s* orbitals (the grey spheres in Figure $12.2.1$) overlap and contain two electrons.

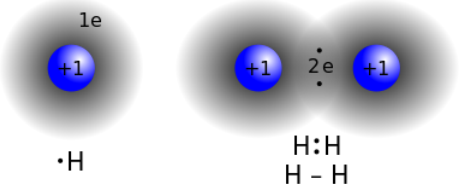

Figure $12.2.1$: These two electrons are now attracted to the positive charge of both of the hydrogen nuclei, with the result that they serve as a sort of 'chemical glue' holding the two nuclei together. from Wikipedia (credit: Jacek FH)

How far apart are the two nuclei? If they are too far apart, their respective 1*s* orbitals cannot overlap, and thus no covalent bond can form - they are still just two separate hydrogen atoms. As they move closer and closer together, orbital overlap begins to occur, and a bond begins to form. This lowers the **potential energy** of the system, as new, *attractive* positive-negative electrostatic interactions become possible between the nucleus of one atom and the electron of the second (Figure $12.2.2$). However, something else is happening at the same time: as the atoms get closer, the *repulsive* positive-positive interaction between the two nuclei also begins to increase.

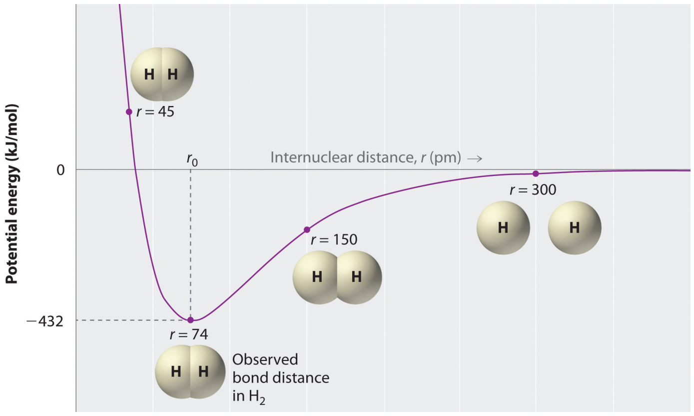

Figure $12.2.2$: A Plot of Potential Energy versus Internuclear Distance for the Interaction between Two Gaseous Hydrogen Atoms. At long distances, both attractive and repulsive interactions are small. As the distance between the atoms decreases, the attractive electron–proton interactions dominate, and the energy of the system decreases. At the observed bond distance, the repulsive electron–electron and proton–proton interactions just balance the attractive interactions, preventing a further decrease in the internuclear distance. At very short internuclear distances, the repulsive interactions dominate, making the system less stable than the isolated atoms.

At first this repulsion is more than offset by the attraction between nuclei and electrons, but at a certain point, as the nuclei get even closer, the repulsive forces begin to overcome the attractive forces, and the potential energy of the system rises quickly. When the two nuclei are 'too close', we have an unstable, high-energy situation. There is a defined optimal distance between the nuclei in which the potential energy is at a minimum, meaning that the combined attractive and repulsive forces add up to the greatest overall attractive force. This optimal internuclear distance is the **bond length**; the distance is 74 pm for H_2. Likewise, the difference in potential energy between the lowest energy state (at the optimal internuclear distance) and the state where the two atoms are completely separated is called the **bond dissociation energy,** or, more simply**, bond strength**; the H_2 bond strength is 435 kJ/mol.

A comparison of some bond lengths and energies is shown in Table $12.2.1$. We can find many of these bonds in a variety of molecules, and this table provides average values. For example, breaking the first C–H bond in CH4 requires 439.3 kJ/mol, while breaking the first C–H bond in $\mathrm{H{-}\,CH_2C_6H_5}$ (a common paint thinner) requires 375.5 kJ/mol.

Table 12.2.1: Representative Bond Energies and Lengths

Bond	Length (pm)	Energy (kJ/mol)		Bond	Length (pm)	Energy (kJ/mol)
H–H	74	436		C–O	140.1	358
H–C	106.8	413		$\mathrm{C=O}$	119.7	745
H–N	101.5	391		$\mathrm{C\equiv O}$	113.7	1072
H–O	97.5	467		H–Cl	127.5	431
C–C	150.6	347		H–Br	141.4	366
$\mathrm{C=C}$	133.5	614		H–I	160.9	298
$\mathrm{C\equiv C}$	120.8	839		O–O	148	146
C–N	142.1	305		$\mathrm{O=O}$	120.8	498
$\mathrm{C=N}$	130.0	615		F–F	141.2	159
$\mathrm{C\equiv N}$	116.1	891		Cl–Cl	198.8	243

✓ Example 12.2.1: A Morse Potential Approximation

The Morse potential, named after physicist Philip M. Morse, is a convenient interatomic interaction approximation for the potential energy of a diatomic molecule.

$$V(r) = D_e\left[1 - e^{-\beta(r-r_e)}\right]^2$$

Here r is the distance between the atoms, r_e is the equilibrium bond distance, D_e is the well depth (defined relative to the dissociated atoms), and β controls the 'width' of the potential (the smaller β is, the larger the well). For H_2, the equilibrium bond length $r_e = 74.1\ pm$, the bond energy $D_e = 7.61 \times 10^{-19}\,J$, and the Morse potential parameter $\beta = 0.0193\ pm^{-1}$.

The force on the system is given by

$$F(r) = -\frac{dV(r)}{dr}$$

Calculate the force for H_2 and explain the status of the system (e.g., compressing, expanding, or stationary) at:

a. 45 pm,
b. 74 pm,
c. 150 pm, and
d. 500 pm.

Overlap

Valence bond theory describes a covalent bond as the overlap of half-filled atomic orbitals (each containing a single electron) that yield a pair of electrons shared between the two bonded atoms. We say that orbitals on two different atoms overlap when a portion of one orbital and a portion of a second orbital occupy the same region of space. According to valence bond theory, a covalent bond results when two conditions are met:

1. an orbital on one atom overlaps an orbital on a second atom and
2. the single electrons in each orbital combine to form an electron pair.

The mutual attraction between this negatively charged electron pair and the two atoms' positively charged nuclei serves to physically link the two atoms through a force we define as a covalent bond. The strength of a covalent bond depends on the extent of overlap of the orbitals involved. Orbitals that overlap extensively form bonds that are stronger than those that have less overlap.

In addition to the distance between two orbitals, the orientation of orbitals also affects their overlap (other than for two *s* orbitals, which are spherically symmetric). Greater overlap is possible when orbitals are oriented such that they overlap on a direct line between the two nuclei. Figure 12.2.3 illustrates this for two *p* orbitals from different atoms; the overlap is greater when the orbitals overlap end to end rather than at an angle.

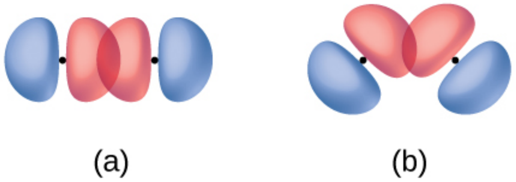

Figure 12.2.3: (a) The overlap of two p orbitals is greatest when the orbitals are directed end to end. (b) Any other arrangement results in less overlap. The dots indicate the locations of the nuclei.

The overlap of two *s* orbitals (as in H_2), the overlap of an *s* orbital and a *p* orbital (as in HCl), and the end-to-end overlap of two *p* orbitals (as in Cl_2) all produce sigma bonds (σ bonds), as illustrated in Figure 12.2.4. A σ bond is a covalent bond in which the electron density is concentrated in the region along the internuclear axis; that is, a line between the nuclei would pass through the center of the overlap region. Single bonds in Lewis structures are described as σ bonds in valence bond theory.

Three diagrams are shown and labeled “a,” “b,” and “c.” Diagram a shows two spherical orbitals lying side by side and overlapping. Diagram b shows one spherical and one peanut-shaped orbital lying near one another so that the spherical orbital overlaps with one end of the peanut-shaped orbital. Diagram c shows two peanut-shaped orbitals lying end to end so that one end of each orbital overlaps the other.

Figure 12.2.4: Sigma (σ) bonds form from the overlap of the following: (a) two s orbitals, (b) an s orbital and a p orbital, and (c) two p orbitals. The dots indicate the locations of the nuclei.

A pi bond (π bond) is a type of covalent bond that results from the side-by-side overlap of two *p* orbitals, as illustrated in Figure 12.2.5. In a π bond, the regions of orbital overlap lie on opposite sides of the internuclear axis. Along the axis itself, there is a node, that is, a plane with no probability of finding an electron.

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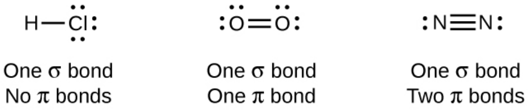
" style="width: 325px; height: 115px;" width="325px" height="115px" src="/@api/deki/files/56400/CNX_Chem_08_01_pi.jpg">

Figure 12.2.5: Pi (π) bonds form from the side-by-side overlap of two p orbitals. The dots indicate the location of the nuclei.

While all single bonds are σ bonds, multiple bonds consist of both σ and π bonds. As the Lewis structures in suggest, O_2 contains a double bond, and N_2 contains a triple bond. The double bond consists of one σ bond and one π bond, and the triple bond consists of one σ bond and two π bonds. Between any two atoms, the first bond formed will always be a σ bond, but there can only be one σ bond in any one location. In any multiple bond, there will be one σ bond, and the remaining one or two bonds will be π bonds. These bonds are described in more detail later in this chapter.



As seen in Table 12.2.2, an average carbon-carbon single bond is 347 kJ/mol, while in a carbon-carbon double bond, the π bond increases the bond strength by 267 kJ/mol. Adding an additional π bond causes a further increase of 225 kJ/mol. We can see a similar pattern when we compare other σ and π bonds. Thus, each individual π bond is generally weaker than a corresponding σ bond between the same two atoms. In a σ bond, there is a greater degree of orbital overlap than in a π bond.

✓ Counting σ and π Bonds

Butadiene, C_6H_6, is used to make synthetic rubber. Identify the number of σ and π bonds contained in this molecule.

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Butadiene

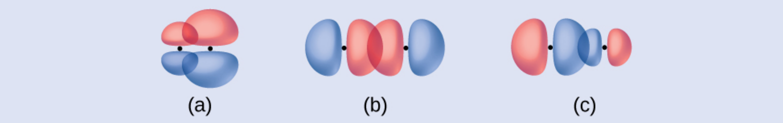
Solution

There are six σ C–H bonds and one σ C–C bond, for a total of seven from the single bonds. There are two double bonds that each have a π bond in addition to the σ bond. This gives a total nine σ and two π bonds overall.

? Exercise 12.2.2

Identify each illustration as depicting a σ or π bond:

a. side-by-side overlap of a 4*p* and a 2*p* orbital
b. end-to-end overlap of a 4*p* and 4*p* orbital
c. end-to-end overlap of a 4*p* and a 2*p* orbital



Answer

(a) is a π bond with a node along the axis connecting the nuclei while (b) and (c) are σ bonds that overlap along the axis.

The Valence Bond Wavefunction

In the hydrogen molecule, VB theory uses two electrons (electron 1 and electron 2) in two 1s atomic orbitals (ψ_a and ψ_b) on the hydrogen atoms(atom a and atom b). The simplest description of a H_2 molecule with two electrons and two nuclei is

$$\psi_{simple} = \psi_a(1)\psi_b(2) \tag{12.2.1}$$

Equation 12.2.1 means electron 1 is in ψ_a of atom a and electron 2 is in ψ_a on the atom b. Where ψ_a and ψ_b may be the $1s$ orbitals as the simplest wavefunction ($n = 1$, $l = 0$, m_l). The ψ_{simple} wavefunction predicts an energy that is about 6% of the experimental value at a bond length of 0.90 pm, which is considerably longer than the experimental value of 0.74 pm (Table 12.2.1). However, Equation 12.2.1 does not address the *indistinguishability* of the problem, i.e, we **cannot** distinguished each electron from the other.

Distinguishable vs. Indistinguishable Particles

Assume you have two particle A and B in states 1 and 2. If the two particle are *distinguishable*, then by exchanging the particles A and B, you will obtain a new state that will have the same properties as the old state. However, for *indistinguishable* particles, exchanging A and B is a transformation that does nothing and you have the same physical state. This means that for indistinguishable particles, particle labels are unphysical and they represent a redundancy in describing the physical state.

To account for the indistinguishable nature of the two electrons in the system, a covalent wavefunction that is better than Equation 12.2.1 can be constructed (ignoring spin effect):

$$\psi_{covalent} = \psi_a(1)\psi_b(2) + \psi_a(2)\psi_b(1) \tag{12.2.2}$$

Equation 12.2.2 means electron 1 is sometimes in ψ_a on atom a and electron 2 is on the atom b (left term of right hand side of Equation) and sometime electron 1 is sometimes in ψ_b on atom b and electron 2 is in ψ_a on the atom a (right term of right hand side of Equation). Notice that in contrast to Equation 12.2.1, if the two electron labels are switched, the wavefunction in Equation 12.2.2 does not change. The potential energy curve for the $\psi_{covalent}$ wavefunction predicts a bond energy that is about 72% at a bond length of 0.87 pm (Table 12.2.2), so the $\psi_{covalent}$ wavefunction is more accurate than ψ_{simple}.

To be more accurate within VB theory, the possibility that both electrons may be on atom a ($\psi_a(1)\psi_a(2)$) or on atom b ($\psi_b(1)\psi_b(2)$) should also be taken into account. This introduces an ionic contribution:

$$\psi_{ionic} = \psi_a(1)\psi_a(2) + \psi_b(2)\psi_b(1) \tag{12.2.3}$$

Notice that Equation 12.2.3 addresses indistinguishability since the wavefunction is unchanged if the two electron labels are switched. The more complete VB wavefunction is a linear combination of both $\psi_{covalent}$ and ψ_{ionic}:

$$\psi_{AB} = \Psi_{covalent} + \lambda\psi_{ionic} \tag{12.2.4}$$

where λ quantifies the amount of ionic character to the bond, e.g., if $\lambda = 0$, then the bond is purely covalent. The potential energy curve for the ψ_{AB} wavefunction predicts a bond energy that is ~80% of the experimental value and a reasonably accurate bond length of 0.77 pm (Table 12.2.1). Additional tinkering with the wavefunction leads to even better results, but is beyond the scope of this discussion. It should be noted that the wavefunctions in Equations 12.2.2, 12.2.3, and 12.2.4 are unnormalized.

Table 12.2.2: Valence Bond Theory Results for H_2

Wavefunction	Bond Energy (kJ mol-1)	Bond Length (pm)
Experiment	435	0.74
ψ_{simple}	25	0.90
$\psi_{covalent}$	301	0.87
ψ_{AB}	335	0.77

Two-Atom Bonds

The central gist of VB theory is that a covalent bond is formed between the **two** atoms by the overlap of half filled valence **atomic orbitals** of each atom containing one unpaired electron.

Example 12.2.3: Percent Ionic Character

Calculate the relative fraction of the contribution of the ionic character to the VB wavefunction. Assuming that the ionic character in HBr bond is 20%.

Solution

From Equation 12.2.4, the percent ionic character is given by:

$$\frac{\lambda^2}{1+\lambda^2} \times 100\%$$

Therefore,

$$20\% = 100\% \frac{\lambda^2}{1+\lambda^2}$$

$$20\% + 20\%\lambda^2 = 100\%\lambda^2$$

$$20\% = 100\%\lambda^2 - 20\lambda^2$$

$$20\% = 80\%\lambda^2$$

Therefore,

$$\lambda^2 = \frac{20}{80}$$

Hence, $\lambda = \sqrt{20/80} = 0.5$ and the fraction of contribution of ionic character to ψ_{AB} is 0.5 or 50%.

Linus Pauling used the pair bonding ideas of Lewis together with Heitler–London theory to develop two key concepts in VB theory: **resonance** and **orbital hybridization**. These will be addressed in later Modules.

Summary

Valence bond theory describes bonding as a consequence of the overlap of two separate atomic orbitals on different atoms that creates a region with one pair of electrons shared between the two atoms. When the orbitals overlap along an axis containing the nuclei, they form a σ bond. When they overlap in a fashion that creates a node along this axis, they form a π bond.

Contributors and Attributions

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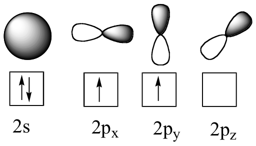
12.3: Hybridization of Atomic Orbitals

Hybridization was introduced to explain molecular structure when the valence bond theory failed to correctly predict them. It is experimentally observed that bond angles in organic compounds are close to 109°, 120°, or 180°. According to Valence Shell Electron Pair Repulsion (VSEPR) theory, electron pairs repel each other and the bonds and lone pairs around a central atom are generally separated by the largest possible angles.

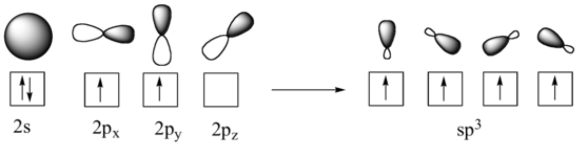
In this section, we will use a model called **valence bond theory** to describe bonding in molecules. In this model, bonds are considered to form from the overlapping of two atomic orbitals on different atoms, each orbital containing a single electron. In looking at simple inorganic molecules such as H_2 or HF, our present understanding of s and p atomic orbitals will suffice. In order to explain the bonding in organic molecules, however, we will need to introduce the concept of **hybrid orbitals**.

Hybrid orbitals: sp^3 hybridization and tetrahedral bonding

Now let’s turn to methane, the simplest organic molecule. Recall the valence electron configuration of the central carbon:



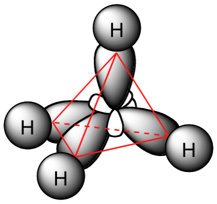
This picture, however, is problematic. How does the carbon form four bonds if it has only two half-filled *p* orbitals available for bonding? A hint comes from the experimental observation that the four C-H bonds in methane are arranged with tetrahedral geometry about the central carbon, and that each bond has the same length and strength. In order to explain this observation, valence bond theory relies on a concept called **orbital hybridization**. In this picture, the four valence orbitals of the carbon (one 2*s* and three 2*p* orbitals) combine mathematically (remember: orbitals are described by equations) to form four equivalent **hybrid orbitals**, which are named **sp^3 orbitals** because they are formed from mixing one s and three p orbitals. In the new electron configuration, each of the four valence electrons on the carbon occupies a single sp^3 orbital.



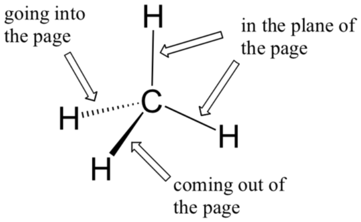
The sp^3 hybrid orbitals, like the *p* orbitals of which they are partially composed, are oblong in shape, and have two lobes of opposite sign. Unlike the *p* orbitals, however, the two lobes are of very different size. The larger lobes of the sp^3 hybrids are directed towards the four corners of a tetrahedron, meaning that the angle between any two orbitals is 109.5º.

This geometric arrangement makes perfect sense if you consider that it is precisely this angle that allows the four orbitals (and the electrons in them) to be as far apart from each other as possible. This is simply a restatement of the Valence Shell Electron Pair Repulsion (VSEPR) theory that you learned in General Chemistry: electron pairs (in orbitals) will arrange themselves in such a way as to remain as far apart as possible, due to negative-negative electrostatic repulsion.

Each C-H bond in methane, then, can be described as an overlap between a half-filled 1*s* orbital in a hydrogen atom and the larger lobe of one of the four half-filled sp^3 hybrid orbitals in the central carbon. The length of the carbon-hydrogen bonds in methane is 1.09 Å (1.09 x 10^{-10} m).



While previously we drew a Lewis structure of methane in two dimensions using lines to denote each covalent bond, we can now draw a more accurate structure in three dimensions, showing the tetrahedral bonding geometry. To do this on a two-dimensional page, though, we need to introduce a new drawing convention: the solid / dashed wedge system. In this convention, a solid wedge simply represents a bond that is meant to be pictured emerging from the plane of the page. A dashed wedge represents a bond that is meant to be pictured pointing into, or behind, the plane of the page. Normal lines imply bonds that lie in the plane of the page.

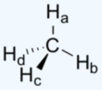


This system takes a little bit of getting used to, but with practice your eye will learn to immediately ‘see’ the third dimension being depicted.

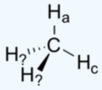
interactive 3D model of the bonding in methane

Exercise

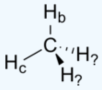
Imagine that you could distinguish between the four hydrogens in a methane molecule, and labeled them H_a through H_d. In the images below, the *exact same* methane molecule is rotated and flipped in various positions. Draw the missing hydrogen atom labels. (It will be much easier to do this if you make a model.)



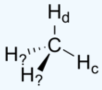
a)



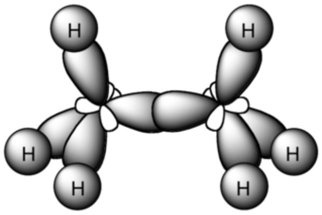
b)

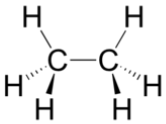


c)

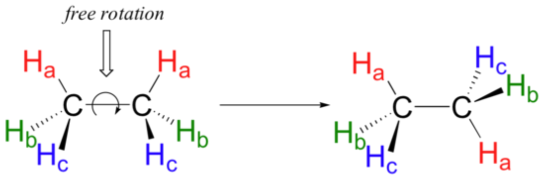


In the ethane molecule, the bonding picture according to valence orbital theory is very similar to that of methane. Both carbons are sp^3-hybridized, meaning that both have four bonds arranged with tetrahedral geometry. The carbon-carbon bond, with a bond length of 1.54 Å, is formed by overlap of one sp^3 orbital from each of the carbons, while the six carbon-hydrogen bonds are formed from overlaps between the remaining sp^3 orbitals on the two carbons and the 1*s* orbitals of hydrogen atoms. All of these are sigma bonds.



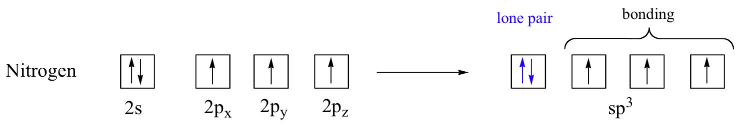


Because they are formed from the end-on-end overlap of two orbitals, *sigma bonds are free to rotate*. This means, in the case of ethane molecule, that the two methyl (CH_3) groups can be pictured as two wheels on a hub, each one able to rotate freely with respect to the other.

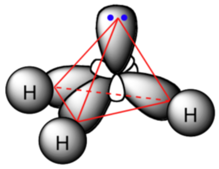


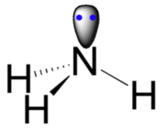
In another module we will learn more about the implications of rotational freedom in sigma bonds, when we discuss the ‘conformation’ of organic molecules.

The sp^3 bonding picture is also used to described the bonding in amines, including ammonia, the simplest amine. Just like the carbon atom in methane, the central nitrogen in ammonia is sp^3-hybridized. With nitrogen, however, there are five rather than four valence electrons to account for, meaning that three of the four hybrid orbitals are half-filled and available for bonding, while the fourth is fully occupied by a (non-bonding) pair of electrons.



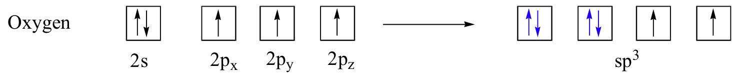
The bonding arrangement here is also tetrahedral: the three N-H bonds of ammonia can be pictured as forming the base of a trigonal pyramid, with the fourth orbital, containing the lone pair, forming the top of the pyramid.

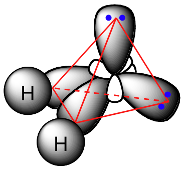


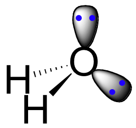


Recall from your study of VSEPR theory in General Chemistry that the lone pair, with its slightly greater repulsive effect, ‘pushes’ the three N-H sigma bonds away from the top of the pyramid, meaning that the H-N-H bond angles are slightly less than tetrahedral, at 107.3˚ rather than 109.5˚.

VSEPR theory also predicts, accurately, that a water molecule is ‘bent’ at an angle of approximately 104.5˚. It would seem logical, then, to describe the bonding in water as occurring through the overlap of sp^3-hybrid orbitals on oxygen with 1*s*orbitals on the two hydrogen atoms. In this model, the two nonbonding lone pairs on oxygen would be located in sp^3 orbitals.







Some experimental evidence, however, suggests that the bonding orbitals on the oxygen are actually unhybridized 2*p* orbitals rather than sp^3 hybrids. Although this would seem to imply that the H-O-H bond angle should be 90˚ (remember that *p* orbitals are oriented perpendicular to one another), it appears that electrostatic repulsion has the effect of distorting this *p*-orbital angle to 104.5˚. Both the hybrid orbital and the nonhybrid orbital models present reasonable explanations for the observed bonding arrangement in water, so we will not concern ourselves any further with the distinction.

? Exercise

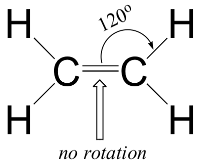
Draw, in the same style as the figures above, an orbital picture for the bonding in methylamine.

Solution

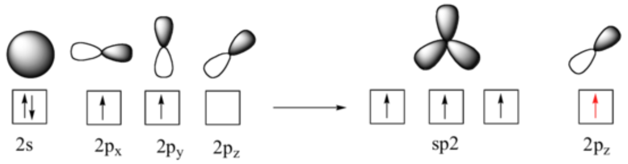
Formation of pi bonds - sp^2 and sp hybridization

The valence bond theory, along with the hybrid orbital concept, does a very good job of describing double-bonded compounds such as ethene. Three experimentally observable characteristics of the ethene molecule need to be accounted for by a bonding model:

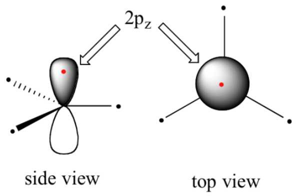
1. Ethene is a planar (flat) molecule.
2. Bond angles in ethene are approximately 120^o, and the carbon-carbon bond length is 1.34 Å, significantly shorter than the 1.54 Å single carbon-carbon bond in ethane.
3. There is a significant barrier to rotation about the carbon-carbon double bond.



Clearly, these characteristics are not consistent with an sp^3 hybrid bonding picture for the two carbon atoms. Instead, the bonding in ethene is described by a model involving the participation of a different kind of hybrid orbital. Three atomic orbitals on each carbon – the 2*s*, 2p_x and 2p_y orbitals – combine to form three sp^2 hybrids, leaving the 2p_z orbital unhybridized.

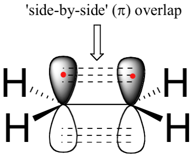


The three sp^2 hybrids are arranged with trigonal planar geometry, pointing to the three corners of an equilateral triangle, with angles of 120°between them. The unhybridized 2p_z orbital is *perpendicular* to this plane (in the next several figures, sp^2 orbitals and the sigma bonds to which they contribute are represented by lines and wedges; only the 2p_z orbitals are shown in the 'space-filling' mode).



another view

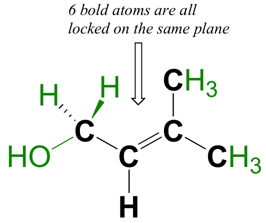
The carbon-carbon double bond in ethene consists of one sigma bond, formed by the overlap of two sp^2 orbitals, and a second bond, called a **π (pi) bond**, which is formed by the *side-by-side* overlap of the two unhybridized 2p_z orbitals from each carbon.



another view

interactive model

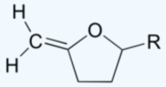
The pi bond does *not* have symmetrical symmetry. Because they are the result of side-by-side overlap (rather then end-to-end overlap like a sigma bond), *pi bonds are not free to rotate.* If rotation about this bond were to occur, it would involve disrupting the side-by-side overlap between the two 2p_z orbitals that make up the pi bond. The presence of the pi bond thus 'locks' the six atoms of ethene into the same plane. This argument extends to larger alkene groups: in each case, the six atoms of the group form a single plane.



Conversely, sigma bonds such as the carbon-carbon single bond in ethane (CH_3CH_3) exhibit free rotation, and can assume many different conformations, or shapes.

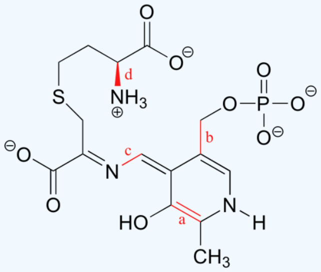
✓ Example

Circle the six atoms in the molecule below that are ‘locked’ into the same plane.

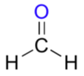


? Exercise

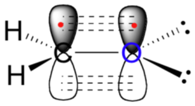
What kinds of orbitals are overlapping in bonds a-d indicated below?



A similar picture can be drawn for the bonding in carbonyl groups, such as formaldehyde. In this molecule, the carbon is sp^2-hybridized, and we will assume that the oxygen atom is also sp^2 hybridized. The carbon has three sigma bonds: two are formed by overlap between two of its sp^2 orbitals with the 1*s*orbital from each of the hydrogens, and the third sigma bond is formed by overlap between the remaining carbon sp^2 orbital and an sp^2 orbital on the oxygen. The two lone pairs on oxygen occupy its other two sp^2 orbitals.



formaldehyde



interactive 3D model

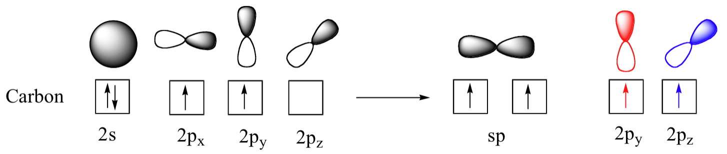
The pi bond is formed by side-by-side overlap of the unhybridized $2p_z$ orbitals on the carbon and the oxygen. Just like in alkenes, the $2p_z$ orbitals that form the pi bond are perpendicular to the plane formed by the sigma bonds.

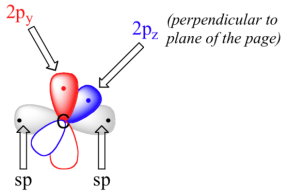
Finally, the hybrid orbital concept applies well to triple-bonded groups, such as alkynes and nitriles. Consider, for example, the structure of ethyne (common name acetylene), the simplest alkyne.

$$H-C\equiv C-H$$

ethyne
(acetylene)

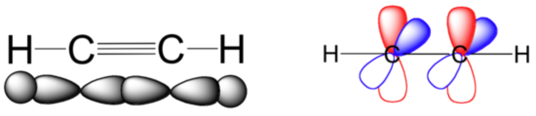
This molecule is linear: all four atoms lie in a straight line. The carbon-carbon triple bond is only 1.20Å long. In the hybrid orbital picture of acetylene, both carbons are **sp-hybridized**. In an sp-hybridized carbon, the 2*s* orbital combines with the $2p_x$ orbital to form two sp hybrid orbitals that are oriented at an angle of 180°with respect to each other (eg. along the x axis). The $2p_y$ and $2p_z$ orbitals remain unhybridized, and are oriented perpendicularly along the y and z axes, respectively.





another view

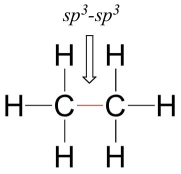
The C-C sigma bond, then, is formed by the overlap of one sp orbital from each of the carbons, while the two C-H sigma bonds are formed by the overlap of the second sp orbital on each carbon with a 1*s* orbital on a hydrogen. Each carbon atom still has two half-filled $2p_y$ and $2p_z$ orbitals, which are perpendicular both to each other and to the line formed by the sigma bonds. These two perpendicular pairs of *p* orbitals form two pi bonds between the carbons, resulting in a triple bond overall (one sigma bond plus two pi bonds).


σ bonding framework

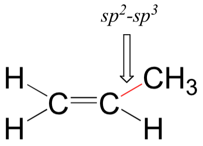
π overlap

another view

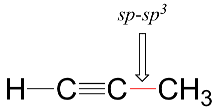
The hybrid orbital concept nicely explains another experimental observation: single bonds adjacent to double and triple bonds are progressively shorter and stronger than 'normal' single bonds, such as the one in a simple alkane. The carbon-carbon bond in ethane (structure A below) results from the overlap of two sp^3 orbitals.



A



B



C

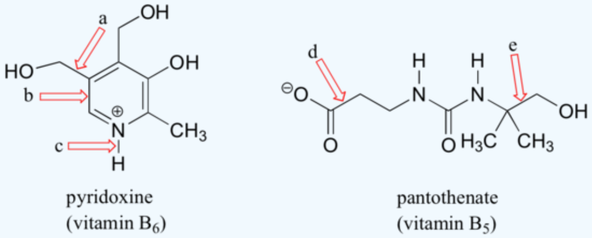
In alkene B, however, the carbon-carbon single bond is the result of overlap between an sp^2 orbital and an sp^3 orbital, while in alkyne C the carbon-carbon single bond is the result of overlap between an sp orbital and an sp^3 orbital. These are all single bonds, but the bond in molecule C is shorter and stronger than the one in B, which is in turn shorter and stronger than the one in A.

The explanation here is relatively straightforward. An sp orbital is composed of one *s* orbital and one *p* orbital, and thus it has 50% *s* character and 50% *p* character. sp^2 orbitals, by comparison, have 33% *s* character and 67% *p* character, while sp^3 orbitals have 25% *s* character and 75% *p* character. Because of their spherical shape, 2*s* orbitals are smaller, and hold electrons closer and 'tighter' to the nucleus, compared to 2*p* orbitals. Consequently, bonds involving sp + sp^3 overlap (as in alkyne C) are shorter and stronger than bonds involving sp^2 + sp^3 overlap (as in alkene B). Bonds involving sp^3-sp^3overlap (as in alkane A) are the longest and weakest of the group, because of the 75% '*p*' character of the hybrids.

✓ Example

For each of the bonds indicated by arrows a-e in the figures below, describe the bonding picture by completing this sentence:

"The sigma bond indicated by this arrow is formed by the overlap of an ________ orbital of a _________atom and an ________orbital of a _______atom."



Solution

Contributors and Attributions

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12.4: Electronegativity and Dipole Moment

Within a group of the periodic table, bond lengths tend to increase with increasing atomic number Z. Consider the Group 17 elements:

$$\begin{array}{ll} F_2 & d = 141.7\ pm \\ Cl_2 & d = 199.1\ pm \\ Br_2 & d = 228.6\ pm \\ I_2 & d = 266.9\ pm \end{array}$$

which corresponds to an increased valence shell size, hence increased electron-electron repulsion. An important result from experiment, which has been corroborated by theory, is that bond lengths tend not to vary much from molecule to molecule. Thus, a CH bond will have roughly the same value in methane, CH_4 as it will in aspirin, $C_9H_8O_4$.

Bond dissociation energies. ΔE_d measured in kJ/mol, measure the energy required to break a mole of a particular kind of bond. A similar periodic trend exists for bond dissociation energies. Consider the hydrogen halides:

$$\begin{array}{lll} HF & \Delta E_d = 565\ kJ/mol & d = 0.926\ pm \\ HCl & \Delta E_d = 429\ kJ/mol & d = 128.4\ pm \\ HBr & \Delta E_d = 363\ kJ/mol & d = 142.4\ pm \\ HI & \Delta E_d = 295\ kJ/mol & d = 162.0\ pm \end{array}$$

Thus, as bond lengths increase with increasing Z, there is a corresponding decrease in the bond dissociation energy.

CC bonds are an exception to the the rule of constancy of bond lengths across different molecules. Because CC bonds can be single, double, or triple bonds, some differences can occur. For example, consider the CC bond in the molecules ethane (C_2H_6), ethylene (C_2H_4) and acetylene (C_2H_2):

$$\begin{array}{llll} C_2H_6 & (single) & d = 1.536\ \overset{\circ}{A} & \Delta E_d = 345\ kJ/mol \\ C_2H_4 & (double) & d = 133.7\ pm & \Delta E_d = 612\ kJ/mol \\ C_2H_2 & (triple) & d = 126.4\ pm & \Delta E_d = 809\ kJ/mol \end{array}$$

The greater the *bond order*, i.e., number of shared electron pairs, the greater the dissociation energy. The same will be true for any kind of bond that can come in such different ``flavors", e.g., NN bonds, OO bonds, NO bonds, CO bonds, etc.

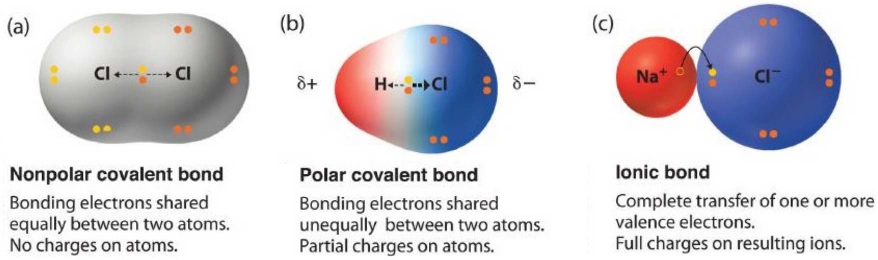

Figure 12.4.1 **:** The Electron Distribution in a Nonpolar Covalent Bond, a Polar Covalent Bond, and an Ionic Bond Using Lewis Electron Structures. In a purely covalent bond (a), the bonding electrons are shared equally between the atoms. In a purely ionic bond (c), an electron has been transferred completely from one atom to the other. A polar covalent bond (b) is intermediate between the two extremes: the bonding electrons are shared unequally between the two atoms, and the electron distribution is asymmetrical with the electron density being greater around the more electronegative atom. Electron-rich (negatively charged) regions are shown in blue; electron-poor (positively charged) regions are shown in red.

The two idealized extremes of chemical bonding:

1. Ionic bonding—in which one or more electrons are transferred completely from one atom to another, and the resulting ions are held together by purely electrostatic forces—and
2. Covalent bonding, in which electrons are shared equally between two atoms.

Most compounds, however, have polar covalent bonds, which means that electrons are shared unequally between the bonded atoms. Figure $12.4.1$ compares the electron distribution in a polar covalent bond with those in an ideally covalent and an ideally ionic bond. Recall that a lowercase Greek delta (δ) is used to indicate that a bonded atom possesses a partial positive charge, indicated by δ^+, or a partial negative charge, indicated by δ^-, and a bond between two atoms that possess partial charges is a polar bond.

Most real chemical bonds in nature are neither truly covalent nor truly ionic. Only homonuclear bonds are truly covalent, and nearly perfect ionic bonds can form between group I and group VII elements, for example, KF. Generally, however, bonds are partially covalent and partially ionic, meaning that there is partial transfer of electrons between atoms and partial sharing of electrons. To quantify how much ionic character (and how much covalent character) a bond possesses, electronegativity differences between the atoms in the bond can be used. In 1936, Linus Pauling came up a method for estimating atomic electronegativities forms the basis of our understanding of electronegativity today.

> Only **homonuclear** bonds are truly covalent, or as covalent as a bond can get. As discussed in Section 12.2, a quantum-mechanical treatment has shown that the two ionic structures (e.g., H^+H^- and H^-H^+ for H_2) also contribute via a resonance with the covalent structure $H-H$. However, this is often to a small extent, for example in H_2, each ionic structure contributes only ~2% to the bonding of the molecule.

Pauling Electronegativity

Linus Pauling described electronegativity as “the power of an atom in a molecule to attract electrons to itself.” Basically, the electronegativity of an atom is a relative value of that atom's ability to attract election density toward itself when it bonds to another atom. The higher the electronegative of an element, the more that atom will attempt to pull electrons towards itself and away from any atom it bonds to. The main properties of an atom dictate it's electronegativity are it's atomic number as well as its atomic radius. The trend for electronegativity is to increase as you move from left to right and bottom to top across the periodic table. This means that the most electronegative atom is Fluorine and the least electronegative is Francium.

Recall the Mulliken's method was based on the arithmetic average of the first ionization energy IE_1 and the electron affinity EA. Both of these energies are properties of individual atoms, hence this method is appealing in its simplicity. However, there is no information about bonding in the Mulliken method. Pauling's method includes such information, and hence is a more effective approach.

To see how the Pauling method works, consider a diatomic AB, which is polar covalent. Let ΔE_{AA} and ΔE_{BB} be the dissociation energies of the diatomics A_2 and B_2, respectively. Since A_2 and B_2 are purely covalent bonds, these two dissociation energies can be used to estimate the pure covalent contribution to the bond AB. Pauling proposed the geometric mean of ΔE_{AA} and ΔE_{BB}, this being more sensitive to large differences between these energies than the arithmetic average:

$$pure\ covalent\ contribution = \sqrt{\Delta E_{AA} \Delta E_{BB}} \tag{12.4.1}$$

If ΔE_{AB} is the true bond dissociation energy, then the difference

$$\Delta E_{AB} - \sqrt{\Delta E_{AA} \Delta E_{BB}} \tag{12.4.2}$$

is a measure of the ionic contribution. Let us define this difference to be Δ:

$$\Delta = \Delta E_{AB} - \sqrt{\Delta E_{AA} \Delta E_{BB}} \tag{12.4.3}$$

Then Pauling defined the electronegativity difference $\chi_A - \chi_B$ between atoms A and B to be

$$\chi_A - \chi_B = 0.102\sqrt{\Delta} \tag{12.4.4}$$

where Δ is measured in kJ/mol, and the constant 0.102 has units $mol^{1/2}/kJ^{1/2}$, so that the electronegativity difference is dimensionless. Thus, with some extra input information, he was able to generate a table of atomic electronegativities that are still used today and is Tablated in Table A2 (Figure $12.4.2$).

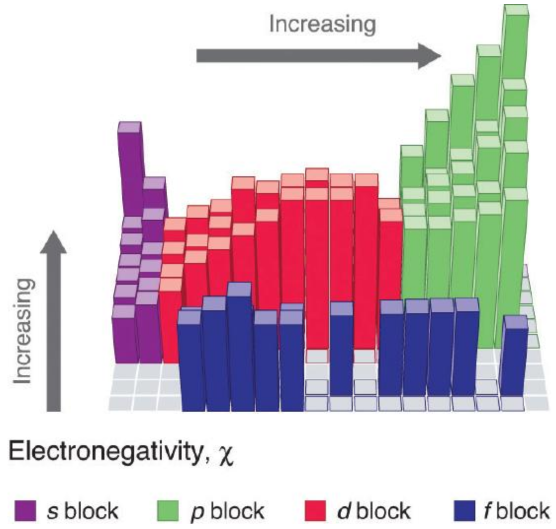

Figure 12.4.2: Pauling Electronegativity Values of the s-, *p*-, *d*-, and *f*-Block Elements. Values for most of the actinides are approximate. Elements for which no data are available are shown in gray. Source: Data from L. Pauling, *The Nature of the Chemical Bond*, 3rd ed. (1960).

To use the electronegativities to estimate degree of ionic character, simply compute the absolute value of the difference for the two atoms in the bond. As an example, consider again the hydrogen halides:

$$\begin{array}{ll} HF & |\chi_F - \chi_H| = 1.78 \\ HCl & |\chi_{Cl} - \chi_H| = 0.96 \\ HBr & |\chi_{Br} - \chi_H| = 0.76 \\ HI & |\chi_I - \chi_H| = 0.46 \end{array}$$

As the electronegativity difference decreases, so does the ionic character of the bond. Hence its covalent character increases. It is possible to predict whether a given bond will be non-polar, polar covalent, or ionic based on the electronegativity difference, since the greater the difference, the more polar the bond (Figure $12.4.3$)

Electronegativity difference, ΔχP	Bond
$\Delta\chi < 0.4$	covalent
$0.4 < \Delta\chi < 1.7$	polar covalent
$\Delta\chi > 1.7$	ionic

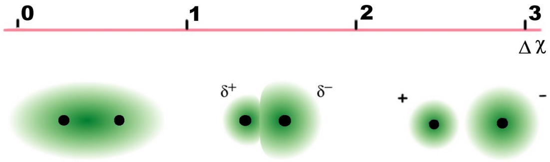

Figure 12.4.3: Range of Bonds Polarity based on difference of Electronegativites

> *As the electronegativity difference decreases, so does the ionic character of the bond. Hence its covalent character increases.*

Dipole moment

In a nearly perfect ionic bond, such as KF, where electron transfer is almost complete, representing the molecule as

$$K^+F^- \tag{12.4.5}$$

is a very good approximation, since the charge on the potassium will be approximately $1e$ and the charge on the fluorine will be approximately $-1e$. For a polar covalent bond, such as HF, in which only partial charge transfer occurs, a more accurate representation would be

$$H^{+\delta}F^{-\delta} \tag{12.4.6}$$

where δ, expressed in units of \(e\), is known as a *partial charge*. It suggests that a fraction of an electron is transferred, although the reality is that there is simply a little more electron density on the more electronegative atom and a little less on the electropositive atom.

How much charge is actually transferred can be quantified by studying the *electric dipole moment* of the bond, which is a quantity that can be measured experimentally. The electric dipole moment for a diatomic with charges $Q_1 = Q = \delta e$ and $Q_2 = -Q = -\delta e$ on atoms 1 and 2, respectively, is

$$\begin{aligned}\mu &= Q_1 r_1 + Q_2 r_2 \\ &= Q r_1 - Q r_2 \\ &= Q(r_1 - r_2)\end{aligned}$$

Hence, the magnitude of the dipole moment is

$$\mu = |\mu| = Q|r_1 - r_2| = QR \tag{12.4.7}$$

where R is the bond length. As an example, consider HF, which has a partial charge on H of 0.41 e, which means $\delta = 0.41$, and a bond length of $0.926\ \overset{\circ}{A}$. Thus, the magnitude of the dipole moment is

$$|\mu| = 0.41(1.602 \times 10^{-19} C)(0.926 \times 10^{-10} m) = 6.08 \times 10^{-30} C \cdot m \tag{12.4.8}$$

Thus, the units of the dipole moment are Coulomb-meters. However, as this example makes clear, this is a very large unit and awkward to work with for molecules. A more convenient unit is the Debye (D), defined to be

$$1\ D = 3.336 \times 10^{-30}\ \text{Coulomb} \cdot \text{meters} \tag{12.4.9}$$

> Historically, the Debye was defined in terms of the dipole moment resulting from two equal charges of opposite sign and separated by 1 Ångstrom ($10^{-10}\ m$) as 4.801 D from Equation 12.4.7. This value arises from
>
> $$\frac{(1.602 \times 10^{-19})(1 \times 10^{-10})}{3.336 \times 10^{-30}}$$
>
> where
>
> $$D = 3.336 \times 10^{-30}\ C\,m$$
>
> or
>
> $$1\ C\,m = 2.9979 \times 10^{29}\ D$$

Thus, for a diatomic with partial charges $+\delta$ and $-\delta$, the dipole moment in D is given by

$$\mu(D) = \frac{\delta * R(\overset{\circ}{A})}{0.2082\ \overset{\circ}{A}\,D^{-1}} \tag{12.4.10}$$

and the percent ionic character is defined in terms of the partial charge δ by

$$percent\ ionic\ character = 100\% * \delta \tag{12.4.11}$$

Typical dipole moments for simple diatomic molecules are in the range of 0 to 11 D (Table 12.4.1). Equation 12.4.11 can be expressed differently in terms of the expected dipole assuming a full charge separation (μ_{ionic}) compared to the experimental dipole moment (μ_{exp})

$$percent\ ionic\ character = 100\% * \frac{\mu_{exp}}{\mu_{ionic}} \tag{12.4.12}$$

✓ Example 12.4.1: KBr

Calculate a theoretical dipole moment for the KBr molecule, assuming opposite charges of one fundamental unit located at each nucleus, and hence the percentage ionic character of KBr.

Solution

From Table 12.4.1, the observed dipole moment of KBr is given as 10.41 D, (3.473 x 10^{-29} Coulomb-meters), which being close to the upper level of 11 indicates that it is a highly polar molecule. The interatomic distance between K^+ and Br^- is 282 pm. From this it is possible to calculate a theoretical dipole moment for the KBr molecule, assuming opposite charges of one fundamental unit located at each nucleus, and hence the percentage ionic character of KBr.

Dipole moment

$$\mu = q \times e \times d \text{ (in Coulomb-meters)} \tag{12.4.13}$$

- q = 1 for complete separation of unit charge
- e = 1.602 x 10^{-19} C
- d = 2.82 x 10^{-10} m for KBr (282 pm)

Hence calculated ionic dipole moment is

$$\mu_{KBr} = (1)(1.602 \times 10^{-19})(2.82 \times 10^{-10}) = 4.518 \times 10^{-29}\ Cm = 13.54\ D$$

The observed dipole moment is

$$\mu_{KBr} = 3.473 \times 10^{-29}\ Cm = 10.41\ D$$

the % ionic character from Equation 12.4.12is

$$KBr = \frac{3.473 \times 10^{-29}}{4.518 \times 10^{-29}} \times 100\% = \frac{10.41\ D}{13.54\ D} \times 100\% = 76.87\%$$

and the % covalent character is therefore about 23% (100% - 77%).

Given the observed dipole moment is 10.41 D (3.473 x 10^{-29}) it is possible to estimate the charge distribution from the same equation by now solving for q.

Dipole moment μ = q * e * d Coulomb metre, but since q is no longer 1 we can substitute in values for μ and d to obtain an estimate for it.

q = μ /(e * d) = 3.473 x 10^{-29} / (1.602 x 10^{-19} * 2.82 x 10^{-10})

thus q = 3.473 x 10^{-29} / (4.518 x 10^{-29}) = 0.77 and the δ- and δ+ are -0.8 and +0.8 respectively.

✓ Example 12.4.2: NaCl

In the gas phase, NaCl has a dipole moment of 9.001 D and an Na–Cl distance of 236.1 pm. Calculate the percent ionic character in NaCl.

Given: chemical species, dipole moment, and internuclear distance

Asked for: percent ionic character

Strategy:

A Compute the charge on each atom using the information given and Equation 8.4.2.

B Find the percent ionic character from the ratio of the actual charge to the charge of a single electron.

Solution:

A The charge on each atom is given by

$$Q = \frac{\mu}{r} = 9.001\ \cancel{D} \left(\frac{3.3356 \times 10^{-30}\ C \cdot \cancel{m}}{1\ \cancel{D}} \right) \left(\frac{1}{236.1\ \cancel{pm}} \right) \left(\frac{1\ \cancel{pm}}{10^{-12}\ \cancel{m}} \right) = 1.272 \times 10^{-19}\ C \tag{12.4.14}$$

Thus NaCl behaves as if it had charges of 1.272×10^{-19} C on each atom separated by 236.1 pm.

B The percent ionic character is given by the ratio of the actual charge to the charge of a single electron (the charge expected for the complete transfer of one electron):

$$\%\ ionic\ character = \left(\frac{1.272 \times 10^{-19}\ \cancel{C}}{1.6022 \times 10^{-19}\ \cancel{C}} \right) (100) = 79.39\% \simeq 79\% \tag{12.4.15}$$

? Exercise 12.4.2: AgCl

In the gas phase, silver chloride (AgCl) has a dipole moment of 6.08 D and an Ag–Cl distance of 228.1 pm. What is the percent ionic character in silver chloride?

Answer

55.5%

Table 12.4.1: Bond characteristics of select diatomics

diatomic	Δ χ	%ionic	bond dist (pm)	μ_{exp} (D)	μ_{ionic} (D)
Cl_2	0.0	0.0	200	0.00	9.60
IBr	0.3	5.9	247	0.70	11.86
HI	0.4	5.7	161	0.44	7.73
ICl	0.5	5.4	232	0.60	11.14
HBr	0.7	12.1	141	0.82	6.77
HCl	0.9	17.7	127	1.08	6.10
ClF	1.0	11.2	163	0.88	7.83
BrF	1.2	15.1	178	1.29	8.55
LiI	1.5	65.0	238	7.43	11.43
HF	1.9	41.2	92	1.82	4.42
LiBr	1.8	69.8	217	7.27	10.42
KI	1.7	73.7	305	10.80	14.65
LiCl	2.0	73.5	202	7.13	9.70
KBr	2.0	76.9	282	10.41	13.54
NaCl	2.1	79.4	236	9.00	11.33
KCl	2.2	80.1	267	10.27	12.82
CsCl	2.3	74.6	291	10.42	13.97
LiF	3.0	86.7	152	6.33	7.30
KF	3.2	82.5	217	8.60	10.42
CsF	3.3	64.4	255	7.88	12.25

Pauling proposed an empirical relationship (instead of the defintion in Equation 12.4.12) which relates the percent ionic character in a bond to the electronegativity difference.

$$percent\ ionic\ character = 100\% \left(1 - e^{(\Delta\chi/2)^2}\right) \tag{12.4.16}$$

This is shown as the curve in Figure 12.4.4 and is compared to the values for some diatomic molecules calculated from observed and calculated dipole moments.

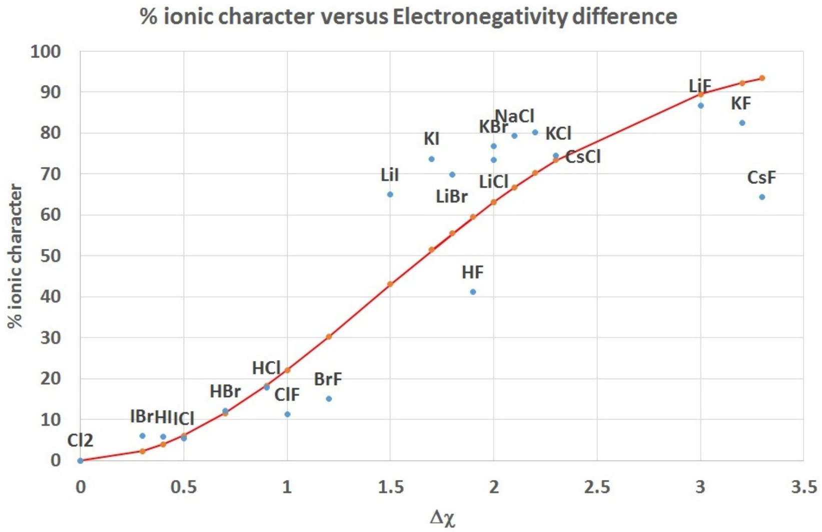

Figure 12.4.4: A Plot of the Percent Ionic Character of a Bond as Determined from Measured Dipole Moments versus the Difference in Electronegativity of the Bonded Atoms.In the gas phase, even CsF, which has the largest possible difference in electronegativity between atoms, is not 100% ionic. Solid CsF, however, is best viewed as 100% ionic because of the additional electrostatic interactions in the lattice.

As an example, consider HF again, for which $\delta = 0.41$. The bond length is $R = 0.926 \overset{\circ}{A}$. Thus, its dipole moment will be

$$\mu(D) = \frac{0.41 * 0.926 \overset{\circ}{A}}{0.2082 \overset{\circ}{A} D^{-1}} = 1.82D \tag{12.4.17}$$

and its percent ionic character is 41%.

✓ Example 12.4.3: Bond Polarity

Without consulting the table of electronegativities (use the periodic table), arrange the following bonds in order of decreasing polarity:

B—Cl, Ba—Cl, Be—Cl, Br—Cl, Cl—Cl.

Solution

We first need to arrange the elements in order of increasing electronegativity. Since the electronegativity increases in going up a column of the periodic table, we have the following relationships:

Ba < Be and Br < Cl

Also since the electronegativity increases across the periodic table, we have

Be < B

Since B is a group III element on the borderline between metals and non-metals, we easily guess that

B < Br

which gives us the complete order

Ba < Be < B < Br < Cl

Among the bonds listed, therefore, the Ba—Cl bond corresponds to the largest difference in electronegativity, i.e., to the most nearly ionic bond. The order of bond polarity is thus

> Ba—Cl > Br—Cl > B—Cl > Br—Cl > Cl—Cl
>
> where the final bond, Cl—Cl,is, of course, purely covalent.

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12.5: Molecular Orbital Theory

None of the approaches we have described so far can adequately explain why some compounds are colored and others are not, why some substances with unpaired electrons are stable, and why others are effective semiconductors. These approaches also cannot describe the nature of resonance. Such limitations led to the development of a new approach to bonding in which electrons are *not* viewed as being localized between the nuclei of bonded atoms but are instead delocalized throughout the entire molecule. Just as with the valence bond theory, the approach we are about to discuss is based on a quantum mechanical model.

Previously, we described the electrons in isolated atoms as having certain spatial distributions, called *orbitals*, each with a particular *orbital energy*. Just as the positions and energies of electrons in *atoms* can be described in terms of *atomic orbitals* (AOs), the positions and energies of electrons in *molecules* can be described in terms of molecular orbitals (MOs) A particular spatial distribution of electrons in a molecule that is associated with a particular orbital energy.—a spatial distribution of electrons *in a molecule* that is associated with a particular orbital energy. As the name suggests, molecular orbitals are not localized on a single atom but extend over the entire molecule. Consequently, the molecular orbital approach, called molecular orbital theory is a *delocalized* approach to bonding.

Although the molecular orbital theory is computationally demanding, the principles on which it is based are similar to those we used to determine electron configurations for atoms. The key difference is that in molecular orbitals, the electrons are allowed to interact with more than one atomic nucleus at a time. Just as with atomic orbitals, we create an energy-level diagram by listing the molecular orbitals in order of increasing energy. We then fill the orbitals with the required number of valence electrons according to the Pauli principle. This means that each molecular orbital can accommodate a maximum of two electrons with opposite spins.

The Hydrogen Molecule-Ion

Molecular orbital theory is a conceptual extension of the orbital model, which was so successfully applied to atomic structure. As was once playfully remarked, "a molecule is nothing more than an atom with more nuclei." This may be overly simplistic, but we do attempt, as far as possible, to exploit analogies with atomic structure. Our understanding of atomic orbitals began with the exact solutions of a prototype problem – the hydrogen atom. We will begin our study of homonuclear diatomic molecules beginning with another exactly solvable prototype, the hydrogen molecule-ion H_2^+. This species actually has a transient existence in electrical discharges through hydrogen gas and has been detected by mass spectrometry. It also has been detected in outer space. The Schrödinger equation for H_2^+ can be solved exactly within the Born-Oppenheimer approximation. For fixed internuclear distance *R*, this reduces to a problem of one electron in the field of two protons, designated A and B. We can write

$$\left\{-\frac{1}{2}\nabla^2\frac{1}{r_A}-\frac{1}{r_B}+\frac{1}{R}\right\}\psi(r)=E\psi(r) \tag{1}$$

where r_A and r_B are the distances from the electron to protons A and B, respectively. This equation was solved by Burrau (1927), after separating the variables in prolate spheroidal coordinates.

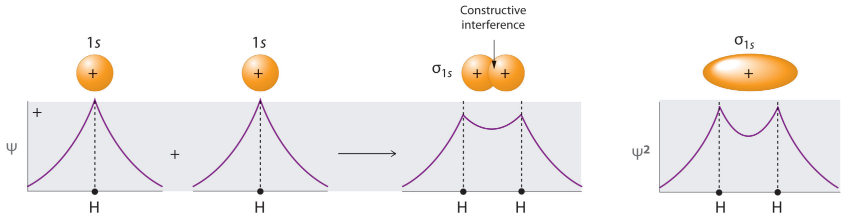
Molecular Orbitals Involving Only *ns* Atomic Orbitals

We begin our discussion of molecular orbitals with the simplest molecule, H_2, formed from two isolated hydrogen atoms, each with a $1s^1$ electron configuration. As discussed before, electrons can behave like waves. In the molecular orbital approach, the overlapping atomic orbitals are described by mathematical equations called *wave functions*. The 1*s* atomic orbitals on the two hydrogen atoms interact to form two new molecular orbitals, one produced by taking the *sum* of the two H 1*s* wave functions, and the other produced by taking their *difference*:

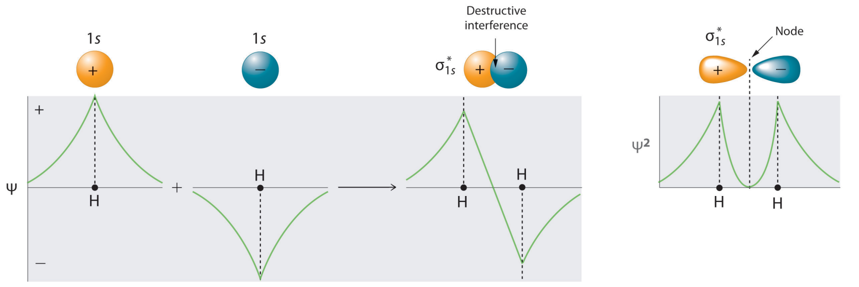
$$\begin{aligned} MO(1) = &\quad AO(atom\ A) &+ &\quad AO(atom B) \\ MO(1) = &\quad AO(atom\ A) &- &\quad AO(atom B) \end{aligned} \tag{12.5.1}$$

The molecular orbitals created from the sum and the difference of two wavefunctions (atomic orbitals) from Equation 12.5.1 are called Linear Combinations of Atomic Orbitals (LCAOs). A molecule **must** have as many molecular orbitals as there are atomic orbitals.

Adding two atomic orbitals corresponds to *constructive* interference between two waves, thus reinforcing their intensity; the internuclear electron probability density is *increased*. The molecular orbital corresponding to the sum of the two H 1*s* orbitals is called a $σ_{1s}$ combination (pronounced “sigma one ess”) (part (a) and part (b) in Figure 12.5.1). In a sigma (σ) orbital, A bonding molecular orbital in which the electron density along the internuclear axis and between the nuclei has cylindrical symmetry, the electron density along the internuclear axis and between the nuclei has cylindrical symmetry; that is, all cross-sections perpendicular to the internuclear axis are circles. The subscript 1*s* denotes the atomic orbitals from which the molecular orbital was derived: The ≈ sign is used rather than an = sign because we are ignoring certain constants that are not important to our argument.



(a) Wave functions combined for σ_{1s} **(b) Bonding probability density**



(c) Wave functions combined for σ^*_{1s} **(d) Antibonding probability density**

Figure 12.5.1: Molecular Orbitals for the H_2 Molecule**.** (a) This diagram shows the formation of a bonding σ_{1s} molecular orbital for H_2 as the sum of the wave functions (Ψ) of two H 1*s* atomic orbitals. (b) This plot of the square of the wave function (Ψ^2) for the bonding σ_{1s} molecular orbital illustrates the increased electron probability density between the two hydrogen nuclei. (Recall that the probability density is proportional to the *square* of the wave function.) (c) This diagram shows the formation of an antibonding *σ^*_{1s} molecular orbital for H_2 as the difference of the wave functions (Ψ) of two H 1s atomic orbitals. (d) This plot of the square of the wave function (Ψ^2) for the σ^*_{1s} antibonding molecular orbital illustrates the node corresponding to zero electron probability density between the two hydrogen nuclei.*

$$\sigma_{1s} \approx 1s\,(A) + 1s\,(B) \tag{12.5.2}$$

Conversely, subtracting one atomic orbital from another corresponds to *destructive* interference between two waves, which reduces their intensity and causes a *decrease* in the internuclear electron probability density (part (c) and part (d) in Figure 12.5.1). The resulting pattern contains a *node* where the electron density is zero. The molecular orbital corresponding to the difference is called σ^*_{1s} ("sigma one ess star"). In a sigma star (σ*) orbital An antibonding molecular orbital in which there is a region of zero electron probability (a nodal plane) perpendicular to the internuclear axis., there is a region of zero electron probability, a nodal plane, perpendicular to the internuclear axis:

$$\sigma^\star_{1s} \approx 1s\,(A) - 1s\,(B) \tag{12.5.3}$$

> A molecule must have as many molecular orbitals as there are atomic orbitals.

The electron density in the σ_{1s} molecular orbital is greatest between the two positively charged nuclei, and the resulting electron–nucleus electrostatic attractions reduce repulsions between the nuclei. Thus the σ_{1s} orbital represents a bonding molecular orbital. A molecular orbital that forms when atomic orbitals or orbital lobes with the same sign interact to give increased electron probability between the nuclei due to constructive reinforcement of the wave functions. In contrast, electrons in the $\sigma^\star_{1s}$ orbital are generally found in the space outside the internuclear region. Because this allows the positively charged nuclei to repel one another, the $\sigma^\star_{1s}$ orbital is an antibonding molecular orbital (a molecular orbital that forms when atomic orbitals or orbital lobes of opposite sign interact to give decreased electron probability between the nuclei due to destructive reinforcement of the wave functions).

> *Antibonding orbitals contain a node perpendicular to the internuclear axis; bonding orbitals do not.*

Energy-Level Diagrams

Because electrons in the σ_{1s} orbital interact simultaneously with both nuclei, they have a lower energy than electrons that interact with only one nucleus. This means that the σ_{1s} molecular orbital has a *lower* energy than either of the hydrogen 1*s* atomic orbitals. Conversely, electrons in the $\sigma^{\star}_{1s}$ orbital interact with only one hydrogen nucleus at a time. In addition, they are farther away from the nucleus than they were in the parent hydrogen 1*s* atomic orbitals. Consequently, the $\sigma^{\star}_{1s}$ molecular orbital has a *higher* energy than either of the hydrogen 1*s* atomic orbitals. The σ_{1s} (bonding) molecular orbital is *stabilized* relative to the 1*s* atomic orbitals, and the $\sigma^{\star}_{1s}$ (antibonding) molecular orbital is *destabilized*. The relative energy levels of these orbitals are shown in the energy-level diagram (a schematic drawing that compares the energies of the molecular orbitals (bonding, antibonding, and nonbonding) with the energies of the parent atomic orbitals) in Figure 12.5.2

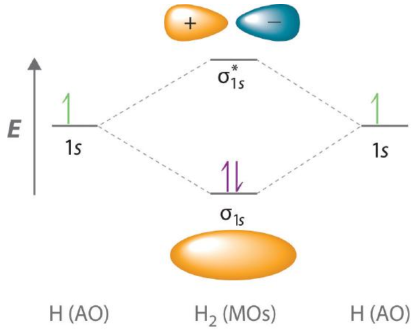


Figure 12.5.2: Molecular Orbital Energy-Level Diagram for H_2. The two available electrons (one from each H atom) in this diagram fill the bonding σ_{1s} molecular orbital. Because the energy of the σ_{1s} molecular orbital is lower than that of the two H 1*s* atomic orbitals, the H_2 molecule is more stable (at a lower energy) than the two isolated H atoms.

> A bonding molecular orbital is *always* lower in energy (more stable) than the component atomic orbitals, whereas an antibonding molecular orbital is *always* higher in energy (less stable).

To describe the bonding in a homonuclear diatomic molecule (a molecule that consists of two atoms of the same element) such as H_2, we use molecular orbitals; that is, for a molecule in which two identical atoms interact, we insert the total number of valence electrons into the energy-level diagram (Figure 12.5.2). We fill the orbitals according to the Pauli principle and Hund's rule: each orbital can accommodate a maximum of two electrons with opposite spins, and the orbitals are filled in order of increasing energy. Because each H atom contributes one valence electron, the resulting two electrons are exactly enough to fill the σ_{1s} bonding molecular orbital. The two electrons enter an orbital whose energy is lower than that of the parent atomic orbitals, so the H_2 molecule is more stable than the two isolated hydrogen atoms. Thus molecular orbital theory correctly predicts that H_2 is a stable molecule. Because bonds form when electrons are concentrated in the space between nuclei, this approach is also consistent with our earlier discussion of electron-pair bonds.

Bond Order in Molecular Orbital Theory

In the Lewis electron structures, the number of electron pairs holding two atoms together was called the *bond order*. In the molecular orbital approach, bond order One-half the net number of bonding electrons in a molecule. is defined as one-half the *net* number of bonding electrons:

$$bond\ order = \frac{number\ of\ bonding\ electrons - number\ of\ antibonding\ electrons}{2} \tag{12.5.4}$$

To calculate the bond order of H_2, we see from Figure 12.5.2 that the σ_{1s} (bonding) molecular orbital contains two electrons, while the $\sigma^{\star}_{1s}$ (antibonding) molecular orbital is empty. The bond order of H_2 is therefore

$$\frac{2-0}{2} = 1 \tag{12.5.5}$$

This result corresponds to the single covalent bond predicted by Lewis dot symbols. Thus molecular orbital theory and the Lewis electron-pair approach agree that a single bond containing two electrons has a bond order of 1. Double and triple bonds contain four or six electrons, respectively, and correspond to bond orders of 2 and 3.

We can use energy-level diagrams such as the one in Figure 12.5.2 to describe the bonding in other pairs of atoms and ions where *n* = 1, such as the H_2^+ ion, the He_2^+ ion, and the He_2 molecule. Again, we fill the lowest-energy molecular orbitals first while being sure not to violate the Pauli principle or Hund's rule.

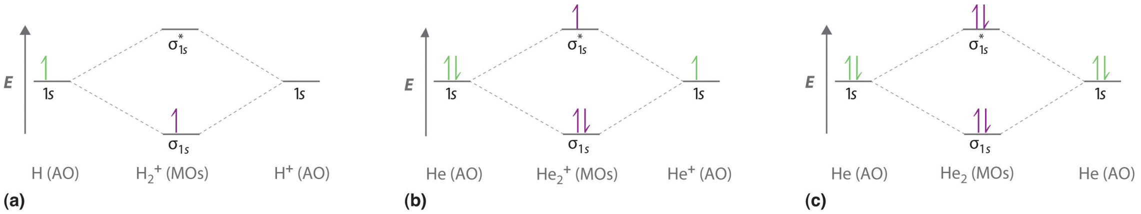


Figure 12.5.3: Molecular Orbital Energy-Level Diagrams for Diatomic Molecules with Only 1 s Atomic Orbitals. (a) The H_2^+ ion, (b) the He_2^+ ion, and (c) the He_2 molecule are shown here.

Part (a) in Figure 12.5.3 shows the energy-level diagram for the H_2^+ ion, which contains two protons and only one electron. The single electron occupies the σ_{1s} bonding molecular orbital, giving a $(\sigma_{1s})^1$ electron configuration. The number of electrons in an orbital is indicated by a superscript. In this case, the bond order is (1-0)/2=1/2 Because the bond order is greater than zero, the H_2^+ ion should be more stable than an isolated H atom and a proton. We can therefore use a molecular orbital energy-level diagram and the calculated bond order to predict the relative stability of species such as H_2^+. With a bond order of only 1/2 the bond in H_2^+ should be weaker than in the H_2 molecule, and the H–H bond should be longer. As shown in Table 12.5.1, these predictions agree with the experimental data.

Part (b) in Figure 12.5.3 is the molecular orbital energy-level diagram for He_2^+. This ion has a total of three valence electrons. Because the first two electrons completely fill the σ_{1s} molecular orbital, the Pauli principle states that the third electron must be in the $\sigma^{\star}_{1s}$ antibonding orbital, giving a $(\sigma_{1s})^2(\sigma^{\star}_{1s})^1$ electron configuration. This electron configuration gives a bond order of (2-1)/2=1/2. As with H_2^+, the He_2^+ ion should be stable, but the He–He bond should be weaker and longer than in H_2. In fact, the He_2^+ ion can be prepared, and its properties are consistent with our predictions (Table 12.5.1).

Table 12.5.1: Molecular Orbital Electron Configurations, Bond Orders, Bond Lengths, and Bond Energies for some Simple Homonuclear Diatomic Molecules and Ions

Molecule or Ion	Electron Configuration	Bond Order	Bond Length (pm)	Bond Energy (kJ/mol)
H_2^+	$(\sigma_{1s})^1$	1/2	106	269
H_2	$(\sigma_{1s})^2$	1	74	436
He_2^+	$(\sigma_{1s})^2(\sigma^{\star}_{1s})^1$	1/2	108	251
He_2	$(\sigma_{1s})^2(\sigma^{\star}_{1s})^2$	0	not observed	not observed

Finally, we examine the He_2 molecule, formed from two He atoms with $1s^2$ electron configurations. Part (c) in Figure 12.5.3 is the molecular orbital energy-level diagram for He_2. With a total of four valence electrons, both the σ_{1s} bonding and $\sigma^{\star}_{1s}$ antibonding orbitals must contain two electrons. This gives a $(\sigma_{1s})^2(\sigma^{\star}_{1s})^1$ electron configuration, with a predicted bond order of (2 − 2) ÷ 2 = 0, which indicates that the He_2 molecule has no net bond and is not a stable species. Experiments show that the He_2 molecule is actually *less* stable than two isolated He atoms due to unfavorable electron–electron and nucleus–nucleus interactions.

In molecular orbital theory, *electrons in antibonding orbitals effectively cancel the stabilization resulting from electrons in bonding orbitals*. Consequently, any system that has equal numbers of bonding and antibonding electrons will have a bond order of 0, and it is predicted to be unstable and therefore not to exist in nature. In contrast to Lewis electron structures and the valence bond approach, molecular orbital theory is able to accommodate systems with an odd number of electrons, such as the H_2^+ ion.

Note

In contrast to Lewis electron structures and the valence bond approach, molecular orbital theory can accommodate systems with an odd number of electrons.

Example 12.5.1

Use a molecular orbital energy-level diagram, such as those in Figure 12.5.3, to predict the bond order in the He_2^{2+} ion. Is this a stable species?

Given: chemical species

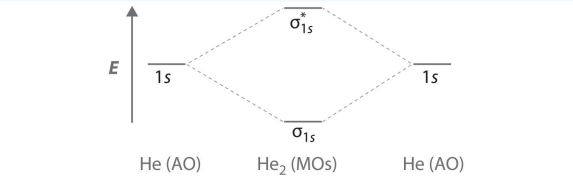
Asked for: molecular orbital energy-level diagram, bond order, and stability

Strategy:

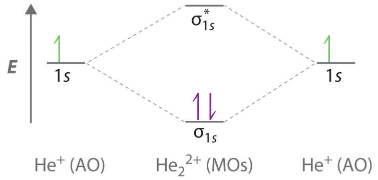
A. Combine the two He valence atomic orbitals to produce bonding and antibonding molecular orbitals. Draw the molecular orbital energy-level diagram for the system.
B. Determine the total number of valence electrons in the He_2^{2+} ion. Fill the molecular orbitals in the energy-level diagram beginning with the orbital with the lowest energy. Be sure to obey the Pauli principle and Hund's rule while doing so.
C. Calculate the bond order and predict whether the species is stable.

Solution:

A Two He 1*s* atomic orbitals combine to give two molecular orbitals: a σ_{1s} bonding orbital at lower energy than the atomic orbitals and a $\sigma^\star_{1s}$ antibonding orbital at higher energy. The bonding in any diatomic molecule with two He atoms can be described using the following molecular orbital diagram:



B The He_2^{2+} ion has only two valence electrons (two from each He atom minus two for the +2 charge). We can also view He_2^{2+} as being formed from two He^+ ions, each of which has a single valence electron in the 1*s* atomic orbital. We can now fill the molecular orbital diagram:



The two electrons occupy the lowest-energy molecular orbital, which is the bonding (σ_{1s}) orbital, giving a $(\sigma_{1s})^2$ electron configuration. To avoid violating the Pauli principle, the electron spins must be paired. **C** So the bond order is

$$\frac{2-0}{2}=1$$

He_2^{2+} is therefore predicted to contain a single He–He bond. Thus it should be a stable species.

Exercise 12.5.1

Use a molecular orbital energy-level diagram to predict the valence-electron configuration and bond order of the H_2^{2-} ion. Is this a stable species?

Answer:

H_2^{2-} has a valence electron configuration of $(\sigma_{1s})^2(\sigma^\star_{1s})^2$ with a bond order of 0. It is therefore predicted to be unstable.

So far, our discussion of molecular orbitals has been confined to the interaction of valence orbitals, which tend to lie farthest from the nucleus. When two atoms are close enough for their valence orbitals to overlap significantly, the filled inner electron shells are largely unperturbed; hence they do not need to be considered in a molecular orbital scheme. Also, when the inner orbitals are completely filled, they contain exactly enough electrons to completely fill both the bonding and antibonding molecular orbitals that arise from their interaction. Thus the interaction of filled shells always gives a bond order of 0, so filled shells are not a factor when predicting the stability of a species. This means that we can focus our attention on the molecular orbitals derived from valence atomic orbitals.

A molecular orbital diagram that can be applied to any **homonuclear diatomic molecule** with two identical alkali metal atoms (Li_2 and Cs_2, for example) is shown in part (a) in Figure 12.5.4, where M represents the metal atom. Only two energy levels are important for describing the valence electron molecular orbitals of these species: a σ_{ns} bonding molecular orbital and a σ^*_{ns} antibonding molecular orbital. Because each alkali metal (M) has an ns^1 valence electron configuration, the M_2 molecule has two valence electrons that fill the σ_{ns} bonding orbital. As a result, a bond order of 1 is predicted for all homonuclear diatomic species formed from the alkali metals (Li_2, Na_2, K_2, Rb_2, and Cs_2). The general features of these M_2 diagrams are identical to the diagram for the H_2 molecule in Figure 12.5.2. Experimentally, all are found to be stable in the gas phase, and some are even stable in solution.

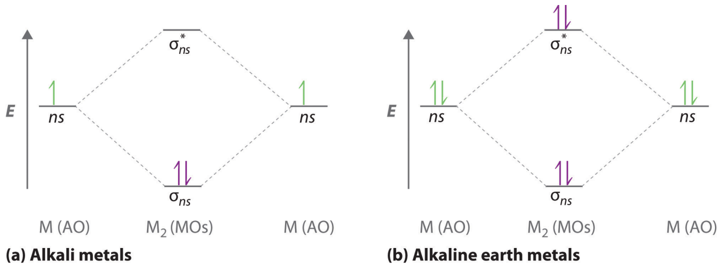


Figure 12.5.4: Molecular Orbital Energy-Level Diagrams for Alkali Metal and Alkaline Earth Metal Diatomic (M_2) Molecules. (a) For alkali metal diatomic molecules, the two valence electrons are enough to fill the σ_{ns} (bonding) level, giving a bond order of 1. (b) For alkaline earth metal diatomic molecules, the four valence electrons fill both the σ_{ns} (bonding) and the $\sigma_{ns}*$ (nonbonding) levels, leading to a predicted bond order of 0.

Similarly, the molecular orbital diagrams for homonuclear diatomic compounds of the alkaline earth metals (such as Be_2), in which each metal atom has an ns^2 valence electron configuration, resemble the diagram for the He_2 molecule in part (c) in Figure 12.5.3. As shown in part (b) in Figure 12.5.4, this is indeed the case. All the homonuclear alkaline earth diatomic molecules have four valence electrons, which fill both the σ_{ns} bonding orbital and the $\sigma_{ns}*$ antibonding orbital and give a bond order of 0. Thus Be_2, Mg_2, Ca_2, Sr_2, and Ba_2 are all expected to be unstable, in agreement with experimental data.In the solid state, however, all the alkali metals and the alkaline earth metals exist as extended lattices held together by metallic bonding. At low temperatures, Be_2 is stable.

Example 12.5.2

Use a qualitative molecular orbital energy-level diagram to predict the valence electron configuration, bond order, and likely existence of the Na_2^- ion.

Given: chemical species

Asked for: molecular orbital energy-level diagram, valence electron configuration, bond order, and stability

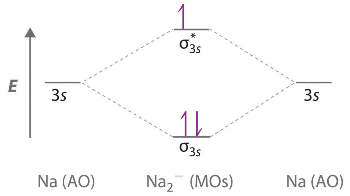
Strategy:

A. Combine the two sodium valence atomic orbitals to produce bonding and antibonding molecular orbitals. Draw the molecular orbital energy-level diagram for this system.
B. Determine the total number of valence electrons in the Na_2^- ion. Fill the molecular orbitals in the energy-level diagram beginning with the orbital with the lowest energy. Be sure to obey the Pauli principle and Hund’s rule while doing so.
C. Calculate the bond order and predict whether the species is stable.

Solution:

A Because sodium has a [Ne]$3s^1$ electron configuration, the molecular orbital energy-level diagram is qualitatively identical to the diagram for the interaction of two 1*s* atomic orbitals.

B The Na_2^- ion has a total of three valence electrons (one from each Na atom and one for the negative charge), resulting in a filled σ_{3s} molecular orbital, a half-filled σ_{3s*} and a $(\sigma_{3s})^2(\sigma^\star_{3s})^1$ electron configuration.



C The bond order is (2-1)÷2=1/2 With a fractional bond order, we predict that the Na_2^- ion exists but is highly reactive.

Exercise 12.5.2

Use a qualitative molecular orbital energy-level diagram to predict the valence electron configuration, bond order, and likely existence of the Ca_2^+ ion.

Answer: Ca_2^+ has a $(\sigma_{4s})^2(\sigma^\star_{4s})^1$ electron configurations and a bond order of 1/2 and should exist.

Contributors

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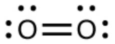
12.6: Diatomic Molecules

For almost every covalent molecule that exists, we can now draw the Lewis structure, predict the electron-pair geometry, predict the molecular geometry, and come close to predicting bond angles. However, one of the most important molecules we know, the oxygen molecule O_2, presents a problem with respect to its Lewis structure. We would write the following Lewis structure for O_2:



This electronic structure adheres to all the rules governing Lewis theory. There is an O=O double bond, and each oxygen atom has eight electrons around it. However, this picture is at odds with the magnetic behavior of oxygen. By itself, O_2 is not magnetic, but it is attracted to magnetic fields. Thus, when we pour liquid oxygen past a strong magnet, it collects between the poles of the magnet and defies gravity. Such attraction to a magnetic field is called paramagnetism, and it arises in molecules that have unpaired electrons. And yet, the Lewis structure of O_2 indicates that all electrons are paired. How do we account for this discrepancy?

Magnetic susceptibility measures the force experienced by a substance in a magnetic field. When we compare the weight of a sample to the weight measured in a magnetic field (Figure $12.6.1$), paramagnetic samples that are attracted to the magnet will appear heavier because of the force exerted by the magnetic field. We can calculate the number of unpaired electrons based on the increase in weight.

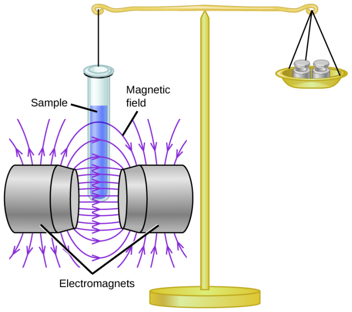


Figure 12.6.1: A Gouy balance compares the mass of a sample in the presence of a magnetic field with the mass with the electromagnet turned off to determine the number of unpaired electrons in a sample.

Experiments show that each O_2 molecule has two unpaired electrons. The Lewis-structure model does not predict the presence of these two unpaired electrons. Unlike oxygen, the apparent weight of most molecules decreases slightly in the presence of an inhomogeneous magnetic field. Materials in which all of the electrons are paired are diamagnetic and weakly repel a magnetic field. Paramagnetic and diamagnetic materials do not act as permanent magnets. Only in the presence of an applied magnetic field do they demonstrate attraction or repulsion.

Video $12.6.1$***:*** *Water, like most molecules, contains all paired electrons. Living things contain a large percentage of water, so they demonstrate diamagnetic behavior. If you place a frog near a sufficiently large magnet, it will levitate. You can see videos of diamagnetic floating frogs, strawberries, and more (https://www.youtube.com/watch?v=A1vyB-O5i6E)*

Molecular orbital theory (MO theory) provides an explanation of chemical bonding that accounts for the paramagnetism of the oxygen molecule. It also explains the bonding in a number of other molecules, such as violations of the octet rule and more molecules with more complicated bonding (beyond the scope of this text) that are difficult to describe with Lewis structures. Additionally, it provides a model for describing the energies of electrons in a molecule and the probable location of these electrons. Unlike valence bond theory, which uses hybrid orbitals that are assigned to one specific atom, MO theory uses the combination of atomic orbitals to yield molecular orbitals that are delocalized over the entire molecule rather than being localized on its constituent atoms. MO theory also helps us understand why some substances are electrical conductors, others are semiconductors, and still others are insulators. Table $12.6.1$ summarizes the main points of the two complementary bonding theories. Both theories provide different, useful ways of describing molecular structure.

Table 12.6.1 : Comparison of Bonding Theories

Valence Bond Theory	Molecular Orbital Theory
considers bonds as localized between one pair of atoms	considers electrons delocalized throughout the entire molecule
creates bonds from overlap of atomic orbitals (*s*, *p*, *d*…) and hybrid orbitals (*sp*, sp^2, sp^3…)	combines atomic orbitals to form molecular orbitals (σ, σ*, π, π*)
forms σ or π bonds	creates bonding and antibonding interactions based on which orbitals are filled
predicts molecular shape based on the number of regions of electron density	predicts the arrangement of electrons in molecules
needs multiple structures to describe resonance	

Molecular Orbitals Formed from *ns* and *np* Atomic Orbitals

Atomic orbitals other than *ns* orbitals can also interact to form molecular orbitals. Because individual *p*, *d*, and *f* orbitals are not spherically symmetrical, however, we need to define a coordinate system so we know which lobes are interacting in three-dimensional space. Recall that for each *np* subshell, for example, there are np_x, np_y, and np_z orbitals. All have the same energy and are therefore degenerate, but they have different spatial orientations.

$$\sigma_{np_z} = np_z(A) - np_z(B) \tag{12.6.1}$$

Just as with *ns* orbitals, we can form molecular orbitals from *np* orbitals by taking their mathematical sum and difference. When two positive lobes with the appropriate spatial orientation overlap, as illustrated for two np_z atomic orbitals in part (a) in Figure $12.6.2$, it is the mathematical *difference* of their wave functions that results in *constructive* interference, which in turn increases the electron probability density between the two atoms. The difference therefore corresponds to a molecular orbital called a σ_{np_z} *bonding molecular orbital* because, just as with the σ orbitals discussed previously, it is symmetrical about the internuclear axis (in this case, the *z*-axis):

$$\sigma_{np_z} = np_z(A) - np_z(B) \tag{12.6.2}$$

The other possible combination of the two np_z orbitals is the mathematical sum:

$$\sigma_{np_z} = np_z(A) + np_z(B) \tag{12.6.3}$$

In this combination, shown in part (b) in Figure $12.6.2$, the positive lobe of one np_z atomic orbital overlaps the negative lobe of the other, leading to *destructive* interference of the two waves and creating a node between the two atoms. Hence this is an antibonding molecular orbital. Because it, too, is symmetrical about the internuclear axis, this molecular orbital is called a $\sigma_{np_z} = np_z(A) - np_z(B)$ *antibonding molecular orbital*. Whenever orbitals combine, *the bonding combination is always lower in energy* (more stable) than the atomic orbitals from which it was derived, and *the antibonding combination is higher in energy* (less stable).

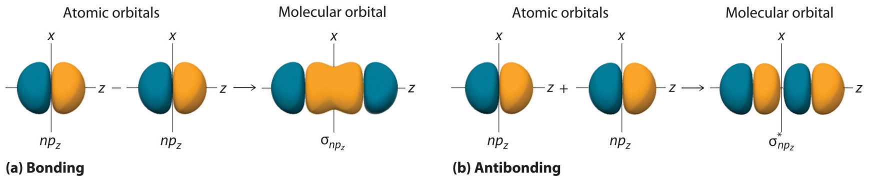


Figure 12.6.2: Formation of Molecular Orbitals from np_z Atomic Orbitals on Adjacent Atoms.(a) By convention, in a linear molecule or ion, the *z*-axis always corresponds to the internuclear axis, with +*z* to the right. As a result, the signs of the lobes of the np_z atomic orbitals on the two atoms alternate − + − +, from left to right. In this case, the σ (bonding) molecular orbital corresponds to the mathematical *difference*, in which the overlap of lobes with the same sign results in increased probability density between the nuclei. (b) In contrast, the σ* (antibonding) molecular orbital corresponds to the mathematical *sum*, in which the overlap of lobes with opposite signs results in a nodal plane of zero probability density perpendicular to the internuclear axis.

> Overlap of atomic orbital lobes with the *same sign* produces a bonding molecular orbital, regardless of whether it corresponds to the sum or the difference of the atomic orbitals.

The remaining *p* orbitals on each of the two atoms, np_x and np_y, do not point directly toward each other. Instead, they are perpendicular to the internuclear axis. If we arbitrarily label the axes as shown in Figure 12.6.3, we see that we have two pairs of *np* orbitals: the two np_x orbitals lying in the plane of the page, and two np_y orbitals perpendicular to the plane. Although these two pairs are equivalent in energy, the np_x orbital on one atom can interact with only the np_x orbital on the other, and the np_y orbital on one atom can interact with only the np_y on the other. These interactions are side-to-side rather than the head-to-head interactions characteristic of σ orbitals. Each pair of overlapping atomic orbitals again forms two molecular orbitals: one corresponds to the arithmetic sum of the two atomic orbitals and one to the difference. The sum of these side-to-side interactions increases the electron probability in the region above and below a line connecting the nuclei, so it is a bonding molecular orbital that is called a pi (π) orbital (a bonding molecular orbital formed from the side-to-side interactions of two or more parallel np atomic orbitals). The difference results in the overlap of orbital lobes with opposite signs, which produces a nodal plane perpendicular to the internuclear axis; hence it is an antibonding molecular orbital, called a pi star (π*) orbital An antibonding molecular orbital formed from the difference of the side-to-side interactions of two or more parallel *np* atomic orbitals, creating a nodal plane perpendicular to the internuclear axis..

$$\pi_{np_x} = np_x\,(A) + np_x\,(B) \tag{12.6.4}$$

$$\pi^\star_{np_x} = np_x\,(A) - np_x\,(B) \tag{12.6.5}$$

The two np_y orbitals can also combine using side-to-side interactions to produce a bonding π_{np_y} molecular orbital and an antibonding $\pi^\star_{np_y}$ molecular orbital. Because the np_x and np_y atomic orbitals interact in the same way (side-to-side) and have the same energy, the π_{np_x} and π_{np_y} molecular orbitals are a degenerate pair, as are the $\pi^\star_{np_x}$ and $\pi^\star_{np_y}$ molecular orbitals.

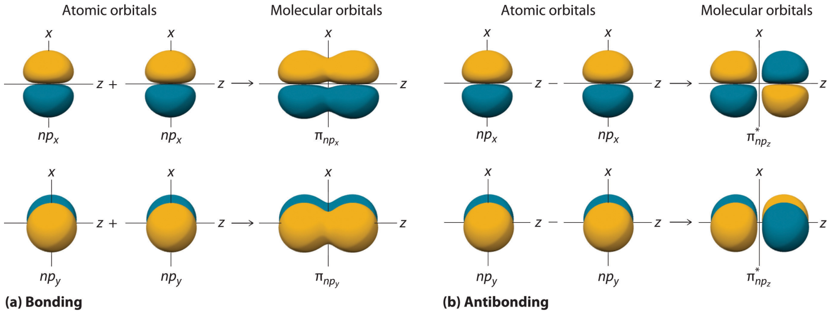


Figure 12.6.3: Formation of π Molecular Orbitals from np_x and np_y Atomic Orbitals on Adjacent Atoms.(a) Because the signs of the lobes of both the np_x and the np_y atomic orbitals on adjacent atoms are the same, in both cases the mathematical sum corresponds to a π (bonding) molecular orbital. (b) In contrast, in both cases, the mathematical difference corresponds to a π* (antibonding) molecular orbital, with a nodal plane of zero probability density perpendicular to the internuclear axis.

Figure 12.6.4 is an energy-level diagram that can be applied to two identical interacting atoms that have three *np* atomic orbitals each. There are six degenerate *p* atomic orbitals (three from each atom) that combine to form six molecular orbitals, three bonding and three antibonding. The bonding molecular orbitals are lower in energy than the atomic orbitals because of the increased stability associated with the formation of a bond. Conversely, the antibonding molecular orbitals are higher in energy, as shown. The energy difference between the σ and σ* molecular orbitals is significantly greater than the difference between the two π and π* sets. The reason for this is that the atomic orbital overlap and thus the strength of the interaction are greater for a σ bond than a π bond, which means that the σ molecular orbital is more stable (lower in energy) than the π molecular orbitals.

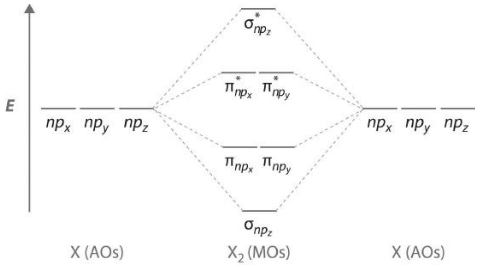


Figure 12.6.4: The Relative Energies of the σ and π Molecular Orbitals Derived from np_x, np_y, and np_z Orbitals on Identical Adjacent Atoms. Because the two np_z orbitals point directly at each other, their orbital overlap is greater, so the difference in energy between the σ and σ* molecular orbitals is greater than the energy difference between the π and π* orbitals.

Although many combinations of atomic orbitals form molecular orbitals, we will discuss only one other interaction: an *ns* atomic orbital on one atom with an np_z atomic orbital on another. As shown in Figure 12.6.5, the sum of the two atomic wave functions ($ns + np_z$) produces a σ bonding molecular orbital. Their difference ($ns - np_z$) produces a σ* antibonding molecular orbital, which has a nodal plane of zero probability density perpendicular to the internuclear axis.

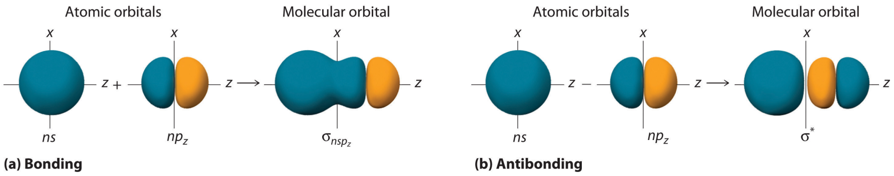


Figure 12.6.5: Formation of Molecular Orbitals from an ns Atomic Orbital on One Atom and an np_z Atomic Orbital on an Adjacent Atom.(a) The mathematical sum results in a σ (bonding) molecular orbital, with increased probability density between the nuclei. (b) The mathematical difference results in a σ* (antibonding) molecular orbital, with a nodal plane of zero probability density perpendicular to the internuclear axis.

Second Row Diatomic Molecules

If we combine the splitting schemes for the 2s and 2p orbitals, we can predict bond order in all of the diatomic molecules and ions composed of elements in the first complete row of the periodic table. Remember that only the valence orbitals of the atoms need be considered; as we saw in the cases of lithium hydride and dilithium, the inner orbitals remain tightly bound and retain their localized atomic character.

We now describe examples of systems involving period 2 homonuclear diatomic molecules, such as N_2, O_2, and F_2. When we draw a molecular orbital diagram for a molecule, there are four key points to remember:

1. The number of molecular orbitals produced is the same as the number of atomic orbitals used to create them (the law of conservation of orbitals).
2. As the overlap between two atomic orbitals increases, the difference in energy between the resulting bonding and antibonding molecular orbitals increases.
3. When two atomic orbitals combine to form a pair of molecular orbitals, the bonding molecular orbital is stabilized about as much as the antibonding molecular orbital is destabilized.
4. The interaction between atomic orbitals is greatest when they have the same energy.

> The number of molecular orbitals is **always** equal to the total number of atomic orbitals we started with.

We illustrate how to use these points by constructing a molecular orbital energy-level diagram for F_2. We use the diagram in part (a) in Figure 12.6.6; the n = 1 orbitals (σ_{1s} and σ_{1s}*) are located well below those of the n = 2 level and are not shown. As illustrated in the diagram, the σ_{2s} and σ_{2s}* molecular orbitals are much lower in energy than the molecular orbitals derived from the 2p atomic orbitals because of the large difference in energy between the 2s and 2p atomic orbitals of fluorine. The lowest-energy molecular orbital derived from the three 2p orbitals on each F is σ_{2p_z} and the next most stable are the two degenerate orbitals, π_{2p_x} and π_{2p_y}. For each bonding orbital in the diagram, there is an antibonding orbital, and the antibonding orbital is destabilized by about as much as the corresponding bonding orbital is stabilized. As a result, the $\sigma^\star_{2p_z}$ orbital is higher in energy than either of the degenerate $\pi^\star_{2p_x}$ and $\pi^\star_{2p_y}$ orbitals. We can now fill the orbitals, beginning with the one that is lowest in energy.

Each fluorine has 7 valence electrons, so there are a total of 14 valence electrons in the F_2 molecule. Starting at the lowest energy level, the electrons are placed in the orbitals according to the Pauli principle and Hund’s rule. Two electrons each fill the σ_{2s} and σ_{2s}* orbitals, 2 fill the σ_{2p_z} orbital, 4 fill the two degenerate π orbitals, and 4 fill the two degenerate π^* orbitals, for a total of 14 electrons. To determine what type of bonding the molecular orbital approach predicts F_2 to have, we must calculate the bond order. According to our diagram, there are 8 bonding electrons and 6 antibonding electrons, giving a bond order of $(8 - 6) \div 2 = 1$. Thus F_2 is predicted to have a stable F–F single bond, in agreement with experimental data.

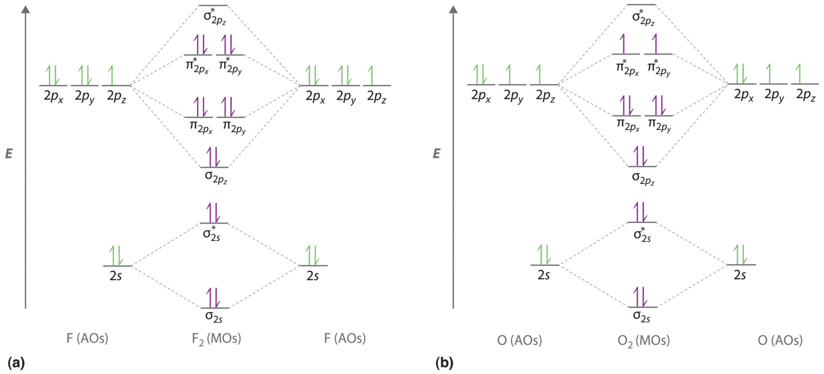
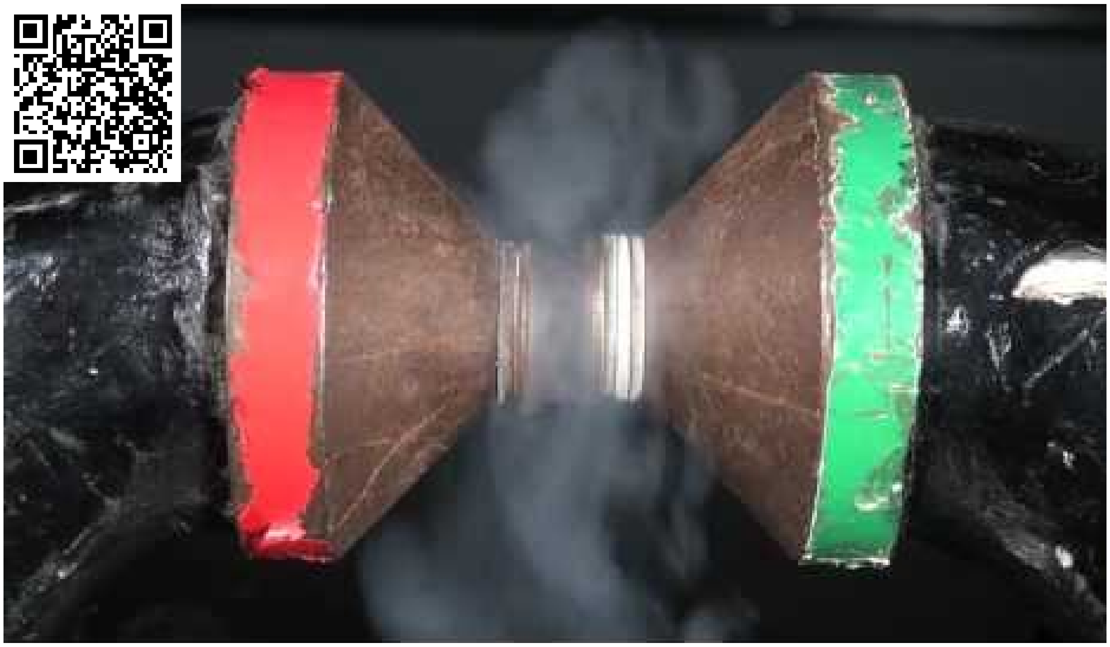


Figure 12.6.6: Molecular Orbital Energy-Level Diagrams for Homonuclear Diatomic Molecules.(a) For F_2, with 14 valence electrons (7 from each F atom), all of the energy levels except the highest, $\sigma^\star_{2p_z}$ are filled. This diagram shows 8 electrons in bonding orbitals and 6 in antibonding orbitals, resulting in a bond order of 1. (b) For O_2, with 12 valence electrons (6 from each O atom), there are only 2 electrons to place in the $\left(\pi^\star_{np_x}, \pi^\star_{np_y}\right)$ pair of orbitals. Hund’s rule dictates that one electron occupies each orbital, and their spins are parallel, giving the O_2 molecule two unpaired electrons. This diagram shows 8 electrons in bonding orbitals and 4 in antibonding orbitals, resulting in a predicted bond order of 2.

We now turn to a molecular orbital description of the bonding in O_2. It so happens that the molecular orbital description of this molecule provided an explanation for a long-standing puzzle that could not be explained using other bonding models. To obtain the molecular orbital energy-level diagram for O_2, we need to place 12 valence electrons (6 from each O atom) in the energy-level diagram shown in part (b) in Figure 12.6.6. We again fill the orbitals according to Hund's rule and the Pauli principle, beginning with the orbital that is lowest in energy. Two electrons each are needed to fill the σ_{2s} and $\sigma_{2s}*$ orbitals, 2 more to fill the σ_{2p_z} orbital, and 4 to fill the degenerate $\pi^\star_{2p_x}$ and $\pi^\star_{2p_y}$ orbitals. According to Hund's rule, the last 2 electrons must be placed in separate π^* orbitals with their spins parallel, giving two unpaired electrons. This leads to a predicted bond order of (8 − 4) ÷ 2 = 2, which corresponds to a double bond, in agreement with experimental data (Table 4.5): the O–O bond length is 120.7 pm, and the bond energy is 498.4 kJ/mol at 298 K.

None of the other bonding models can predict the presence of two unpaired electrons in O_2. Chemists had long wondered why, unlike most other substances, liquid O_2 is attracted into a magnetic field. As shown in Video 12.6.2, it actually remains suspended between the poles of a magnet until the liquid boils away. The only way to explain this behavior was for O_2 to have unpaired electrons, making it paramagnetic, exactly as predicted by molecular orbital theory. This result was one of the earliest triumphs of molecular orbital theory over the other bonding approaches we have discussed.



***Video 12.6.2**: Liquid O_2 Suspended between the Poles of a Magnet.Because the O_2 molecule has two unpaired electrons, it is paramagnetic. Consequently, it is attracted into a magnetic field, which allows it to remain suspended between the poles of a powerful magnet until it evaporates. Full video can be found at* https://www.youtube.com/watch?featur...&v=Lt4P6ctf06Q.

The magnetic properties of O_2 are not just a laboratory curiosity; they are absolutely crucial to the existence of life. Because Earth's atmosphere contains 20% oxygen, all organic compounds, including those that compose our body tissues, should react rapidly with air to form H_2O, CO_2, and N_2 in an exothermic reaction. Fortunately for us, however, this reaction is very, very slow. The reason for the unexpected stability of organic compounds in an oxygen atmosphere is that virtually all organic compounds, as well as H_2O, CO_2, and N_2, have only paired electrons, whereas oxygen has two unpaired electrons. Thus the reaction of O_2 with organic compounds to give H_2O, CO_2, and N_2 would require that at least one of the electrons on O_2 change its spin during the reaction. This would require a large input of energy, an obstacle that chemists call a *spin barrier*. Consequently, reactions of this type are usually exceedingly slow. If they were not so slow, all organic substances, including this book and you, would disappear in a puff of smoke!

For period 2 diatomic molecules to the left of N_2 in the periodic table, a slightly different molecular orbital energy-level diagram is needed because the σ_{2p_z} molecular orbital is slightly *higher* in energy than the degenerate $\pi^\star_{np_x}$ and $\pi^\star_{np_y}$ orbitals. The difference in energy between the 2*s* and 2*p* atomic orbitals increases from Li_2 to F_2 due to increasing nuclear charge and poor screening of the 2*s* electrons by electrons in the 2*p* subshell. The bonding interaction between the 2*s* orbital on one atom and the 2*pz* orbital on the other is most important when the two orbitals have similar energies. This interaction decreases the energy of the σ_{2s} orbital and increases the energy of the σ_{2p_z} orbital. Thus for Li_2, Be_2, B_2, C_2, and N_2, the σ_{2p_z} orbital is higher in energy than the σ_{3p_z} orbitals, as shown in Figure 12.6.7 Experimentally, it is found that the energy gap between the *ns* and *np* atomic orbitals *increases* as the nuclear charge increases (Figure 12.6.7). Thus for example, the σ_{2p_z} molecular orbital is at a lower energy than the $\pi_{2p_{x,y}}$ pair.

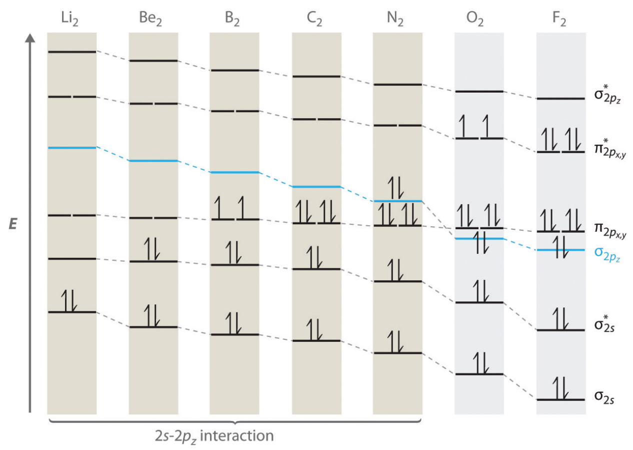


Figure 12.6.7: Molecular Orbital Energy-Level Diagrams for the Diatomic Molecules of the Period 2 Elements. Unlike earlier diagrams, only the molecular orbital energy levels for the molecules are shown here. For simplicity, the atomic orbital energy levels for the component *atoms* have been omitted. For Li_2 through N_2, the σ_{2p_z} *orbital is higher in energy than the* $\pi_{2p_{x,y}}$ *orbitals. In contrast, the* σ_{2p_z} *orbital is lower in energy than the* $\pi_{2p_{x,y}}$ *orbitals for* O_2 *and* F_2 *due to the increase in the energy difference between the 2s and 2p atomic orbitals as the nuclear charge increases across the row.*

Completing the diagram for N_2 in the same manner as demonstrated previously, we find that the 10 valence electrons result in 8 bonding electrons and 2 antibonding electrons, for a predicted bond order of 3, a triple bond. Experimental data show that the N–N bond is significantly shorter than the F–F bond (109.8 pm in N_2 versus 141.2 pm in F_2), and the bond energy is much greater for N_2 than for F_2 (945.3 kJ/mol versus 158.8 kJ/mol, respectively). Thus the N_2 bond is much shorter and stronger than the F_2 bond, consistent with what we would expect when comparing a triple bond with a single bond.

✓ Example 12.6.1

Use a qualitative molecular orbital energy-level diagram to predict the electron configuration, the bond order, and the number of unpaired electrons in S_2, a bright blue gas at high temperatures.

Given: chemical species

Asked for: molecular orbital energy-level diagram, bond order, and number of unpaired electrons

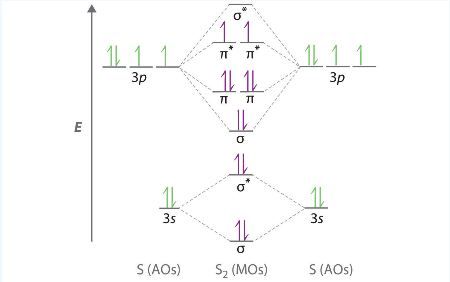
Strategy:

A. Write the valence electron configuration of sulfur and determine the type of molecular orbitals formed in S_2. Predict the relative energies of the molecular orbitals based on how close in energy the valence atomic orbitals are to one another.
B. Draw the molecular orbital energy-level diagram for this system and determine the total number of valence electrons in S_2.
C. Fill the molecular orbitals in order of increasing energy, being sure to obey the Pauli principle and Hund's rule.
D. Calculate the bond order and describe the bonding.

Solution:

A Sulfur has a [Ne]$3s^2 3p^4$ valence electron configuration. To create a molecular orbital energy-level diagram similar to those in Figure 12.6.6 and Figure 12.6.7, we need to know how close in energy the 3*s* and 3*p* atomic orbitals are because their energy separation will determine whether the $\pi_{3p_{x,y}}$ or the σ_{3p_z}> molecular orbital is higher in energy. Because the *ns*–*np* energy gap *increases* as the nuclear charge increases (Figure 12.6.7), the σ_{3p_z} molecular orbital will be lower in energy than the $\pi_{3p_{x,y}}$ pair.

B The molecular orbital energy-level diagram is as follows:



Each sulfur atom contributes 6 valence electrons, for a total of 12 valence electrons.

C Ten valence electrons are used to fill the orbitals through π_{3p_x} and π_{3p_y}, leaving 2 electrons to occupy the degenerate $\pi^\star_{3p_x}$ and $\pi^\star_{3p_y}$ pair. From Hund's rule, the remaining 2 electrons must occupy these orbitals separately with their spins aligned. With the numbers of electrons written as superscripts, the electron configuration of S_2 is $(\sigma_{3s})^2(\sigma^\star_{3s})^2(\sigma_{3p_z})^2(\pi_{3p_{x,y}})^4(\pi_{3p^\star_{x,y}})^2$ with 2 unpaired electrons. The bond order is (8 − 4) ÷ 2 = 2, so we predict an S=S double bond.

Exercise 12.6.1

Use a qualitative molecular orbital energy-level diagram to predict the electron configuration, the bond order, and the number of unpaired electrons in the peroxide ion ($O_2{}^{2-}$).

Answer

$(\sigma_{2s})^2(\sigma^\star_{2s})^2(\sigma_{2p_z})^2(\pi_{2p_{x,y}})^4(\pi_{2p^\star_{x,y}})^4$ bond order of 1; no unpaired electrons

Molecular Orbitals for Heteronuclear Diatomic Molecules

Diatomic molecules with two different atoms are called heteronuclear diatomic molecules. When two nonidentical atoms interact to form a chemical bond, the interacting atomic orbitals do not have the same energy. If, for example, element B is more electronegative than element A ($\chi_B > \chi_A$), the net result is a "skewed" molecular orbital energy-level diagram, such as the one shown for a hypothetical A–B molecule in Figure 12.6.8. The atomic orbitals of element B are uniformly lower in energy than the corresponding atomic orbitals of element A because of the enhanced stability of the electrons in element B. The molecular orbitals are no longer symmetrical, and the energies of the bonding molecular orbitals are more similar to those of the atomic orbitals of B. Hence the electron density of bonding electrons is likely to be closer to the more electronegative atom. In this way, molecular orbital theory can describe a polar covalent bond.

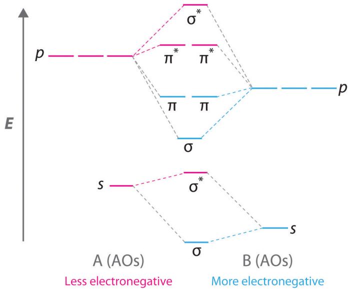


Figure 12.6.8: Molecular Orbital Energy-Level Diagram for a Heteronuclear Diatomic Molecule AB, Where $\chi_B > \chi_A$. The bonding molecular orbitals are closer in energy to the atomic orbitals of the more electronegative B atom. Consequently, the electrons in the bonding orbitals are not shared equally between the two atoms. On average, they are closer to the B atom, resulting in a polar covalent bond.

> A molecular orbital energy-level diagram is always skewed toward the more electronegative atom.

An Odd Number of Valence Electrons: NO

Nitric oxide (NO) is an example of a heteronuclear diatomic molecule. The reaction of O_2 with N_2 at high temperatures in internal combustion engines forms nitric oxide, which undergoes a complex reaction with O_2 to produce NO_2, which in turn is responsible for the brown color we associate with air pollution. Recently, however, nitric oxide has also been recognized to be a vital biological messenger involved in regulating blood pressure and long-term memory in mammals.

Because NO has an odd number of valence electrons (5 from nitrogen and 6 from oxygen, for a total of 11), its bonding and properties cannot be successfully explained by either the Lewis electron-pair approach or valence bond theory. The molecular orbital energy-level diagram for NO (Figure 12.6.9) shows that the general pattern is similar to that for the O_2 molecule (Figure 12.6.7). Because 10 electrons are sufficient to fill all the bonding molecular orbitals derived from 2*p* atomic orbitals, the 11th electron must occupy one of the degenerate π^* orbitals. The predicted bond order for NO is therefore (8-3) ÷ 2 = 2 1/2 . Experimental data, showing an N–O bond length of 115 pm and N–O bond energy of 631 kJ/mol, are consistent with this description. These values lie between those of the N_2 and O_2 molecules, which have triple and double bonds, respectively. As we stated earlier, molecular orbital theory can therefore explain the bonding in molecules with an odd number of electrons, such as NO, whereas Lewis electron structures cannot.

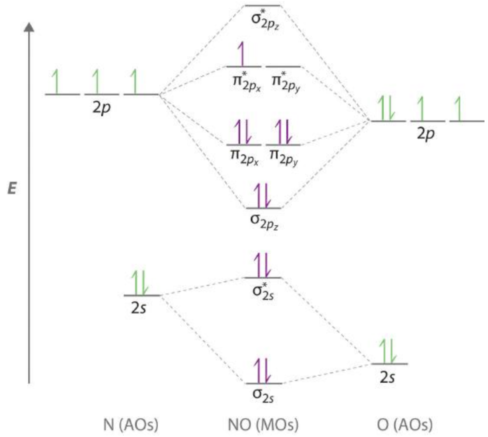


Figure 12.6.9: Molecular Orbital Energy-Level Diagram for NO. Because NO has 11 valence electrons, it is paramagnetic, with a single electron occupying the $\left(\pi^{\star}_{2p_x},\ \pi^{\star}_{2p_y}\right)$ pair of orbitals.

Molecular orbital theory can also tell us something about the *chemistry* of NO. As indicated in the energy-level diagram in Figure 12.6.9, NO has a single electron in a relatively high-energy molecular orbital. We might therefore expect it to have similar reactivity as alkali metals such as Li and Na with their single valence electrons. In fact, NO is easily oxidized to the NO^{+} cation, which is isoelectronic with N_2 and has a bond order of 3, corresponding to an N≡O triple bond.

Nonbonding Molecular Orbitals

Molecular orbital theory is also able to explain the presence of lone pairs of electrons. Consider, for example, the HCl molecule, whose Lewis electron structure has three lone pairs of electrons on the chlorine atom. Using the molecular orbital approach to describe the bonding in HCl, we can see from Figure 12.6.10 that the 1*s* orbital of atomic hydrogen is closest in energy to the 3*p* orbitals of chlorine. Consequently, the filled Cl 3*s* atomic orbital is not involved in bonding to any appreciable extent, and the only important interactions are those between the H 1*s* and Cl 3*p* orbitals. Of the three *p* orbitals, only one, designated as $3p_z$, can interact with the H 1*s* orbital. The $3p_x$ and $3p_y$ atomic orbitals have no net overlap with the 1*s* orbital on hydrogen, so they are not involved in bonding. Because the energies of the Cl 3*s*, $3p_x$, and $3p_y$ orbitals do not change when HCl forms, they are called **nonbonding molecular orbitals**. A nonbonding molecular orbital occupied by a pair of electrons is the molecular orbital equivalent of a lone pair of electrons. By definition, electrons in nonbonding orbitals have no effect on bond order, so they are not counted in the calculation of bond order. Thus the predicted bond order of HCl is (2 − 0) ÷ 2 = 1. Because the σ bonding molecular orbital is closer in energy to the Cl $3p_z$ than to the H 1*s* atomic orbital, the electrons in the σ orbital are concentrated closer to the chlorine atom than to hydrogen. A molecular orbital approach to bonding can therefore be used to describe the polarization of the H–Cl bond to give $H^{\delta+}-Cl^{\delta-}$.

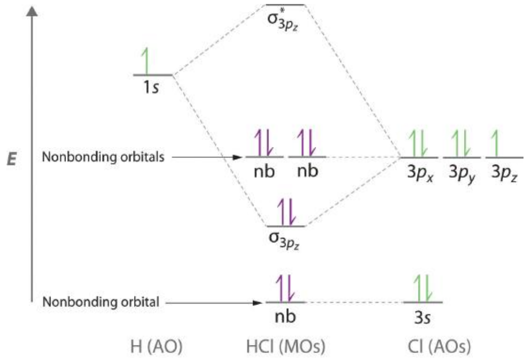


Figure 12.6.10: Molecular Orbital Energy-Level Diagram for HCl. The hydrogen 1 s atomic orbital interacts most strongly with the $3p_z$ orbital on chlorine, producing a bonding/antibonding pair of molecular orbitals. The other electrons on Cl are best viewed as nonbonding. As a result, only the bonding σ orbital is occupied by electrons, giving a bond order of 1.

> Electrons in nonbonding molecular orbitals have **no effect** on bond order.

✓ Example 12.6.2

Use a “skewed” molecular orbital energy-level diagram like the one in Figure 12.6.8 to describe the bonding in the cyanide ion (CN⁻). What is the bond order?

Given: chemical species

Asked for: “skewed” molecular orbital energy-level diagram, bonding description, and bond order

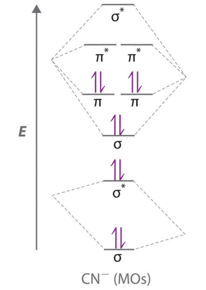
Strategy:

A. Calculate the total number of valence electrons in CN^-. Then place these electrons in a molecular orbital energy-level diagram like Figure 12.6.8 in order of increasing energy. Be sure to obey the Pauli principle and Hund's rule while doing so.

B. Calculate the bond order and describe the bonding in CN^-.

Solution:

A The CN^- ion has a total of 10 valence electrons: 4 from C, 5 from N, and 1 for the −1 charge. Placing these electrons in an energy-level diagram like Figure 12.6.8 fills the five lowest-energy orbitals, as shown here:



Because $\chi_N > \chi_C$, the atomic orbitals of N (on the right) are lower in energy than those of C. **B** The resulting valence electron configuration gives a predicted bond order of (8 − 2) ÷ 2 = 3, indicating that the CN^- ion has a triple bond, analogous to that in N_2.

? Exercise 12.6.2

Use a qualitative molecular orbital energy-level diagram to describe the bonding in the hypochlorite ion (OCl^-). What is the bond order?

Answer

All molecular orbitals except the highest-energy σ* are filled, giving a bond order of 1.

Although the molecular orbital approach reveals a great deal about the bonding in a given molecule, the procedure quickly becomes computationally intensive for molecules of even moderate complexity. Furthermore, because the computed molecular orbitals extend over the entire molecule, they are often difficult to represent in a way that is easy to visualize. Therefore we do not use a pure molecular orbital approach to describe the bonding in molecules or ions with more than two atoms. Instead, we use a valence bond approach and a molecular orbital approach to explain, among other things, the concept of resonance, which cannot adequately be explained using other methods.

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12.7: Resonance and Electron Delocalization

Resonance is a mental exercise and method within the Valence Bond Theory of bonding that describes the delocalization of electrons within molecules. It compares and contrasts two or more possible Lewis structures that can represent a particular molecule. Resonance structures are used when one Lewis structure for a single molecule cannot fully describe the bonding that takes place between neighboring atoms relative to the empirical data for the actual bond lengths between those atoms. The net sum of valid resonance structures is defined as a resonance hybrid, which represents the overall delocalization of electrons within the molecule. A molecule that has several resonance structures is more stable than one with fewer. Some resonance structures are more favorable than others.

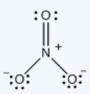
Introduction

Electrons have no fixed position in atoms, compounds and molecules (see image below) but have probabilities of being found in certain spaces (orbitals). Resonance forms illustrate areas of higher probabilities (electron densities). This is like holding your hat in either your right hand or your left. The term Resonance is applied when there are two or more possibilities available. Chemists use Lewis diagrams to depict structure and bonding of covalent entities, such as molecules and polyatomic ions, henceforth, molecules. The Lewis diagram of many a molecule, however, is not consistent with the observed properties of the molecule.

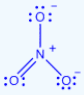
✓ Example 12.7.1: Nitrate Ion

The nitrate ion, according to its Lewis diagram, has two types of nitrogen-oxygen bonds, one double bond and two single bonds, suggesting that one nitrogen-oxygen bond in the nitrate ion is shorter and stronger than each of the other two. Also, the Lewis structure implies, with respect to formal charge, that there are two types of oxygen atoms in the nitrate ion, one formally neutral and each of the other two bearing a formal charge of –1. Experimentally, however, the three nitrogen-oxygen bonds in the nitrate ion have the same bond length and the same bond energy, and the three oxygen atoms are indistinguishable. The Lewis diagram fails to explain the structure and bonding of the nitrate ion satisfactorily.

Two additional Lewis diagrams can be drawn for the nitrate ion.



1



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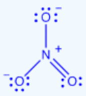


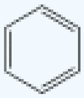
3

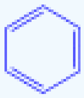
However, none of them are consistent with the observed properties of the nitrate ion and, therefore, does not correctly depict the nitrate ion.

✓ Example 12.7.2: Benzene

Benzene, according to its Lewis diagram, has two types of carbon-carbon bonds, three double bonds and three single bonds, suggesting that each of three carbon-carbon bonds in benzene is shorter and stronger than each of the other three. Experimentally, however, the six carbon-carbon bonds in benzene have the same bond length and the same bond energy. The Lewis diagram fails to explain the structure and bonding of benzene satisfactorily.

An attribute of molecules of which the classical Lewis diagram is not consistent with the observed properties is that other valid Lewis diagrams can be generated for them. One additional Lewis diagram can be drawn for benzene.

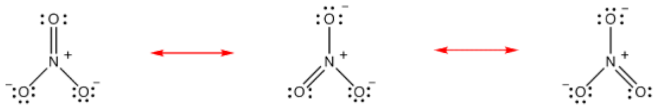




However, none of them are consistent with the observed properties of benzene and, therefore, does not correctly depict benzene.

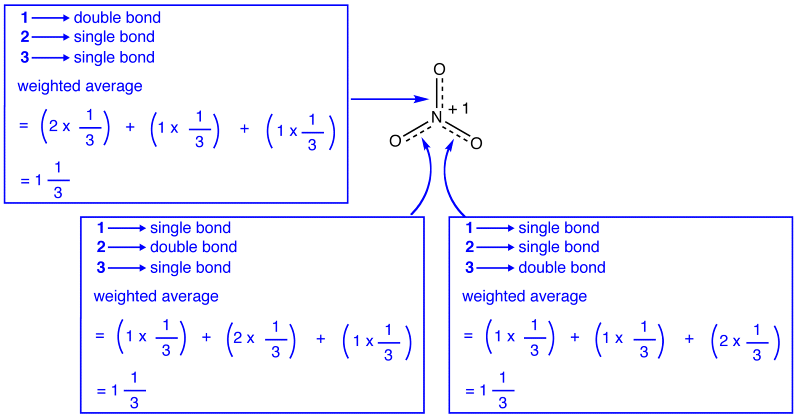
Resonance theory is an attempt to explain the structure of a species, like the nitrate ion or benzene, no Lewis diagram of which is consistent with the observed properties of the species. The major advantage of resonance theory is that, although based on rigorous mathematical analysis, resonance theory can be applied successfully invoking little or no math. Resonance theory is explained below using the nitrate ion as the example.

According to resonance theory, the structure of the nitrate ion is not 1 nor 2 nor 3 but the average of all three of them, weighted by stability. Lewis diagrams 1, 2, and 3 are called resonance forms, resonance structures, or resonance contributors of the nitrate ion. The structure of the nitrate ion is said to be a resonance hybrid or, simply, hybrid of resonance forms 1, 2, and 3. Whenever it is necessary to show the structure of the nitrate ion, resonance forms 1, 2, and 3 are drawn, connected by a double-headed arrows.

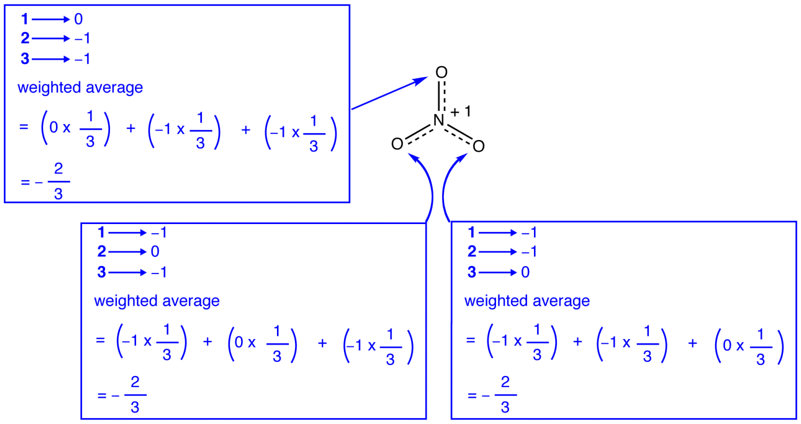


1 **2** **3**

The three resonance forms of the nitrate ion, 1, 2, and 3, are identical, so they have the same stability and, therefore, contribute equally to the hybrid. Since the exact extent to which each resonance form of the nitrate ion contributes to the hybrid is known, the bond order of each nitrogen-oxygen bond as well as the formal charge on each oxygen atom in the hybrid can be easily determined:



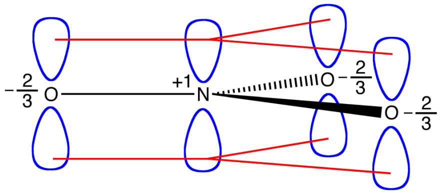
According to resonance theory, each bond in the nitrate ion is one and one-third of a bond, which is consistent with the observation that the three bonds in the nitrate ion have the same bond length and the same bond energy.



According to resonance theory, each oxygen atom in the nitrate ion has a formal charge of –2/3, which, in conjunction with the fact that the three nitrogen-oxygen bonds are identical, is consistent with the observation that the three oxygen atoms in the nitrate ion are indistinguishable. In each resonance form of the nitrate ion, there are two π electrons, and they are shared only by two atoms. An electron shared only by two atoms is said to be localized. Thus, the two π electrons in each resonance form of the nitrate ion are localized. The nitrate ion, as represented by the hybrid, has two π electrons:

- # electrons in one π bond = 2
- # electrons in one-third of a π bond = 2/3
- # electrons in three of them = 3 x (2/3) = 2

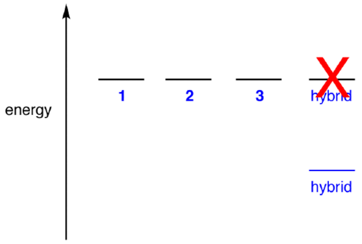
The two π electrons in the nitrate ion are shared by a total of four atoms, one nitrogen atom and three oxygen atoms. An electron shared by more than two atoms is said to be delocalized. Thus, the two π electrons in the nitrate ion are delocalized. Delocalization of π electrons in the nitrate ion requires that the four atoms be on the same plane, allowing lateral overlap of the p orbitals on them.



If the energy of the nitrate ion were the weighted average of the energies of its three resonance forms, just as the structure of the nitrate ion is the weighted average of the structures of its three resonance forms, it should be equal to the energy of one of the three identical resonance forms:

$$\begin{aligned}
&\text{energy of } \mathbf{1} = x\\
&\text{energy of } \mathbf{2} = x\\
&\text{energy of } \mathbf{3} = x\\
&\text{weighted average} = \left(x \cdot \frac{1}{3}\right) + \left(x \cdot \frac{1}{3}\right) + \left(x \cdot \frac{1}{3}\right)\\
&\qquad\qquad\qquad\quad = x
\end{aligned}$$

If the energy of the hybrid were equal to that of a resonance form, given that all chemical entities (elementary particles, atoms, molecules, etc.) naturally tend to be in the lowest possible energy state, there would be no advantage for the nitrate ion to exist as the hybrid; it could simply exist as a resonance form. Since the nitrate ion exists as the hybrid, not as a resonance form, it can be inferred that the energy of the hybrid is lower than that of any of the resonance forms.

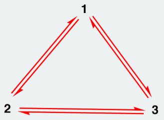


According to resonance theory then, the energy of a molecule is lower than that of the lowest-energy resonance form. Since the nitrate ion has lower energy and, therefore, is more stable than any of its resonance forms, the nitrate ion is said to be resonance stabilized.

Common Misconceptions

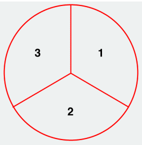
There are two misconceptions about resonance theory among beginning students, likely due to literal interpretation of the word resonance. They are described below, using the nitrate ion as the example.

Misconception 1: The nitrate ion exists as resonance form 1 for a moment and then changes either to resonance form 2 or to resonance form 3, which interconvert, or revert to 1.



The structure of the nitrate ion is not 1 nor 2 nor 3 but the hybrid and does not change with time unless undergoing a reaction.

Misconception 2: In a sample of nitrate ions, at a given moment, one-third of the ions exist as resonance form 1, another one-third as resonance form 2, and the remaining one-third as resonance form 3.



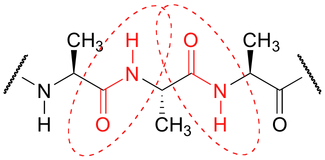
In a sample of nitrate ions, at a given moment, all ions have the same structure, which is the hybrid.

Mules and Rhinoceros

The classic analogy used to clarify these two misconceptions is the mule (Morrison, R. T.; Boyd, R.N. Organic Chemistry, fifth edition; Allyn and Bacon: Boston, 1987, pg. 373). Biologically, a mule is a hybrid of a horse and a donkey. This does not mean that a mule resembles a horse for a moment and then changes to resemble a donkey. The appearance of a mule is a combination of that of a horse and that of a donkey and does not change with time. Nor does it mean that, in a herd, some mules resemble a horse and the others a donkey. In a herd, all mules have the same appearance, which is a combination of a horse and a donkey. The weakness of this analogy is that horses and donkeys do exist, whereas resonance forms are strictly hypothetical. A better analogy, cited in Morrison and Boyd, is the rhinoceros. Upon seeing a rhinoceros, one could describe it as the hybrid of a dragon and a unicorn, two creatures that do not exist.

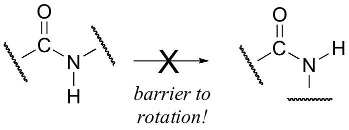
Peptide Bonds

A consideration of resonance contributors is crucial to any discussion of the amide functional group. One of the most important examples of amide groups in nature is the 'peptide bond' that links amino acids to form polypeptides and proteins.

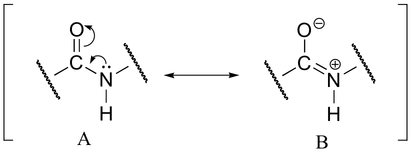


peptide bonds in a polypeptide

Critical to the structure of proteins is the fact that, although it is conventionally drawn as a single bond, the C-N bond in a peptide linkage has a significant barrier to rotation, almost as if it were a double bond.



This, along with the observation that the bonding around the peptide nitrogen has trigonal planar geometry, strongly suggests that the nitrogen is sp^2-hybridized. An important resonance contributor has a C=N double bond and a C-O single bond, with a separation of charge between the oxygen and the nitrogen.



Although B is a minor contributor due to the separation of charges, it is still very relevant in terms of peptide and protein structure – our proteins would simply not fold up properly if there was free rotation about the peptide C-N bond.

Contributors and Attributions

- ◦ Gamini Gunawardena from the OChemPal site (Utah Valley University)
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

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12.8: Coordination Compounds

Learning Objectives

- To know the most common structures observed for metal complexes.
- To predict the relative stabilities of metal complexes with different ligands

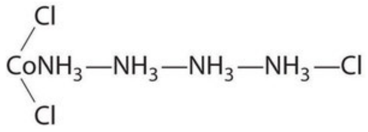
One of the most important properties of metallic elements is their ability to act as Lewis acids that form complexes with a variety of Lewis bases. A metal complex consists of a central metal atom or ion that is bonded to one or more ligands (from the Latin ligare, meaning “to bind”), which are ions or molecules that contain one or more pairs of electrons that can be shared with the metal. Metal complexes can be neutral, such as $Co(NH_3)_3Cl_3$; positively charged, such as $[Nd(H_2O)_9]^{3+}$; or negatively charged, such as $[UF_8]^{4-}$. Electrically charged metal complexes are sometimes called *complex ions*. A *coordination compound* contains one or more metal complexes.

Coordination compounds are important for at least three reasons. First, most of the elements in the periodic table are metals, and almost all metals form complexes, so metal complexes are a feature of the chemistry of more than half the elements. Second, many industrial catalysts are metal complexes, and such catalysts are steadily becoming more important as a way to control reactivity. For example, a mixture of a titanium complex and an organometallic compound of aluminum is the catalyst used to produce most of the polyethylene and polypropylene “plastic” items we use every day. Finally, transition-metal complexes are essential in biochemistry. Examples include hemoglobin, an iron complex that transports oxygen in our blood; cytochromes, iron complexes that transfer electrons in our cells; and complexes of Fe, Zn, Cu, and Mo that are crucial components of certain enzymes, the catalysts for all biological reactions.

History of the Coordination Compounds

Coordination compounds have been known and used since antiquity; probably the oldest is the deep blue pigment called Prussian blue: $\mathrm{KFe_2(CN)_6}$. The chemical nature of these substances, however, was unclear for a number of reasons. For example, many compounds called “double salts” were known, such as $\mathrm{AlF_3 \cdot 3\,KF}$, $\mathrm{Fe(CN)_2 \cdot 4\,KCN}$, and $\mathrm{ZnCl_2 \cdot 2\,CsCl}$, which were combinations of simple salts in fixed and apparently arbitrary ratios. Why should $\mathrm{AlF_3 \cdot 3\,KF}$ exist but not $\mathrm{AlF_3 \cdot 4\,KF}$ or $\mathrm{AlF_3 \cdot 2\,KF}$? And why should a 3:1 KF:AlF3 mixture have different chemical and physical properties than either of its components? Similarly, adducts of metal salts with neutral molecules such as ammonia were also known—for example, $\mathrm{CoCl_3 \cdot 6\,NH_3}$, which was first prepared sometime before 1798. Like the double salts, the compositions of these adducts exhibited fixed and apparently arbitrary ratios of the components. For example, $\mathrm{CoCl_3 \cdot 6\,NH_3}$, $\mathrm{CoCl_3 \cdot 5\,NH_3}$, $\mathrm{CoCl_3 \cdot 4\,NH_3}$, and $\mathrm{CoCl_3 \cdot 3\,NH_3}$ were all known and had very different properties, but despite all attempts, chemists could not prepare $\mathrm{CoCl_3 \cdot 2\,NH_3}$ or $\mathrm{CoCl_3 \cdot NH_3}$.

Although the chemical composition of such compounds was readily established by existing analytical methods, their chemical nature was puzzling and highly controversial. The major problem was that what we now call valence (i.e., the oxidation state) and coordination number were thought to be identical. As a result, highly implausible (to modern eyes at least) structures were proposed for such compounds, including the “Chattanooga choo-choo” model for $CoCl_3{\cdot}4NH_3$ shown here.



$\mathbf{CoCl_3 \cdot 4NH_3}$

The modern theory of coordination chemistry is based largely on the work of Alfred Werner (1866–1919; Nobel Prize in Chemistry in 1913). In a series of careful experiments carried out in the late 1880s and early 1890s, he examined the properties of several series of metal halide complexes with ammonia. For example, five different “adducts” of ammonia with $PtCl_4$ were known at the time: $PtCl_4{\cdot}nNH_3$ (n = 2–6). Some of Werner’s original data on these compounds are shown in Table 12.8.1. The electrical conductivity of aqueous solutions of these compounds was roughly proportional to the number of ions formed per mole, while the number of chloride ions that could be precipitated as AgCl after adding $Ag^+(aq)$ was a measure of the number of “free” chloride ions present. For example, Werner’s data on $PtCl_4{\cdot}6NH_3$ in Table 12.8.1 showed that all the chloride ions were present as free chloride. In contrast, $PtCl_4{\cdot}2NH_3$ was a neutral molecule that contained no free chloride ions.

Alfred Werner (1866–1919)

Werner, the son of a factory worker, was born in Alsace. He developed an interest in chemistry at an early age, and he did his first independent research experiments at age 18. While doing his military service in southern Germany, he attended a series of chemistry lectures, and he subsequently received his PhD at the University of Zurich in Switzerland, where he was appointed professor of chemistry at age 29. He won the Nobel Prize in Chemistry in 1913 for his work on coordination compounds, which he performed as a graduate student and first presented at age 26. Apparently, Werner was so obsessed with solving the riddle of the structure of coordination compounds that his brain continued to work on the problem even while he was asleep. In 1891, when he was only 25, he woke up in the middle of the night and, in only a few hours, had laid the foundation for modern coordination chemistry.

Table 12.8.1: Werner's Data on Complexes of Ammonia with $PtCl_4$

Complex	Conductivity (ohm^{-1})	Number of Ions per Formula Unit	Number of Cl$^-$ Ions Precipitated by Ag$^+$
$PtCl_4·6NH_3$	523	5	4
$PtCl_4·5NH_3$	404	4	3
$PtCl_4·4NH_3$	299	3	2
$PtCl_4·3NH_3$	97	2	1
$PtCl_4·2NH_3$	0	0	0

These data led Werner to postulate that metal ions have two different kinds of valence: (1) a primary valence (**oxidation state**) that corresponds to the positive charge on the metal ion and (2) a secondary valence (**coordination number**) that is the total number of ligand-metal bonds bound to the metal ion. If Pt had a primary valence of 4 and a secondary valence of 6, Werner could explain the properties of the $\mathrm{PtCl_4 \cdot NH_3}$ adducts by the following reactions, where the metal complex is enclosed in square brackets:

$$\mathrm{[Pt(NH_3)_6]Cl_4 \rightarrow [Pt(NH_3)_6]^{4+}(aq) + 4Cl^-(aq)}$$

$$\mathrm{[Pt(NH_3)_5Cl]Cl_3 \rightarrow [Pt(NH_3)_5Cl]^{3+}(aq) + 3Cl^-(aq)}$$

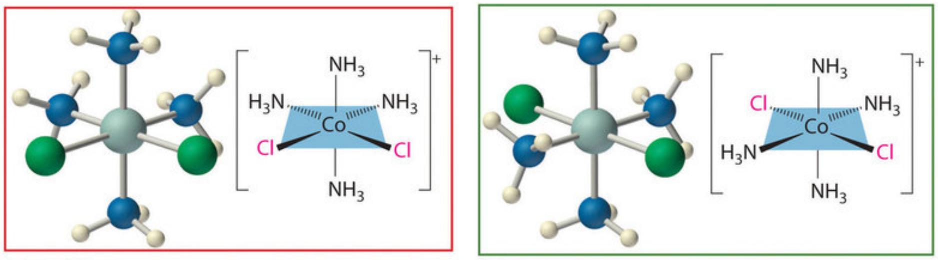
$$\mathrm{[Pt(NH_3)_4Cl_2]Cl_2 \rightarrow [Pt(NH_3)_4Cl_2]^{2+}(aq) + 2Cl^-(aq)}$$

$$\mathrm{[Pt(NH_3)_3Cl_3]Cl \rightarrow [Pt(NH_3)_3Cl_3]^{+}(aq) + Cl^-(aq)}$$

$$\mathrm{[Pt(NH_3)_2Cl_4] \rightarrow [Pt(NH_3)_2Cl_4]^{0}(aq)}$$

Further work showed that the two missing members of the series—$[Pt(NH_3)Cl_5]^-$ and $[PtCl_6]^{2-}$—could be prepared as their mono- and dipotassium salts, respectively. Similar studies established coordination numbers of 6 for Co^{3+} and Cr^{3+} and 4 for Pt^{2+} and Pd^{2+}.

Werner's studies on the analogous Co^{3+} complexes also allowed him to propose a structural model for metal complexes with a coordination number of 6. Thus he found that $[Co(NH_3)_6]Cl_3$ (yellow) and $[Co(NH_3)_5Cl]Cl_2$ (purple) were 1:3 and 1:2 electrolytes. Unexpectedly, however, two different $[Co(NH_3)_4Cl_2]Cl$ compounds were known: one was red, and the other was green (Figure $12.8.1a$). Because both compounds had the same chemical composition and the same number of groups of the same kind attached to the same metal, there had to be something different about the arrangement of the ligands around the metal ion. Werner's key insight was that the six ligands in $[Co(NH_3)_4Cl_2]Cl$ had to be arranged at the vertices of an octahedron because that was the only structure consistent with the existence of two, and only two, arrangements of ligands (Figure $12.8.1b$ His conclusion was corroborated by the existence of only two different forms of the next compound in the series: $Co(NH_3)_3Cl_3$.



(a) Red form **(b) Green form**

Figure 12.8.1: Complexes with Different Arrangements of the Same Ligands Have Different Properties. The $[Co(NH_3)_4Cl_2]^+$ ion can have two different arrangements of the ligands, which results in different colors: if the two Cl^- ligands are next to each other, the complex is red (a), but if they are opposite each other, the complex is green (b).

✓ Example 12.8.1

In Werner's time, many complexes of the general formula MA_4B_2 were known, but no more than two different compounds with the same composition had been prepared for any metal. To confirm Werner's reasoning, calculate the maximum number of different structures that are possible for six-coordinate MA_4B_2 complexes with each of the three most symmetrical possible structures: a hexagon, a trigonal prism, and an octahedron. What does the fact that no more than two forms of any MA_4B_2 complex were known tell you about the three-dimensional structures of these complexes?

Given: three possible structures and the number of different forms known for MA_4B_2 complexes

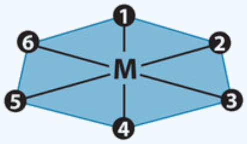
Asked for: number of different arrangements of ligands for MA_4B_2 complex for each structure

Strategy:

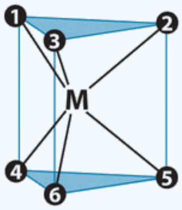
Sketch each structure, place a B ligand at one vertex, and see how many different positions are available for the second B ligand.

Solution

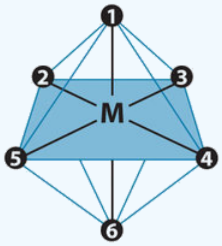
The three regular six-coordinate structures are shown here, with each coordination position numbered so that we can keep track of the different arrangements of ligands. For each structure, all vertices are equivalent. We begin with a symmetrical MA_6 complex and simply replace two of the A ligands in each structure to give an MA_4B_2 complex:



Hexagon



Trigonal prism



Octahedron

For the hexagon, we place the first B ligand at position 1. There are now three possible places for the second B ligand: at position 2 (or 6), position 3 (or 5), or position 4. These are the only possible arrangements. The (1, 2) and (1, 6) arrangements are chemically identical because the two B ligands are adjacent to each other. The (1, 3) and (1, 5) arrangements are also identical because in both cases the two B ligands are separated by an A ligand.

Turning to the trigonal prism, we place the first B ligand at position 1. Again, there are three possible choices for the second B ligand: at position 2 or 3 on the same triangular face, position 4 (on the other triangular face but adjacent to 1), or position 5 or 6 (on the other triangular face but not adjacent to 1). The (1, 2) and (1, 3) arrangements are chemically identical, as are the (1, 5) and (1, 6) arrangements.

In the octahedron, however, if we place the first B ligand at position 1, then we have only two choices for the second B ligand: at position 2 (or 3 or 4 or 5) or position 6. In the latter, the two B ligands are at opposite vertices of the octahedron, with the metal lying directly between them. Although there are four possible arrangements for the former, they are chemically identical because in all cases the two B ligands are adjacent to each other.

The number of possible MA_4B_2 arrangements for the three geometries is thus: hexagon, 3; trigonal prism, 3; and octahedron, 2. The fact that only two different forms were known for all MA_4B_2 complexes that had been prepared suggested that the correct structure was the octahedron but did not prove it. For some reason one of the three arrangements possible for the other two structures could have been less stable or harder to prepare and had simply not yet been synthesized. When combined with analogous results for other types of complexes (e.g., MA_3B_3), however, the data were best explained by an octahedral structure for six-coordinate metal complexes.

? Exercise 12.8.1

Determine the maximum number of structures that are possible for a four-coordinate MA_2B_2 complex with either a square planar or a tetrahedral symmetrical structure.

Answer

square planar, 2; tetrahedral, 1

Structures of Metal Complexes

The coordination numbers of metal ions in metal complexes can range from 2 to at least 9. In general, the differences in energy between different arrangements of ligands are greatest for complexes with low coordination numbers and decrease as the coordination number increases. Usually only one or two structures are possible for complexes with low coordination numbers, whereas several different energetically equivalent structures are possible for complexes with high coordination numbers ($n > 6$). The following presents the most commonly encountered structures for coordination numbers 2–9. Many of these structures should be familiar to you from our discussion of the valence-shell electron-pair repulsion (VSEPR) model because they correspond to the lowest-energy arrangements of n electron pairs around a central atom.

> *Compounds with low coordination numbers exhibit the greatest differences in energy between different arrangements of ligands.*

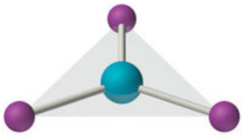
Coordination Number 2

Although it is rare for most metals, this coordination number is surprisingly common for d^{10} metal ions, especially Cu^+, Ag^+, Au^+, and Hg^{2+}. An example is the $[Au(CN)_2]^-$ ion, which is used to extract gold from its ores. As expected based on VSEPR considerations, these complexes have the linear L–M–L structure shown here.

Linear ML_2

Coordination Number 3

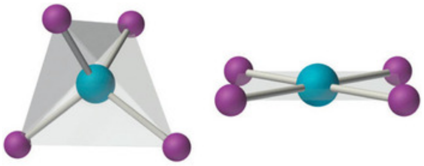
Although it is also rare, this coordination number is encountered with d^{10} metal ions such as Cu^+ and Hg^{2+}. Among the few known examples is the HgI_3^- ion. Three-coordinate complexes almost always have the trigonal planar structure expected from the VSEPR model.



Trigonal planar ML_3

Coordination Number 4

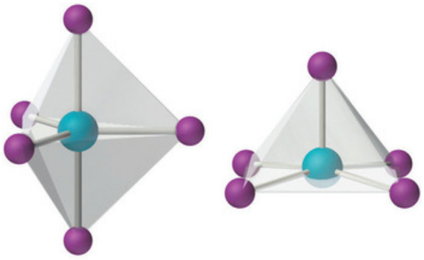
Two common structures are observed for four-coordinate metal complexes: tetrahedral and square planar. The tetrahedral structure is observed for all four-coordinate complexes of nontransition metals, such as $[BeF_4]^{2-}$, and d^{10} ions, such as $[ZnCl_4]^{2-}$. It is also found for four-coordinate complexes of the first-row transition metals, especially those with halide ligands (e.g., $[FeCl_4]^-$ and $[FeCl_4]^{2-}$). In contrast, square planar structures are routinely observed for four-coordinate complexes of second- and third-row transition metals with d^8 electron configurations, such as Rh^+ and Pd^{2+}, and they are also encountered in some complexes of Ni^{2+} and Cu^{2+}.



Tetrahedral and square planar ML_4

Coordination Number 5

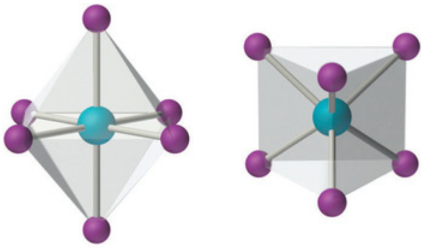
This coordination number is less common than 4 and 6, but it is still found frequently in two different structures: trigonal bipyramidal and square pyramidal. Because the energies of these structures are usually rather similar for most ligands, many five-coordinate complexes have distorted structures that lie somewhere between the two extremes.



Trigonal bipyramidal and
square pyramidal ML_5

Coordination Number 6

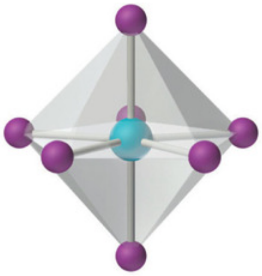
This coordination number is by far the most common. The six ligands are almost always at the vertices of an octahedron or a distorted octahedron. The only other six-coordinate structure is the trigonal prism, which is very uncommon in simple metal complexes.



Octahedral and trigonal prismatic ML_6

Coordination Number 7

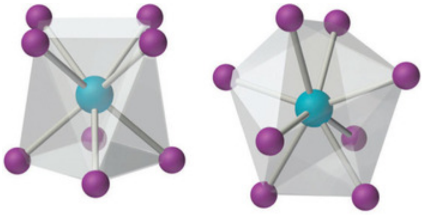
This relatively uncommon coordination number is generally encountered for only large metals (such as the second- and third-row transition metals, lanthanides, and actinides). At least three different structures are known, two of which are derived from an octahedron or a trigonal prism by adding a ligand to one face of the polyhedron to give a “capped” octahedron or trigonal prism. By far the most common, however, is the pentagonal bipyramid.



Pentagonal bipyramidal ML_7

Coordination Number 8

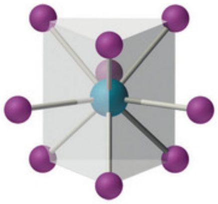
This coordination number is relatively common for larger metal ions. The simplest structure is the cube, which is rare because it does not minimize interligand repulsive interactions. Common structures are the square antiprism and the dodecahedron, both of which can be generated from the cube.



Square antiprismatic and trigonal dodecahedral ML_8

Coordination Number 9

This coordination number is found in larger metal ions, and the most common structure is the tricapped trigonal prism, as in $[Nd(H_2O)_9]^{3+}$.



Tricapped trigonal prismatic ML_9

Key Takeaways

- Coordination compounds are a major feature of the chemistry of over half the elements.
- Coordination compounds have important roles as industrial catalysts in controlling reactivity, and they are essential in biochemical processes.

Summary

Transition metals form metal complexes, polyatomic species in which a metal ion is bound to one or more ligands, which are groups bound to a metal ion. Complex ions are electrically charged metal complexes, and a coordination compound contains one or more metal complexes. Metal complexes with low coordination numbers generally have only one or two possible structures, whereas those with coordination numbers greater than six can have several different structures. Coordination numbers of two and three are common for d^{10} metal ions. Tetrahedral and square planar complexes have a coordination number of four; trigonal bipyramidal and square pyramidal complexes have a coordination number of five; and octahedral complexes have a coordination number of six. At least three structures are known for a coordination number of seven, which is generally found for only large metal ions. Coordination numbers of eight and nine are also found for larger metal ions.

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12.9: Coordination Compounds in Biological Systems

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12.E: The Chemical Bond (Exercises)

12.1: Lewis Structures

Q12.1

Which of the following molecules has the shortest bond length?

- O_2
- Cl_2
- Br_2
- I_2

Q12.2

Draw a plausible Lewis structure for 1,3-Bisphosphoglyerate (1,3-BPG), (C3H8O10P2).

Q12.3

Draw resonance structures for NO3- and ClO3-, please show formal charges in drawings.

Q12.4

Calculate the dipole moment (μ) of a two ions of +2e and -2e that are separated by 100 pm. Express dipole moment in both units of $C\,m$ and D.

S12.4

$$\mu = Q \times r = 2(1.602 \times 10^{-19})(8 \times 10^{-10}) = 2.56 \times 10^{-28} C\,m \tag{12.E.1}$$

$$(2.56 \times 10^{-28}\ C\,\cancel{m})\left(\frac{1\ D}{3.336 \times 10^{-30}\ C\,\cancel{m}}\right) = 76.8\ D \tag{12.E.2}$$

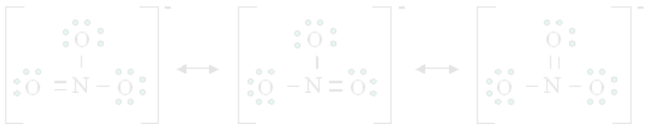
12.2: Valence Bond Theory

Q12.5

What are the resonance of NO_3^0?

S12.5

Resonance structure in basic means that there are multiple way to draw a Lewis structure. For example:

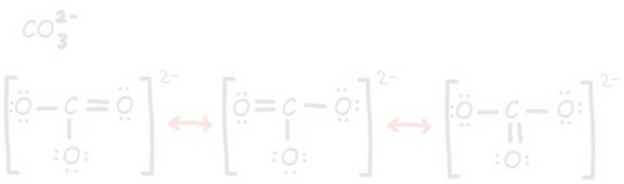


*Source from Michael Blaber

Q12.6

Draw resonance structures for the carbonate ion (CO_3^{-2}).

S12.6



Q12.7a

How is it that this structure, PF_5, have P have 5 bonds to it?

S12.7a

The d orbitals are available to make extra bonds allowing the P to bond to 5 Flourines instead of just Four.

Q12.7b

Draw the Lewis structure for nitric acid (HNO_3). This may or may not include resonance structures.

S12.7b

12.3: Hybridization of Atomic Orbitals

Q12.8a

What is the hybridization of carbon in CH_4?

S12.8a

Carbon has the electron configuration $1s^22s^2sp^{2.}$ In the excited state, because the 2s and 2p orbitals are so close one of the s electrons is able to fill the empty 2p orbital. All the carbon bonds are identical so the four unpaired electrons will be in a sp3 hybridization. The sp3 hybridization is the only hybridization that accounts for four identical orbitals.

Q12.8b

Describe the pattern of valence electrons across the periodic table (left to right and top to bottom), excluding the transition metals.

S12.8b

The number of valence electrons increases going left to right along the same row and stays constant going from top to bottom along the same column.

Q12.9a

What is the difference between covalent bond and ionic bond wave functions?

S12.9a

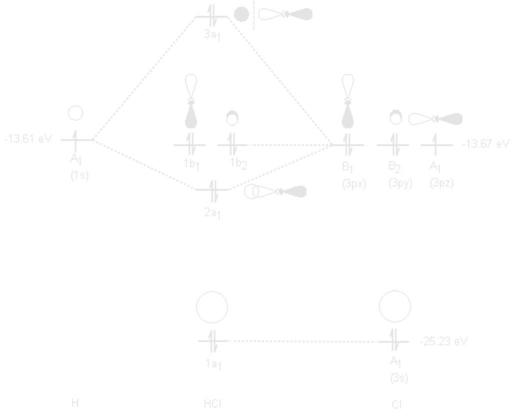
An ionic bond wave function takes into account the probability that the electrons of a multiatomic molecule might exist on the same atom; the covalent bond wave function assumes they exist on separate atoms.

Q12.9b

What is the hybridization of HCl?

S12.9b

There is no orbital hybridization in HCl. The $3p_z$ of Cl can overlap with the 1s of H just fine; they are only 0.06 eV apart in energy However, the 3s of Cl and the 1s of H are too far away in energy to interact, so there is no reason why the 3p of Cl can interact with the 3s of Cl anyway.



Q13.7

Calculate the potential energy of interaction between an electron situated 5.5 Å away from an HF molecule with a dipole moment of 2.5 D.

S13.7

$$\mu = 2.5D \times \frac{3.3356 \times 10^{30} Cm}{D} = 8.39 \times 10^{-30} Cm \tag{12.E.3}$$

$$r = 5.5 \; angstroms = 5.5 \times 10^{-10} m \tag{12.E.4}$$

$$V = \frac{q\mu}{4\pi\varepsilon_o r^2} = \frac{(+1.602 \times 10^{-19} C)(8.39 \times 10^{-30} Cm)}{4\pi(8.851 \times 10^{-12} C^{-2} N^{-1} m^{-2})(5.5 \times 10^{-10})} = 2.196 \times 10^{-11} J \tag{12.E.5}$$

Q12.10

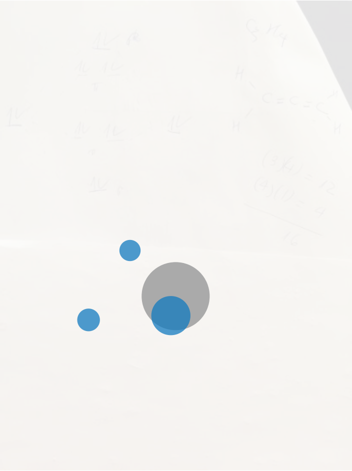
Give two types of bonding that present in the molecule CH_2. how do you do this?

S12.10

1 is C atom to be not hydrid, no paired electrons and the molecule will be diamagnetic.
2 is C atom is sp^3 hybbridized with 2 of the hybrid orbitals used for bonding to H's , unpaired electron. this is paramagnetic.

Q12.11

Describe bonding CO_2 and C_3H_4 as hybridization. Draw diagram of forming of sigma and pi bond of C_3H_4 there is a double bond CO2 and its hydridization is sp and C3H4 is sp2 belong to CH2 and 1 sp of C=C=C.



Q12.12

Give the bonding scheme in term of molecular orbital H_{2^+}, H_2, He_2^+, He. Besides, give the species in the following decreasing stability.

Q12.13

Between F2 and F_2^+ which one has longer bond?

S12.13

F_2^+ has bond order 1.5, F_2 has bond order 1.0. The bond lengths are inverse to the bond order, so the order is F2+ < F2 .There is 1 unpaired electron in F2+, 0 unpaired electrons in F2

Q12.14

Which of the following molecules have the shortest bond: F_2, N_2, O_2? Why?

S12.14

N_2 has the shortest bond because the bond order is 3 while O_2 is 2 and F_2 is 1.

12.5: Molecular Orbital Theory

Q12.15

Draw the molecular orbital diagram for F_2 with the atomic orbitals labeled and find the bond order.

Q12.16

Comparing benezene and cyclopentadiene, which one has a lesser degree of π-electron delocalization?

Q12.19

Draw the molecular orbital energy diagram for the F_2 Then compare the relative stability of the molecule to F_2^+.

Answer

BOND ORDER OF F_2 = (8-6)/2 =1

BOND ORDER OF F_2^+ (8-5)/2 =1.5

Based on bond order F_2^+ is stable than F_2

Q12.21

Diatomic carbon (C_2) exists at very high temperatures. What type or types of bonds do you expect a molecule of diatomic carbon to have?

S12.21

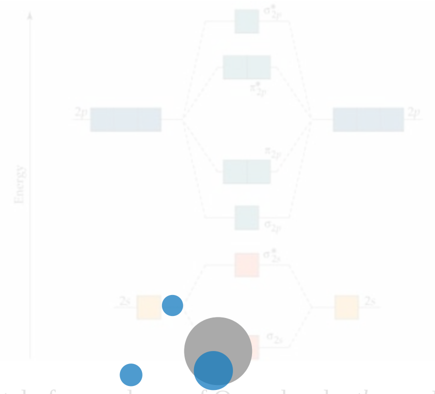
1. Draw a molecular orbital diagram.

Answer: The molecular orbital diagram predicts that there will be a double bond consisting of two π bonds.

Q12.21

Determine the second period for molecule O_2 by using molecular orbital?

S12.21



Based on general diagram for molecular orbital of second row of O_2 molecule, *the $_{2p}$ MO is below the $_{2p}$ molecular orbitals.*

Q12.30

Though there are some exceptions, the double bond rule states that atoms of period 3 and greater do not form double or triple bonds. Explain why this is generally true. *Hint: What properties of elements change with increasing period?*

S12.30

Pi bonds are usually weaker than sigma bonds because there is less orbital overlap. The larger atomic radius of period 3 and greater elements means that there is even less overlap between the orbitals that would form pi bonds. There is not enough overlap to form the pi bonds that would make for double or triple bonds.

Q12.30

Explain why the Si=Si double bond is not stable than the C=C. Given the covalent radius of carbon is 77 pm and Silicon is 111pm?

S12.30

Silicon is significantly bigger than carbon. Thus the Si-Si bond is longer than C-C bond. However, the longer bond result in lowering the effective overlap of 3p orbital to form a π bonds. In contrast, C atoms can form the π bond from 2p orbital. Thus the Si=Si is less stable despite its larger size.

Q12.33

Myohemerythrin is an iron-containing protein that binds oxygen in marine invertebrates. The protein is monomeric (has one subunit) and contains 0.8107% iron by mass. Estimate the molar mass of myohemerythrin. Is your answer the same as the known molar mass of myohemerythrin, 13,780 grams per mole? If it is not, account for the difference between your estimate and the known value.

Myohemerythrin ribbon schematic, a 4-helix bundle protein structure with a bound iron. Hand drawn by Jane Richardson in 1980, from PDB file 2MHR.

S12.33

1. Find the mass of the protein if there is one atom of iron per protein.

$$55.85\ g\,Fe/mol \times \frac{100.0\ g\,protein}{0.8107\ g\,Fe} \tag{12.E.6}$$

$$6889 g/mol \tag{12.E.7}$$

2. This is much less than the known molar mass. In fact, it is half.

$$\frac{13780\ g/mol}{6889\ g/mol} = 2.000 \tag{12.E.8}$$

We know the protein is monomeric, so there must be two atoms of iron in each protein.

Q12.19

Neon is a noble gas. Draw the molecular orbital diagram of Ne_2 and Ne_2. From that, describe the bonding scheme of those two molecules based on molecular orbital theory.

S12.19

Based on the molecular orbital diagram, there are more anti-bonding than bonding state. The bonding order of Ne$_2$ is:

BO = 1/2 (8-8) = 0

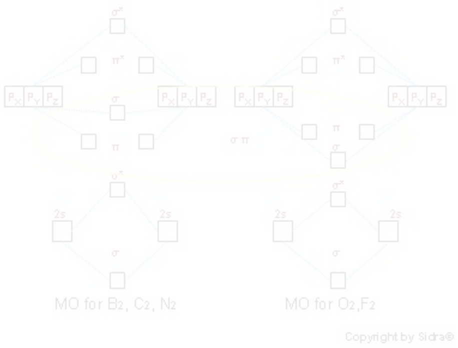
Therefore, Ne_2 does not exist in nature.

Q12.21

What is the difference between the last three group, including O$_2$, F$_2$ and the other diatomic molecules in the second row of Periodic table in term of Molecular orbital theory?

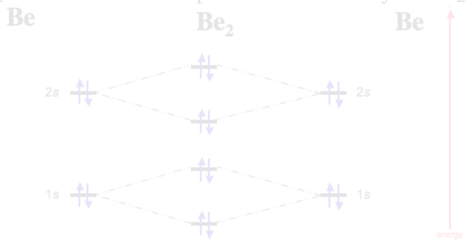
S12.21

For O$_2$ and F$_2$, the pi bonds(2p) have higher energy than the sigma bonds (2p). Whereas, a group of B$_2$, C$_2$, and N$_2$, the sigma bonds(2p) have higher energy than the pi bonds(2p)



Q12.30

Be is in the second period, and very rare Be_2 exist in nature. Explain the instability of Be_2 , and calculate the bond order.



S12.30

Be_2 molecule has 2 valence electrons. The bonding order, BO= 1/2 (2-2)= 0 Therefore, diatomic Be_2 is not stable! Not exist in nature

12.4: Electronegativity and Dipole Moment

Q12.36

Will the dipole moment of a cis-dichloroethylene molecule increase or decrease upon heating? Why?

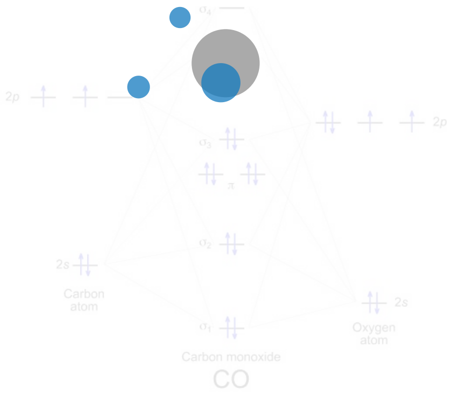
S12.36

The dipole moment will decrease because cis-trans isomerization will occur when heated. This is because the trans isomer of the molecule does not have a dipole moment present.

Q12.37

Draw the σ and σ^* molecular orbital of CO. Draw the MO energy level diagram and write the electron coefficient. Calculate the Bond order.

S12.37



Electron Configuration:

$$(\sigma 1s)^2(\sigma^* 1s)^2(\sigma 2s)^2(\sigma^* 2s)^2(\pi x)^2(\pi y)^2(\sigma 2sp)^2$$

Bond Order: 1/2(Bonding Electrons-Antibonding Electrons)

$$=1/2(8-2) = 3$$

12.6: Diatomic Molecules

12.7: Resonance and Electron Delocalization

12.8: Coordination Compounds

12.9: Coordination Compounds in Biological Systems

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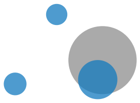

CHAPTER OVERVIEW

13: Intermolecular Forces

Intermolecular forces are forces of attraction or repulsion which act between neighboring particles (atoms, molecules, or ions). They are weak compared to the intramolecular forces, the forces which keep a molecule together.

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13.1: Intermolecular Interactions

Learning Objectives

- Classify intermolecular forces as ionic, covalent, London dispersion, dipole-dipole, or hydrogen bonding.
- Explain properties of material in terms of type of intermolecular forces.
- Predict the properties of a substance based on the dominant intermolecular force.

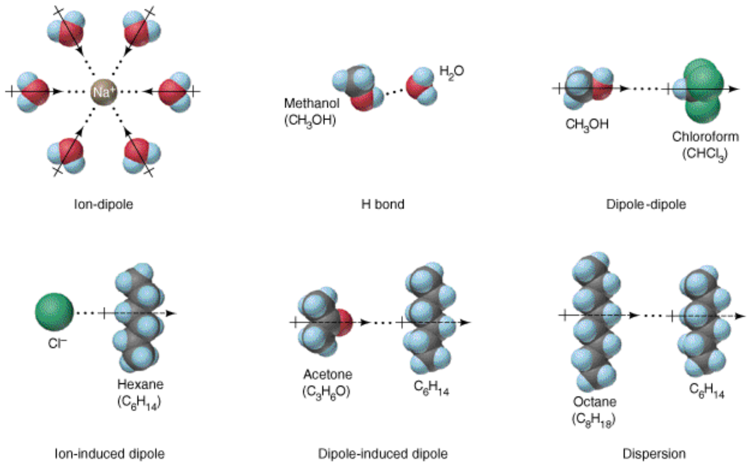
Forces binding atoms in a molecule are due to chemical bonding. The energy required to break a bond is called the bond-energy. For example, the average bond-energy for $\ce{O-H}$ bonds in water is 463 kJ/mol. On average, 463 kJ is required to break 6.023x10^{23} $\ce{O-H}$ bonds, or 926 kJ to convert 1.0 mole of water into 1.0 mol of $\ce{O}$ and 2.0 mol of $\ce{H}$ atoms. The forces holding molecules together are generally called intermolecular forces. The energy required to break molecules apart is much smaller than a typical bond-energy, but intermolecular forces play important roles in determining the properties of a substance. Intermolecular forces are particularly important in terms of how molecules interact and form biological organisms or even life. This link gives an excellent introduction to the interactions between molecules.

Classifying Intermolecular Forces

In general, intermolecular forces can be divided into several categories. The four prominent types are:

- **Ion-Ion Interactions**: Recall lattice energy and its relation to properties of solids. The more ionic, the higher the lattice energy. Examine the following list and see if you can explain the observed values by way of ionic attraction: $\ce{LiF} = 1036$; $\ce{LiI} = 737$; $\ce{KF} = 821$; $\ce{MgF2} = 2957\, kJ/mol$
- **Dipole-dipole Interactions**: Substances whose molecules have dipole moment have a higher melting point or boiling point than those of similar molecular mass, but whose molecules have no dipole moment.
- **London dispersion forces or van der Waal's force:** These forces always operate in any substance. The force arisen from induced dipole and the interaction is weaker than the dipole-dipole interaction. In general, the heavier the molecule, the stronger the van der Waal's force of interaction. For example, the boiling points of inert gases increase as their atomic masses increase due to stronger London dispersion interactions.
- **Hydrogen bonds:** Certain substances such as $\ce{H2O}$, $\ce{HF}$, and $\ce{NH3}$ form hydrogen bonds, which affects properties (mp, bp, solubility) of the substance. Other compounds containing $\ce{OH}$ and $\ce{NH2}$ groups also form hydrogen bonds. Molecules of many organic compounds such as alcohols, acids, amines, and amino acids contain these groups, and thus hydrogen bonding plays a important role in biological science.
- **Covalent bonding:** Covalent bonding is really intramolecular force rather than intermolecular force. It is mentioned here, because some solids are formed due to covalent bonding. For example, in diamond, silicon, quartz etc., all the atoms in the entire crystal are linked together by covalent bonding. These solids are hard, brittle, and have high melting points. Covalent bonding holds atoms tighter than ionic attraction.
- **Metallic bonding:** Forces between atoms in metallic solids belong to another category. Valence electrons in metals are rampant. They are not restricted to certain atoms or bonds. Rather they run freely in the entire solid, providing good conductivity for heat and electric energy. This behavior of electrons gives special properties such as ductility and mechanical strength to metals.

The division into types is for convenience in their discussion. Of course all types can be present simultaneously for many substances. Usually, intermolecular forces are discussed together with The States of Matter. Intermolecular forces also play important roles in solutions, a discussion of which is given in Hydration, solvation in water. A summary of the interactions is illustrated in the following diagram:



See if you can answer the following questions.

- What are dipoles?
- What are dipole moments?
- How do dipoles interact?
- Why do molecules attract one another?
- How do London dispersion forces come about?
- What parameters cause an increase of the London dispersion forces?
- What is a hydrogen bond?
- What type of hydrogen bonds are strong?
- What chemical groups are hydrogen acceptors for hydrogen bonds?

If you are looking for specific information, your study will be efficient. Some answers can be found in the Confidence Building Questions. Consider carefully the purpose of each question, and figure out what there is to be learned in it.

Confidence Building Questions

1. Which of the following molecules have a permanent dipole moment?
   a. H_2O
   b. CO_2
   c. CH_4
   d. N_2
   e. CO
   f. NH_3

   Hint: a e f

   Discussion -
   CO_2, CH_4, and N_2 are symmetric, and hence they have no permanent dipole moments. A molecule with polar bonds unsymmetrically arranged will possess a permanent dipole.

2. Which has the higher boiling point, Br_2 or ICl?

   Hint: ICl

   Discussion -
   They have similar molecular weights: $Br_2 = 160$; $ICl = 162$. Their boiling points are 332 K and 370 K respectively.

3. An atom or molecule can be temporarily polarized by a nearby species. Polarization separates centers of charge giving
   a. permanent dipole

b. temporary charges
c. hydrogen bonding
d. induced dipole
e. induced ions
f. radicals

Hint: d.

Discussion -
Induced dipoles are responsible for the London dispersion forces. The heavier the molecule, the larger the induced dipole will be. Thus, London dispersion forces are strong for heavy molecules.

4. Which has a higher boiling point, I_2 or Br_2?

Hint: iodine, I_2.

Discussion -
Atomic weights for Br and I are 80 and 127 respectively. The higher the molecular weight, the stronger the London dispersion forces.

5. If only London dispersion forces are present, which should have a lower boiling point, H_2O or H_2S?

Hint: water, H_2O

Discussion -
The b.p. for H_2O is 100 deg C, and that of H_2S is -70 deg C. Very strong hydrogen bonding is present in liquid H_2O, but no hydrogen bonding is present in liquid H_2S.

6. Contrary to most other substances, the density of water decreases as temperature decreases between 4 and 0 deg C. This is due to

a. dipole-dipole interaction
b. London dispersion
c. decreasing number of hydrogen bonds
d. increasing number of hydrogen bonds formed

Hint: d.

Discussion -
As more hydrogen bonds form when the temperature decreases, the volume expands, causing a decrease in density. Above 4 deg C, the thermal expansion is more prominent than the effect of hydrogen bonds.

7. Ethanol (C_2H_5OH, molar mass 46) boils at 351 K, but water (H_2O, molar mass 18) boils at higher temperature, 373 K. This is because:

a. water is denser
b. water has stronger London dispersion forces
c. water has stronger hydrogen bonds
d. water molecules contain no carbon

Hint: c.

Discussion -
A hydrogen atom between two small, electronegative atoms (such as F, O, N) causes a strong intermolecular interaction known as the hydrogen bond. The strength of a hydrogen bond depends upon the electronegativities and sizes of the two atoms.

8. Ethanol (C_2H_5OH) and methyl ether (CH_3OCH_3) have the same molar mass. Which has a higher boiling point?

Hint: Ethanol has a higher boiling point.

Discussion -
$R-OH$ group is both proton donor and acceptor for hydrogen bonding. Methyl groups have very weak hydrogen bonding, if any.

Contributors and Attributions

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13.2: The Ionic Bond

The interactions between ions (ion - ion interactions) are the easiest to understand: like charges repel each other and opposite charges attract. These Coulombic forces operate over relatively long distances in the gas phase. The force depends on the product of the charges (Z_1, Z_2) divided by the square of the distance of separation (d^2):

$$F \propto \frac{-Z_1 Z_2}{d^2} \tag{1}$$

Two oppositely-charged particles flying about in a vacuum will be attracted toward each other, and the force becomes stronger and stronger as they approach until eventually they will stick together and a considerable amount of energy will be required to separate them.

Figure 1: *Ion - Ion Interactions in the Gas Phase*

They form an *ion-pair*, a new particle which has a positively-charged area and a negatively-charged area. There are fairly strong interactions between these ion pairs and free ions, so that these the clusters tend to grow, and they will eventually fall out of the gas phase as a liquid or solid (depending on the temperature).

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- Gary L Bertrand, Professor of Chemistry, University of Missouri-Rolla

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13.3: Types of Intermolecular Forces

Intermolecular Forces

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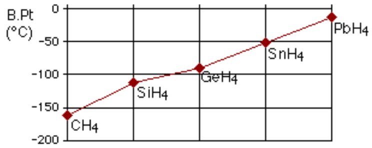
13.4: Hydrogen Bonding

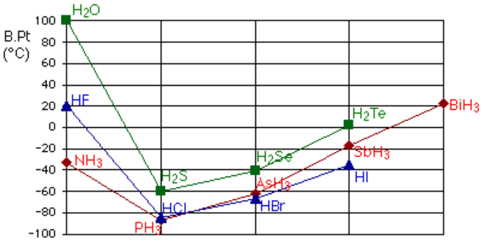
This page explains the origin of hydrogen bonding - a relatively strong form of intermolecular attraction.

The evidence for hydrogen bonding

Many elements form compounds with hydrogen. If you plot the boiling points of the compounds of the Group 4 elements with hydrogen, you find that the boiling points increase as you go down the group.



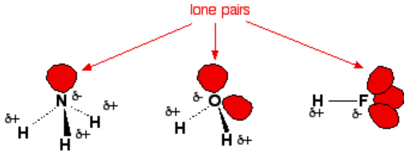
The increase in boiling point happens because the molecules are getting larger with more electrons, and so van der Waals dispersion forces become greater. If you repeat this exercise with the compounds of the elements in Groups 5, 6 and 7 with hydrogen, something odd happens.



Although for the most part the trend is exactly the same as in group 4 (for exactly the same reasons), the boiling point of the compound of hydrogen with the first element in each group is abnormally high. In the cases of NH_3, H_2O and HF there must be some additional intermolecular forces of attraction, requiring significantly more heat energy to break. These relatively powerful intermolecular forces are described as hydrogen bonds.

The origin of hydrogen bonding

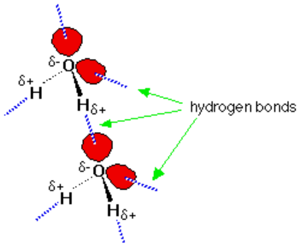
The molecules which have this extra bonding are:



The solid line represents a bond in the plane of the screen or paper. Dotted bonds are going back into the screen or paper away from you, and wedge-shaped ones are coming out towards you. Notice that in each of these molecules:

- The hydrogen is attached directly to one of the most electronegative elements, causing the hydrogen to acquire a significant amount of positive charge.
- Each of the elements to which the hydrogen is attached is not only significantly negative, but also has at least one "active" lone pair.
- Lone pairs at the 2-level have the electrons contained in a relatively small volume of space which therefore has a high density of negative charge. Lone pairs at higher levels are more diffuse and not so attractive to positive things.

Consider two water molecules coming close together.

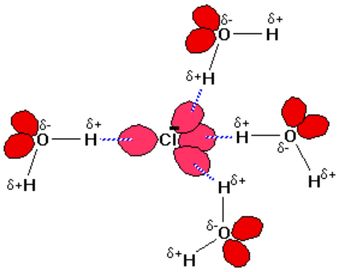


The δ+ hydrogen is so strongly attracted to the lone pair that it is almost as if you were beginning to form a co-ordinate (dative covalent) bond. It doesn't go that far, but the attraction is significantly stronger than an ordinary dipole-dipole interaction. Hydrogen bonds have about a tenth of the strength of an average covalent bond, and are being constantly broken and reformed in liquid water. If you liken the covalent bond between the oxygen and hydrogen to a stable marriage, the hydrogen bond has "just good friends" status.

Water as a "perfect" example of hydrogen bonding

Notice that each water molecule can potentially form four hydrogen bonds with surrounding water molecules. There are exactly the right numbers of δ+ hydrogens and lone pairs so that every one of them can be involved in hydrogen bonding. This is why the boiling point of water is higher than that of ammonia or hydrogen fluoride. In the case of ammonia, the amount of hydrogen bonding is limited by the fact that each nitrogen only has one lone pair. In a group of ammonia molecules, there aren't enough lone pairs to go around to satisfy all the hydrogens. In hydrogen fluoride, the problem is a shortage of hydrogens. In water, there are exactly the right number of each. Water could be considered as the "perfect" hydrogen bonded system.

The diagram shows the potential hydrogen bonds formed to a chloride ion, Cl^-. Although the lone pairs in the chloride ion are at the 3-level and wouldn't normally be active enough to form hydrogen bonds, in this case they are made more attractive by the full negative charge on the chlorine.

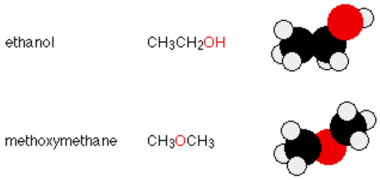


However complicated the negative ion, there will always be lone pairs that the hydrogen atoms from the water molecules can hydrogen bond to.

Hydrogen bonding in alcohols

An alcohol is an organic molecule containing an -O-H group. Any molecule which has a hydrogen atom attached directly to an oxygen or a nitrogen is capable of hydrogen bonding. Such molecules will always have higher boiling points than similarly sized molecules which don't have an -O-H or an -N-H group. The hydrogen bonding makes the molecules "stickier", and more heat is necessary to separate them.

Ethanol, CH_3CH_2-O-H, and methoxymethane, CH_3-O-CH_3, both have the same molecular formula, C_2H_6O.



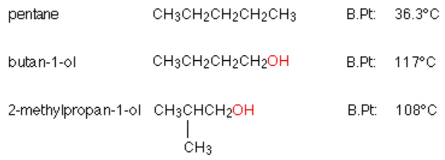
They have the same number of electrons, and a similar length to the molecule. The van der Waals attractions (both dispersion forces and dipole-dipole attractions) in each will be much the same. However, ethanol has a hydrogen atom attached directly to an oxygen - and that oxygen still has exactly the same two lone pairs as in a water molecule. Hydrogen bonding can occur between ethanol molecules, although not as effectively as in water. The hydrogen bonding is limited by the fact that there is only one hydrogen in each ethanol molecule with sufficient δ+ charge.

In methoxymethane, the lone pairs on the oxygen are still there, but the hydrogens aren't sufficiently δ+ for hydrogen bonds to form. Except in some rather unusual cases, the hydrogen atom has to be attached directly to the very electronegative element for hydrogen bonding to occur. The boiling points of ethanol and methoxymethane show the dramatic effect that the hydrogen bonding has on the stickiness of the ethanol molecules:

ethanol (with hydrogen bonding)		78.5°C
methoxymethane (without hydrogen bonding)		-24.8°C

The hydrogen bonding in the ethanol has lifted its boiling point about 100°C.

It is important to realize that hydrogen bonding exists in addition to van der Waals attractions. For example, all the following molecules contain the same number of electrons, and the first two are much the same length. The higher boiling point of the butan-1-ol is due to the additional hydrogen bonding.



pentane	$CH_3CH_2CH_2CH_2CH_3$	B.Pt:	36.3°C
butan-1-ol	$CH_3CH_2CH_2CH_2OH$	B.Pt:	117°C
2-methylpropan-1-ol	$CH_3\underset{\substack{\vert \\ CH_3}}{CH}CH_2OH$	B.Pt:	108°C

Comparing the two alcohols (containing -OH groups), both boiling points are high because of the additional hydrogen bonding due to the hydrogen attached directly to the oxygen - but they are not the same. The boiling point of the 2-methylpropan-1-ol isn't as high as the butan-1-ol because the branching in the molecule makes the van der Waals attractions less effective than in the longer butan-1-ol.

Hydrogen bonding in nitrogen containing organic molecules

Hydrogen bonding also occurs in organic molecules containing N-H groups - in the same sort of way that it occurs in ammonia. Examples range from simple molecules like CH_3NH_2 (methylamine) to large molecules like proteins and DNA. The two strands of the famous double helix in DNA are held together by hydrogen bonds between hydrogen atoms attached to nitrogen on one strand, and lone pairs on another nitrogen or an oxygen on the other one.

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13.5: The Structure and 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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2. Petrucci, et al. General Chemistry: Principles & Modern Applications: AIE (Hardcover). Upper Saddle River: Pearson/Prentice Hall, 2007.

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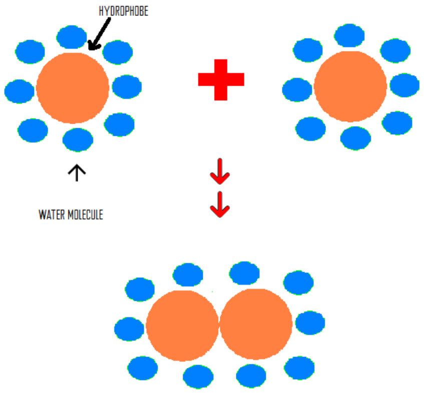
13.6: Hydrophobic Interaction

Hydrophobic interactions describe the relations between water and **hydrophobes** (low water-soluble molecules). Hydrophobes are nonpolar molecules and usually have a long chain of carbons that do not interact with water molecules. The mixing of fat and water is a good example of this particular interaction. The common misconception is that water and fat doesn't mix because the **Van der Waals forces** that are acting upon both water and fat molecules are too weak. However, this is not the case. The behavior of a fat droplet in water has more to do with the enthalpy and entropy of the reaction than its intermolecular forces.

Causes of Hydrophobic Interactions

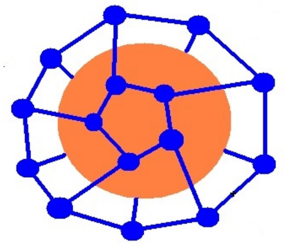
American chemist **Walter Kauzmann** discovered that nonpolar substances like fat molecules tend to clump up together rather than distributing itself in a water medium, because this allow the fat molecules to have minimal contact with water.



The image above indicates that when the hydrophobes come together, they will have less contact with water. They interact with a total of 16 water molecules before they come together and only 10 atoms after they interact.

Thermodynamics of Hydrophobic Interactions

When a hydrophobe is dropped in an aqueous medium, hydrogen bonds between water molecules will be broken to make room for the hydrophobe; however, water molecules do not react with hydrophobe. This is considered an endothermic reaction, because when bonds are broken heat is put into the system. Water molecules that are distorted by the presence of the hydrophobe will make new hydrogen bonds and form an ice-like cage structure called a *clathrate* cage around the hydrophobe. This orientation makes the system (hydrophobe) more structured with an decrease of the total entropy of the system; therefore $\Delta S < 0$.



The change in enthalpy (ΔH) of the system can be negative, zero, or positive because the new hydrogen bonds can partially, completely, or over compensate for the hydrogen bonds broken by the entrance of the hydrophobe. The change in enthalpy, however, is insignificant in determining the spontaneity of the reaction (mixing of hydrophobic molecules and water) because the change in entropy (ΔS) is large.

According to the Gibbs Energy formula

$$\Delta G = \Delta H - T\Delta S \tag{13.6.1}$$

with a small unknown value of ΔH and a large negative value of ΔS, the value of ΔG will turn out to be positive. A positive ΔG indicates that the mixing of the hydrophobe and water molecules is not spontaneous.

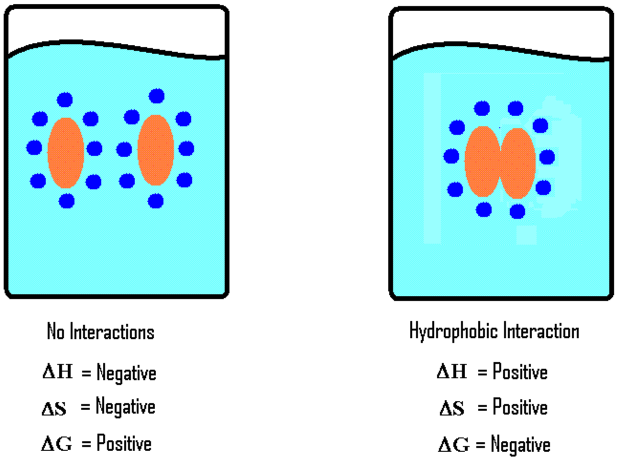
Formation of Hydrophobic Interactions

The mixing hydrophobes and water molecules is not spontaneous; however, hydrophobic interactions between hydrophobes are spontaneous. When hydropobes come together and interact with each other, enthalpy increases (ΔH is positive) because some of hydrogen bonds that form the clathrate cage will be broken. Tearing down a portion of the clathrate cage will cause the entropy to increase (ΔS is positive), since forming it decreases the entropy.

According to the Equation 13.6.1

- ΔH = small positive value
- ΔS = large positive value

Result: ΔG is negative and hence hydrophobic interactions are spontaneous.



Strength of Hydrophobic Interactions

Hydrophobic interactions are relatively stronger than other weak intermolecular forces (i.e., Van der Waals interactions or Hydrogen bonds). The strength of Hydrophobic Interactions depend on several factors including (in order of strength of influence):

1. **Temperature**: As temperature increases, the strength of hydrophobic interactions increases also. However, at an extreme temperature, hydrophobic interactions will denature.
2. **Number of carbons on the hydrophobes**: Molecules with the greatest number of carbons will have the strongest hydrophobic interactions.
3. **The shape of the hydrophobes**: Aliphatic organic molecules have stronger interactions than aromatic compounds. Branches on a carbon chain will reduce the hydrophobic effect of that molecule and linear carbon chain can produce the largest hydrophobic interaction. This is so because carbon branches produce steric hindrance, so it is harder for two hydrophobes to have very close interactions with each other to minimize their contact to water.

Biological Importance of Hydrophobic Interactions

Hydrophobic Interactions are important for the folding of proteins. This is important in keeping a protein stable and biologically active, because it allow to the protein to decrease in surface are and reduce the undesirable interactions with water. Besides from proteins, there are many other biological substances that rely on hydrophobic interactions for its survival and functions, like the phospholipid bilayer membranes in every cell of your body!

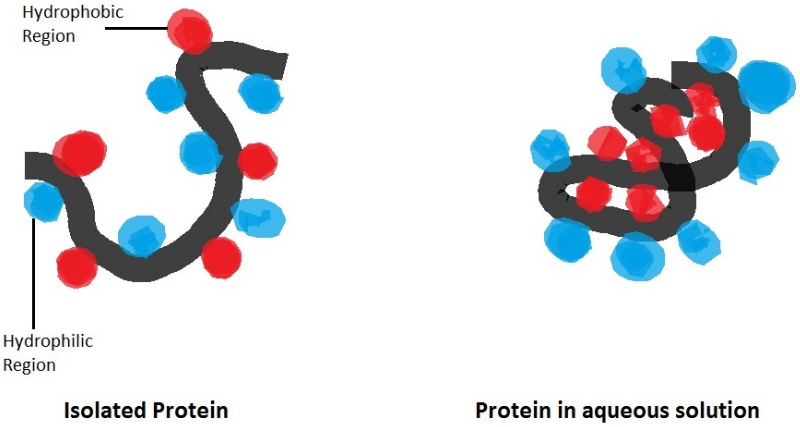


Illustration of how protein changes shape to allow polar regions (blue) to interact with water while non-polar hydrophobic regions (red) do not interact with the water. (CC BY-SA 3.0; Treshphrd via Wikipedia).

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3. Garrett, Reginald H. and Charles M. Grisham. Biochemistry. Belmont, CA: Thomas Brooks/Cole. 2005. 15.

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13.E: Intermolecular Forces (Exercises)

13.1: Intermolecular Interactions

Q13.1a

List all the intermolecular interactions that take place in each of the follow kings of molecules: CCl_3F, CCl_2F_2, $CClF_3$, and CF_4.

Q13.1b

Determine what type of intermolecular forces exist in the following molecules: LiF, MgF_2, H_2O, and HF.

S13.1b

- H_2O: London Force, Dipole-Dipole interaction, Hydrogen bonds.
- HF: Dipole-Dipole intermolecular forces, Hydrogen bonds.
- MgF_2 and LiF: strong ionic attraction.

Q13.2a

Arrange the follow species in order of decreasing melting points: CsBr, KI, KCL, MgF2.

Q13.2b

Which has the highest boiling point I_2, Br_2, and Cl_2. Explain why?

S13.2b

The atomic weigh of Iodine = 127, Bromine = 80, and Chlorine = 35.5. The weigh is proportion to the London dispersion force, and the higher molecular weigh, the larger the force. Thus, I_2 has a highest boiling point.

Q13.3

1-Propanol C_3H_7OH and methoxyethane CH_3O C_2H_5 have the same molecular weigh. Which has the higher boiling point?

S13.3

The 1-Propanol can form London Force, Dipole- Dipole, and H- bonding due to the H bonded to O atom of OH group, whereas the methoxyethane can not form the H-bonding. Therefore, the 1-Propanol has higher intermolecular attractive force and thus a higher boiling point.

Q13.3

Why do the lightest compounds such as NH3, H2O, and HF have the highest boiling points?

Q13.4a

What kind of attractive interaction exists between atoms and between nonpolar molecules?

Q13.4b

Why nature gas CH_4 is a good choice to storage tank in winter?

S13.4b

It's about boiling point. The methane has the boiling point at -161 °C, making it to be a good choice for winter season.

Q13.4

Explain why methane (CH_$_{4\backslash)}$ is used as the primary heating gas in Alaska during wintertime instead of the more commonly used butant or propane gases use in the lower 48 states.

S13.4

Methane (CH_4) remains gas because its boiling point is about -160°C. Other gases, such as propane or butane, would liquefy under freezing condition. Therefore, methane is more likely to be used during wintertime at Alaska

Q13.5

Define types of intermolecular forces and give example for each.

S13.5

There are 3 types of intermolecular force: London Dispersion, Dipole-Dipole (Example: Two $NaCl$) and Ion-Dipole (Example: Mg^{+} and HCl)

- Dipole- Dipole occurs between polar molecules
- Ion- Dipole occurs between an ion and polar molecules
- London Dispersion occurs between the nonpolar molecules.

Q13.6

How does the intermolecular determine the boiling point?

S13.6

The weakest intermolecular, the lowest boiling point.

Q13.7a

What is their dipole-dipole interaction of wo HCl molecules are co-linear head-to tail.

Given: The dipole moment of HF is 1.86 D. The dipole moment of HCl is 1.05 D. The distance between the two is 1.78

H^{+}-F^{-} - - - - H^{+}-Cl^{-}

S13.7a

$$V = -\frac{2\mu_A\mu_B}{4\pi\varepsilon_0 r^3} \tag{13.E.1}$$

$$V = -\frac{2(1.05)(1.86)}{4\pi(8.854187817\cdot 10^{-12})(1.78)^3} \tag{13.E.2}$$

13.2: The Ionic Bond

Q13.7b

Calculate an ion-ion interaction energy between K^{+} and Cl^{-} at a distance of 600 pm.

S13.7b

The ion-ion interaction energy is given by Coulomb's law.

$$V = \frac{q_1 q_2}{4\pi\epsilon_o r} \tag{13.E.3}$$

$$V = \frac{-(1.602\times 10^{-19}\ \cancel{C})(1.602\times 10^{-19}\ \cancel{C})}{4\pi(8.853\times 10^{-12}\ \cancel{C^2}\cdot N^{-1}\cdot m^{\cancel{-2}})(6\times 10^{-10}\ \cancel{m})} = -3.84\times 10^{-19}\ J \tag{13.E.4}$$

Q13.7

Calculate an ion-dipole interaction energy between K^{+} and HCl at a distance of 600 pm. HCl has a dipole moment of 1.08 D.

S13.7

$$\mu = 1.08\ \cancel{D} \times \frac{3.3356\times 10^{30}\ C\cdot m}{1\ \cancel{D}} = 3.6\times 10^{-30}\ C\cdot m \tag{13.E.5}$$

$$V = \frac{-q\,\mu}{4\pi\epsilon_o r^2} = \frac{-(1.602\times 10^{-19}\ \cancel{C})(3.6\times 10^{-30}\ \cancel{C}\cdot\ \cancel{m})}{4\pi(8.853\times 10^{-12}\ \cancel{C^2}\cdot N^{-1}\cdot m^{\cancel{-2}})(6\times 10^{-10}\ \cancel{m})^2} = -1.44\times 10^{-20}\ J \tag{13.E.6}$$

As expected this is appreciably smaller in energy than covalent bonds (e..g, HCl has a bond enthalpy of $7.0\times 10^{-19}\ J$).

13.3: Types of Intermolecular Forces

Q13.8a

Rank the interactions from weakest to strongest:

a. H_2O - - OH_2
b. Li^+ - - F^-
c. Li^+ - - OH_2

S13.8a

a. ion-ion interaction: Li^+ - - F^-
b. ion-dipole interaction: Li^+ - - OH_2
c. dipole-dipole interaction: H_2O - - OH_2

Q13.8b

A low concentration electrolytic solution behaves non-ideally while a high concentration of the same solution behaves ideally. Explain this phenomenon in terms of forces, noting that Coulomb forces depend on $1/r^2$ while van der Waals forces depend on $1/r^7$. Which of these forces are low concentration electrolytic solutions likely to follow? High concentration?

S13.8b

The interatomic distances in a low concentration electrolytic solution are greater than those in a high concentration solution. They follow van der Waals forces and thus behave less ideally. High concentration electrolytic solutions follow Coulomb forces.

Q13.9a

Calculate the ion-dipole interaction between H_2O and Li^+. You are given the dipole moment of H_2O is 1.82 D. The distance between these two is 2 Å.

S13.9a

$$V = -\frac{q\mu}{4\pi\varepsilon_0 r^2} \tag{13.E.7}$$

$$= \frac{1.82D \cdot (\frac{3.3356\cdot 10^{-30}\,Cm)}{1D}}{4\pi(8.85 \cdot 10^{-12})(2 \cdot 10^{-10} m)^2} = 1.36\ kJ/mol \tag{13.E.8}$$

Q13.9b

Calculate the potential energy of interaction between a Cl^- ion situated 120 pm away from an H_2O molecule with a dipole moment of 1.85 D.

S13.9b

$$\mu = 1.85\ \cancel{D} \times \frac{3.3356 \times 10^{30}\ C \cdot m}{1\ \ \cancel{D}} = 6.18 \times 10^{-30}\ C \cdot m \tag{13.E.9}$$

$$r = 1.2 \times 10^{-10}\ m \tag{13.E.10}$$

$$V = \frac{q\mu}{4\pi\varepsilon_o r^2} = \frac{(-1.602 \times 10^{-19}\ C)(6.18 \times 10^{-30}\ C \cdot m)}{4\pi(8.851 \times 10^{-12}\ C^{-2}N^{-1}m^{-2})(1.2 \times 10^{-10}\ m)^2} \tag{13.E.11}$$

Q13.10

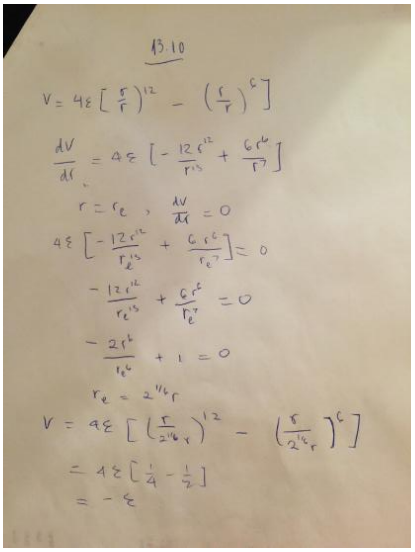
Do you expect a greater dipole-dipole interaction between two molecules that are antiparallel or between two molecules that are co-linear head-to-tail?

S13.10

You expect a stronger interaction when the two are co-linear head-to tail. This can be seen by looking at the formula or in the images of the two.

Q13.10

Express the equilibrium distance r_e in term ð and show V = - €



13.10

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

$$\frac{dV}{dr} = 4\varepsilon\left[-\frac{12\sigma^{12}}{r^{13}} + \frac{6\sigma^{6}}{r^{7}}\right]$$

$$r = r_e, \quad \frac{dV}{dr} = 0$$

$$4\varepsilon\left[-\frac{12\sigma^{12}}{r_e^{13}} + \frac{6\sigma^{6}}{r_e^{7}}\right] = 0$$

$$-\frac{12\sigma^{12}}{r_e^{13}} + \frac{6\sigma^{6}}{r_e^{7}} = 0$$

$$-\frac{2\sigma^{6}}{r_e^{6}} + 1 = 0$$

$$r_e = 2^{1/6}\sigma$$

$$V = 4\varepsilon\left[\left(\frac{\sigma}{2^{1/6}\sigma}\right)^{12} - \left(\frac{\sigma}{2^{1/6}\sigma}\right)^{6}\right]$$

$$= 4\varepsilon\left[\frac{1}{4} - \frac{1}{2}\right]$$

$$= -\varepsilon$$

Q13.12

a. Determine Vander Waals radius of Argon.
b. Use this radius to find fraction of volume by 2 mole of argon at room temperature at 1 atm.

S13.12

a. r= σ/2 = 3.40 A^0 /2 = 1.70 A^0

b. Volume of 2 mole of Ar

4/3 πr^3 ((6.022 x 10^23)/(2 mol))= 4/3 π (1.70 x 10^(-10) m)^3 ((6.022 x 10^23)/(2 mol))

= 6.19 x 10-6 L mol-1

V/n=RT/P= ((0.08206 L atm K^(-1) mol^(-1) (298.2 K))/1atm

= 24.5 L mol-1

The fraction of this volume occupied by 2 mole of Ar

(1.239 x 10^-2 L mol^{-1})/ 24.47 L mol^{-1} = 2.5 $x10^{-7}$

Q13.15

a) What is the original of polarity in a molecule?

b) Is CO_2 polar? Explain.

Q13.16

Of the following compound, which one(s) is/are soluble?

a. CH_4
b. NCl_3
c. C_6H6
d. $CO(NH_2)_2$

Q13.17

What makes a compound soluble in water? Explain using examples.

Q13.18

Explain why does water have a high specific heat.

Q13.20

The energy of a hydrogen bond for each base pair in DNA is 15 kJ/mol. Two complimentary strands has 50 base pairs each. What is the ratio of the 2 different strands to hydrogen double helix in a solution given a temperature of 300 K.

S13.20

First calculate the ratio of the two different strands for just one pair.

$$e^{\Delta E/RT} = exp[(15 \times 10^3\ J/mol)/(8.314\ J/K*mol)(300\ K) = 2.4 \times 10^{-3} \tag{13.E.12}$$

Since there are 50 base pairs, we need to multiply by 50 to account for all the base pairs.

$$\text{exp}[100X(15X10^3\ J/mol)/(8.314\ J/K*mol)(300K) = 0$$

Q13.24

Consider two pure liquids. One has strong intermolecular interactions, and the other has relatively weak intermolecular interactions. For the following properties, indicate which of the liquids you would expect to have a higher value (answer with "strong" or "weak").

a. viscosity
b. vapor pressure
c. freezing point
d. surface tension

S13.24

a. Strong. Higher viscosity results from stronger interactions between the liquid molecules.
b. Weak. The liquid with weaker bonds takes less energy to turn into vapor, so it will exert a higher vapor pressure.
c. Strong. The freezing point is the same as the melting point; it takes more energy to melt a solid with stronger intermolecular interactions.
d. Strong. Surface tension is a result of intermolecular interactions. The stronger these interactions, the greater the surface tension.

Q13.25

Fun fact: if the DNA in a single human cell were stretched out (but still in its familiar double helix conformation), it would be approximately 2 meters long. The distance, along the helix, between nucleotides is 3.4 Å.

a. Estimate the number of basepairs in the haploid human genome, from the 2 meter fun fact.
b. The human body contains about 100 trillion cells. About a quarter of these are erythrocytes (red blood cells) and contain no genomic DNA. Use the average molar mass for a basepair, 650 grams per mole, to estimate how much of a human's mass is human genomic DNA.
c. At its closest, Pluto is 4.28 billion km from Earth. Do you have enough DNA to reach Pluto?

Hint: Humans are diploid.

S13.25

(a)

$$ 2\ m/cell \times \dfrac{bp}{3.4\ Å} \times \dfrac{10^{10}\ Å}{m} \times \dfrac{cell}{2\ haploid\ genomes} = 3 \times 10^{9} \dfrac{bp}{haploid\ genome} \]

Three billion basepairs.

(b) 75 trillion of the human cells in your body have genomic DNA.

$$ 75 \times 10^{20}\ cells \times \dfrac{haploid\ genomes}{cell} \times \dfrac{3 \times 10^9\ bp}{haploid\ genome} \times \dfrac{mol}{6.022 \times 10^{23}} \times 650 \dfrac{g}{mol\ bp} = 200\ g \]

That's about half a pound.

(c)

$$\dfrac{2\ m}{cell} \times 75 \times 10^{12}\ cells \times \dfrac{km}{1000\ m} = 2 \times 10^{11}\ km$$

Yes, you have way more DNA than you need to stretch it from Earth to Pluto.

13.4: Hydrogen Bonding

13.5: The Structure and Properties of Water

13.6: Hydrophobic Interaction

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CHAPTER OVERVIEW

14: Spectroscopy

The focus of this chapter is on the interaction of ultraviolet, visible, and infrared radiation with matter. Because these techniques use optical materials to disperse and focus the radiation, they often are identified as optical spectroscopies. For convenience we will use the simpler term **spectroscopy** in place of optical spectroscopy; however, you should understand that we are considering only a limited part of a much broader area of analytical techniques.

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14.1: Vocabulary

Electromagnetic radiation—light—is a form of energy whose behavior is described by the properties of both waves and particles. Some properties of electromagnetic radiation, such as its refraction when it passes from one medium to another are explained best by describing light as a wave. Other properties, such as absorption and emission, are better described by treating light as a particle. The exact nature of electromagnetic radiation remains unclear, as it has since the development of quantum mechanics in the first quarter of the 20th century.[1] Nevertheless, the dual models of wave and particle behavior provide a useful description for electromagnetic radiation.

Electromagnetic radiation consists of oscillating electric and magnetic fields that propagate through space along a linear path and with a constant velocity. In a vacuum electromagnetic radiation travels at the speed of light, c, which is 2.997×10^8 m/s. When electromagnetic radiation moves through a medium other than a vacuum its velocity, v, is less than the speed of light in a vacuum. The difference between v and c is sufficiently small (<0.1%) that the speed of light to three significant figures, 3.00×10^8 m/s, is accurate enough for most purposes.

The oscillations in the electric and magnetic fields are perpendicular to each other, and to the direction of the wave's propagation. Figure 14.1.1 shows an example of plane-polarized electromagnetic radiation, consisting of a single oscillating electric field and a single oscillating magnetic field.

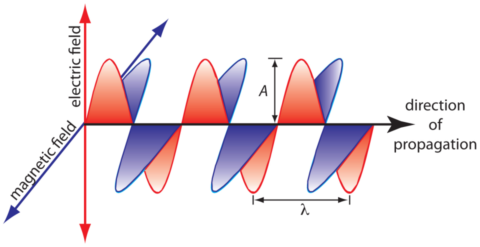


Figure 14.1.1: Plane-polarized electromagnetic radiation showing the oscillating electric field in red and the oscillating magnetic field in blue. The radiation's amplitude, A, and its wavelength, λ, are shown. Normally, electromagnetic radiation is unpolarized, with oscillating electric and magnetic fields present in all possible planes perpendicular to the direction of propagation.

An electromagnetic wave is characterized by several fundamental properties, including its velocity, amplitude, frequency, phase angle, polarization, and direction of propagation.[2] For example, the amplitude of the oscillating electric field at any point along the propagating wave is

$$A_{\mathrm{t}}=A_{\mathrm{e}} \sin (2 \pi \nu t+\phi) \tag{14.1.1}$$

where A_t is the magnitude of the electric field at time t, A_e is the electric field's maximum **amplitude**, ν is the wave's **frequency**—the number of oscillations in the electric field per unit time—and ϕ is a **phase angle**, which accounts for the fact that A_t need not have a value of zero at $t = 0$. The identical equation for the magnetic field is

$$A_{\mathrm{t}}=A_{\mathrm{m}} \sin (2 \pi \nu t+\phi) \tag{14.1.2}$$

where A_m is the magnetic field's maximum amplitude.

Units

Other properties also are useful for characterizing the wave behavior of electromagnetic radiation. The **wavelength**, λ, is defined as the distance between successive maxima (Figure 14.1.1). For ultraviolet and visible electromagnetic radiation the wavelength is usually expressed in nanometers (1 nm = 10^{-9} m), and for infrared radiation it is given in microns (1 μm = 10^{-6} m). The relationship between wavelength and frequency is

$$\lambda=\frac{c}{\nu} \tag{14.1.3}$$

Another unit useful unit is the **wavenumber**, $\tilde{\nu}$, which is the reciprocal of wavelength

$$\tilde{\nu}=\frac{1}{\lambda} \tag{14.1.4}$$

Wavenumbers are frequently used to characterize infrared radiation, with the units given in cm^{-1}.

Example 14.1.1

In 1817, Josef Fraunhofer studied the spectrum of solar radiation, observing a continuous spectrum with numerous dark lines. Fraunhofer labeled the most prominent of the dark lines with letters. In 1859, Gustav Kirchhoff showed that the D line in the sun's spectrum was due to the absorption of solar radiation by sodium atoms. The wavelength of the sodium D line is 589 nm. What are the frequency and the wavenumber for this line?

Solution

The frequency and wavenumber of the sodium D line are

$$\nu = \frac{c}{\lambda} = \frac{3.00 \times 10^{8} \text{ m/s}}{589 \times 10^{-9} \text{ m}} = 5.09 \times 10^{14} \text{ s}^{-1} \tag{14.1.5}$$

$$\tilde{\nu} = \frac{1}{\lambda} = \frac{1}{589 \times 10^{-9} \text{ m}} \times \frac{1 \text{ m}}{100 \text{ cm}} = 1.70 \times 10^{4} \text{ cm}^{-1} \tag{14.1.6}$$

Exercise 14.1.1

Another historically important series of spectral lines is the Balmer series of emission lines form hydrogen. One of the lines has a wavelength of 656.3 nm. What are the frequency and the wavenumber for this line?

Click here to review your answer to this exercise.

Regions of the Spectrum

The frequency and wavelength of electromagnetic radiation vary over many orders of magnitude. For convenience, we divide electromagnetic radiation into different regions—the **electromagnetic spectrum**—based on the type of atomic or molecular transition that gives rise to the absorption or emission of photons (Figure 14.1.2). The boundaries between the regions of the electromagnetic spectrum are not rigid, and overlap between spectral regions is possible.

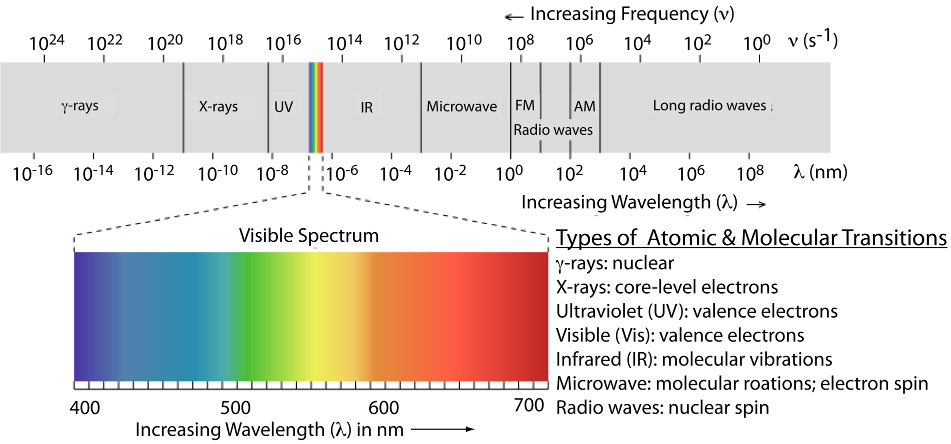


Figure 14.1.2: The electromagnetic spectrum showing the boundaries between different regions and the type of atomic or molecular transition responsible for the change in energy. The colored inset shows the visible spectrum. Source: modified from Zedh (www.commons.Wikipedia.org).

Above, we defined several characteristic properties of electromagnetic radiation, including its energy, velocity, amplitude, frequency, phase angle, polarization, and direction of propagation. A spectroscopic measurement is possible only if the photon's interaction with the sample leads to a change in one or more of these characteristic properties. We can divide spectroscopy into two broad classes of techniques. In one class of techniques there is a transfer of energy between the photon and the sample. Table 14.1.1 provides a list of several representative examples.

Table 14.1.1: Examples of Spectroscopic Techniques Involving an Exchange of Energy Between a Photon and the Sample

Type of Energy Transfer	Region of Electromagnetic Spectrum	Spectroscopic Techniquea

Type of Energy Transfer	Region of Electromagnetic Spectrum	Spectroscopic Techniquea
absorption	γ-ray	Mossbauer spectroscopy
	X-ray	X-ray absorption spectroscopy
	UV/Vis	*UV/Vis spectroscopy atomic absorption spectroscopy*
	IR	*infrared spectroscopy* raman spectroscopy
	Microwave	microwave spectroscopy
	Radio wave	electron spin resonance spectroscopy nuclear magnetic resonance spectroscopy
emission (thermal excitation)	UV/Vis	*atomic emission spectroscopy*
photoluminescence	X-ray	X-ray fluorescence
	UV/Vis	*fluorescence spectroscopy phosphorescence spectroscopy* atomic fluorescence spectroscopy
chemiluminescence	UV/Vis	chemiluminescence spectroscopy

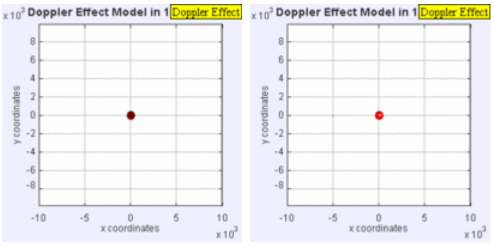
Line Widths

A spectral line extends over a range of frequencies, not a single frequency (i.e., it has a nonzero linewidth). There are multiple reasons for this broadening and shifts and only two are discussed below.

- **Lifetime Broadening.** This mechanism ordinates directly from the Heisenberg Principle, which the lifetime of an excited state (due to the spontaneous radiative decay) with the uncertainty of its energy Δt. Since the system is changing in time, it is impossible to estimate the energies of wavefunctions exactly (ΔE.

  $$\Delta E \Delta t \geq \frac{\hbar}{2} \tag{14.1.7}$$

  Hence, systems with excited-states that have short lifetimes will have a large energy uncertainty and a broad emission. This broadening effect results in an broadened profile. As expected, the lifetime broadening can be experimentally if the decay rates can be artificially suppressed or enhanced.
- **Doppler Broadening**. This mechanism is intrinsic to atoms in a gas which are emitting radiation will have a distribution of velocities. Each photon emitted will be "red"- or "blue"-shifted by the Doppler effect depending on the velocity of the atom relative to the observer. The Doppler effect is the change in frequency of a wave (or other periodic event) for an observer moving relative to its source. It is commonly heard when a vehicle sounding a siren or horn approaches, passes, and recedes from an observer. Compared to the emitted frequency, the received frequency is higher during the approach, identical at the instant of passing by, and lower during the recession.

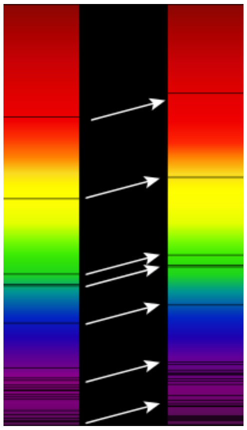


Doppler Broadening example with sound, but applies to light too. (left): Stationary sound source produces sound waves at a constant frequency u*, and the wave-fronts propagate symmetrically away from the source at a constant speed c (assuming speed of sound, c = 330 m/s), which is the speed of sound in the medium. The distance between wave-fronts is the wavelength. All observers* *will hear the same frequency, which will be equal to the actual frequency of the source where $u = u - o$ (right): The same sound source is radiating sound waves at a constant frequency in the same medium. However, now the sound source is moving with a speed so the center of each new wavefront is now slightly displaced to the right. As a result, the wave-fronts begin to bunch up on the right side (in front of) and spread further apart on the left side (behind) of the source. An observer in front of the source will hear a higher frequency. Images used with permission from Wikipedia (credit Lookang).*

If the speeds are small compared to the speed of the wave, the relationship between observed frequency u_o and emitted frequency u is approximately

$$u = \left(1 + \frac{\Delta v}{c}\right) v_0 \tag{14.1.8}$$

The Doppler effect also applies for spectroscopy. For example, the higher the temperature of the gas, the wider the distribution of velocities in the gas (via the Maxwell-Bolztmann Distribution). Since the spectral line is a combination of all of the emitted radiation, the higher the temperature of the gas, the broader the spectral line emitted from that gas. If the average velocity of a gas is non-zero, then a Doppler shift will be observed that is correlated with the amplitude of this average velocity.



Redshift of spectral lines in the optical spectrum of a supercluster of distant galaxies (right), as compared to that of the Sun (left) since the sun is not moving with respect to Earth (or weakly) and the galaxy is moving away. from Wikipedia (Credit Georg Wiora).

Doppler broadening is one of the explanations for the broadening of spectral lines, and as such gives an indication for the temperature of observed material. Other causes of velocity distributions may exist, though, for example due to turbulent motion. Doppler broadening can also be used to determine the velocity distribution of a gas given its absorption spectrum. In particular, this has been used to determine the velocity distribution of interstellar gas clouds.

✓ Example 14.1.2

Find the uncertainty of simultaneously measuring the frequency and wavelength of an emission from an excited molecule, if the wavelength is 430 nm and the excited state lifetime is 0.50 nanoseconds.

Soluton

1. Use Heisenberg's uncertainty principle and the relationship between energy and frequency to find the uncertainty of frequency.

$$\Delta E \Delta t \geq \frac{h}{4\pi}$$

$$\Delta E = h \Delta u$$

$$h \Delta u \Delta t \geq \frac{h}{4\pi}$$

$$\Delta u \geq \frac{1}{4\pi \Delta t}$$

The maximum value for Δt is the lifetime of the excited state.

$$\Delta u \geq \frac{1}{4\pi 0.50 ns \times \frac{s}{10^9\ ns}}$$

$$\Delta u \geq 1.6 \times 10^8\ s^{-1}$$

2. Use the uncertainty of frequency and the relationship between frequency and wavelength to find the uncertainty of the wavelength.

$$\lambda = \frac{c}{u}$$

$$|\Delta\lambda| = \frac{c}{u^2}|\Delta u|$$

$$|\Delta\lambda| = \frac{\lambda^2|\Delta u|}{c}$$

$$|\Delta\lambda| = \frac{(430\ nm)^2 \times 1.6 \times 10^8\ s^{-1}}{2.998 \times 10^8\ m/s} \times \frac{m}{10^9\ nm}$$

$$|\Delta\lambda| = 2.3 \times 10^{-7}\ nm$$

Absorption and Emission

In absorption spectroscopy a photon is absorbed by an atom or molecule, which undergoes a transition from a lower-energy state to a higher-energy, or excited state (Figure 14.1.3). The type of transition depends on the photon's energy. The electromagnetic spectrum in Figure 14.1.2, for example, shows that absorbing a photon of visible light promotes one of the atom's or molecule's valence electrons to a higher-energy level. When an molecule absorbs infrared radiation, on the other hand, one of its chemical bonds experiences a change in vibrational energy.

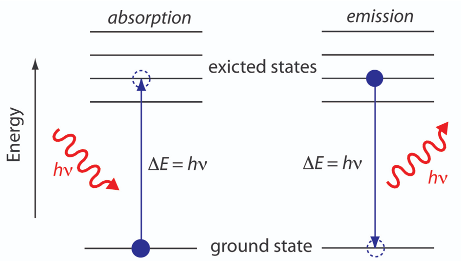


Figure 14.1.3: Simplified energy diagram showing the absorption and emission of a photon by an atom or a molecule. When a photon of energy hν strikes the atom or molecule, absorption may occur if the difference in energy, ΔE, between the ground state and the excited state is equal to the photon's energy. An atom or molecule in an excited state may emit a photon and return to the ground state. The photon's energy, hν, equals the difference in energy, ΔE, between the two states.

When it absorbs electromagnetic radiation the number of photons passing through a sample decreases. The measurement of this decrease in photons, which we call **absorbance**, is a useful analytical signal. Note that the each of the energy levels in Figure 14.1.3 has a well-defined value because they are quantized. Absorption occurs only when the photon's energy, $h\nu$, matches the difference in energy, ΔE, between two energy levels. A plot of absorbance as a function of the photon's energy is called an **absorbance spectrum**. Figure 14.1.4, for example, shows the absorbance spectrum of cranberry juice.

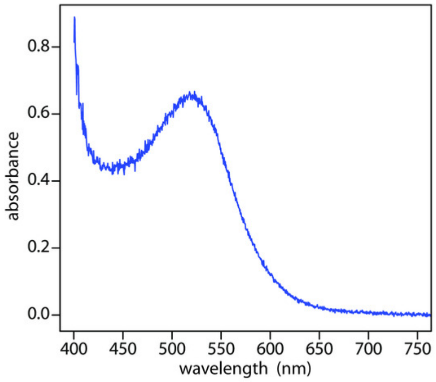


Figure 14.1.3). As a result, the juice appears red.

When an atom or molecule in an excited state returns to a lower energy state, the excess energy often is released as a photon, a process we call **emission** (Figure 14.1.4). There are several ways in which an atom or molecule may end up in an excited state, including thermal energy, absorption of a photon, or by a chemical reaction. Emission following the absorption of a photon is also called **photoluminescence**, and that following a chemical reaction is called **chemiluminescence**. A typical emission spectrum is shown in Figure 14.1.6.

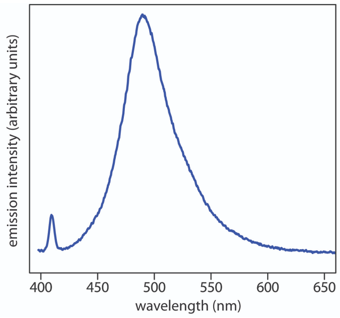


Figure 14.1.5: Photoluminescence spectrum of the dye coumarin 343, which is incorporated in a reverse micelle suspended in cyclohexanol. The dye's absorbance spectrum (not shown) has a broad peak around 400 nm. The sharp peak at 409 nm is from the laser source used to excite coumarin 343. The broad band centered at approximately 500 nm is the dye's emission band. Because the dye absorbs blue light, a solution of coumarin 343 appears yellow in the absence of photoluminescence. Its photoluminescent emission is blue-green. Source: data from Bridget Gourley, Department of Chemistry & Biochemistry, DePauw University).

Selection Rules

The transition probability is defined as the probability of particular spectroscopic transition to take place. When an atom or molecule absorbs a photon, the probability of an atom or molecule to transit from one energy level to another depends on two things: the nature of initial and final state wavefunctions and how strongly photons interact with an wavefunction. Transition strengths are used to describe transition probability. Selection rules are utilized to determine whether a transition is allowed or not. Electronic dipole transitions are by far the most important for the topics covered in this module.

In an atom or molecule, an electromagnetic wave (for example, visible light) can induce an oscillating electric or magnetic moment. If the frequency of the induced electric or magnetic moment is the same as the energy difference between one wavefunction ψ_1 and another wavefunction ψ_2, the interaction between an atom or molecule and the electromagnetic field is resonant (which means these two have the same frequency). Typically, the amplitude of this (electric or magnetic) moment is called the transition moment. In quantum mechanics, the transition probability of one molecule from one wavefunction ψ_1 to another wavefunction ψ_2 is given by $|\vec{M}_{21}|^2$, and $\vec{M}_{21}$ is called the **transition dipole moment**, or transition moment, from ψ_1 to ψ_2. $\vec{M}_{21}$ can be written as

$$\vec{M}_{21} = \int \psi_2 \vec{\mu} \psi_1 d\tau \tag{14.1.9}$$

where ψ_1 and ψ_2 are two different wavefunctions in one molecule, and $\vec{M}_{21}$ is the **electric dipole moment operator**. If we have a system with n atoms and each has charge q_n, and the dipole moment operator is can be written as

$$\vec{\mu} = \sum_n q_n \vec{r}_n \tag{14.1.10}$$

the $\vec{r}_n$ is the position vector operator for the ith charge. The nature of ψ_1 and ψ_1 change (e..g, the quantum numbers associated with each wavefunction) $\vec{M}_{21}$. Large values of $\vec{M}_{21}$ signify transitions with strong probabilities and small $\vec{M}_{21}$ values represent weak probabilities. A zero probability for a transition is a forbidden transition.

For electronic wavefucntion (either atoms or molecules), the two primary selection rules governing transitions between electronic energy wavefunctions are:

1. $\Delta S = 0$ (The Spin Rule)
2. $\Delta l = \pm 1$ (The Orbital Rule (or Laporte rule))

The spin multiplicity can be calculated from the quantum number S of the total spin or from the number of unpaired electrons (like when determining paramagnetic properties of molecules). The spin-multiplicity is $(2S+1)$, where

$$S = \sum_{\text{spin quantum } \#} s \tag{14.1.11}$$

The Spin Rule says that allowed transitions must involve the promotion of electrons **without** a change in their spin. The Orbital Rule says that transitions within a given set of p or d orbitals (i.e. those which only involve a redistribution of electrons within a given subshell) are forbidden. The orbital rule can be used to construct Grotrian diagrams, which show the allowed electronic transitions between the energy levels of atoms (Figure 14.1.6) by taking into account the specific selection rules related to the system (e..g, the Orbital or Spin Rules).

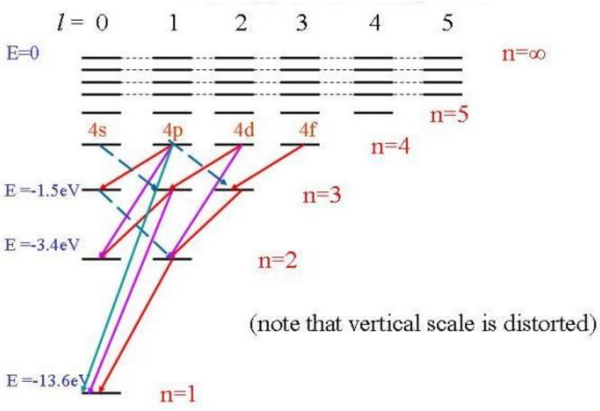


Figure 14.1.6: A Grotrian diagram of the hydrogen atom. Only transitions between adjacent columns are allowed, as per the selection rule $\Delta l = \pm 1$. from Tufts OCW (CC SA-BY; Gary Goldstein).

> Transitions not permitted by selection rules are said forbidden, which means that theoretically they must not occur. However, in practice they may occur, but very low probabilities (see 14.1.3 below).

The Beers-Lambert Law

The Beer-Lambert law relates the attenuation of light to the properties of the material through which the light is traveling. This page takes a brief look at the Beer-Lambert Law and explains the use of the terms absorbance and molar absorptivity relating to UV-visible absorption spectrometry. For each wavelength of light passing through the spectrometer, the intensity of the light passing through the reference cell is measured. This is usually referred to as I_o - that's I for Intensity.

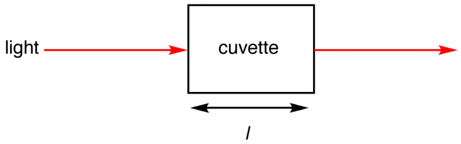


Figure 14.1.6: Light absorbed by sample in a cuvetter

The intensity of the light passing through the sample cell is also measured for that wavelength - given the symbol, I. If I is less than I_o, then the sample has absorbed some of the light (neglecting reflection of light off the cuvetter surface). A simple bit of math is then done in the computer to convert this into something called the absorbance of the sample - given the symbol, A.

Note

The absorbance of a transition depends on two external assumptions.

1. The absorbance is directly proportional to the concentration (c) of the solution of the the sample used in the experiment.
2. The absorbance is directly proportional to the length of the light path (l), which is equal to the width of the cuvette.

Assumption one relates the absorbance to concentration and can be expressed as

$$A \propto c \tag{14.1.12}$$

The absorbance (A) is defined via the incident intensity I_o and transmitted intensity I by

$$A = \log_{10}\left(\frac{I_o}{I}\right) \tag{14.1.13}$$

Assumption two can be expressed as

$$A \propto l \tag{14.1.14}$$

Combining Equations 14.1.12and 14.1.14:

$$A \propto cl \tag{14.1.15}$$

This proportionality can be converted into an equality by including a proportionality constant.

$$A = \epsilon cl \tag{14.1.16}$$

This formula is the common form of the *Beer-Lambert Law*, although it can be also written in terms of intensities:

$$A = \log_{10}\left(\frac{I_o}{I}\right) = \epsilon lc \tag{14.1.17}$$

The constant ϵ is called molar absorptivity or molar extinction coefficient and is a measure of the probability of the electronic transition. On most of the diagrams you will come across, the absorbance ranges from 0 to 1, but it can go higher than that. An absorbance of 0 at some wavelength means that no light of that particular wavelength has been absorbed. The intensities of the sample and reference beam are both the same, so the ratio I_o/I is 1. Log_{10} of 1 is zero.

Example 14.1.3

In a sample with an absorbance of 1 at a specific wavelength, what is the relative amount of light that was absorbed by the sample?

Solution

This question does not need Beer-Lambert Law (Equation 14.1.16) to solve, but only the definition of absorbance (Equation 14.1.13)

$$A = \log_{10}\left(\frac{I_o}{I}\right)$$

The relative loss of intensity is

$$\frac{I - I_o}{I_o} = 1 - \frac{I}{I_o}$$

Equation 14.1.13can be rearranged using the properties of logarithms to solved for the relative loss of intensity:

$$10^A = \frac{I_o}{I}$$

$$10^{-A} = \frac{I}{I_o}$$

$$1 - 10^{-A} = 1 - \frac{I}{I_o}$$

Substituting in $A = 1$

$$1 - \frac{I}{I_o} = 1 - 10^{-1} = 1 - \frac{1}{10} = 0.9$$

Hence 90% of the light at that wavelength has been absorbed and that the transmitted intensity is 10% of the incident intensity

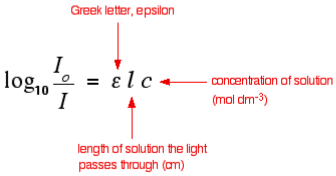
To confirm, substituting these values into Equation 14.1.13to get the absorbance back:

$$\frac{I_o}{I} = \frac{100}{10} = 10$$

and

$$\log_{10} 10 = 1$$

You will find that various different symbols are given for some of the terms in the equation - particularly for the concentration and the solution length.



The Greek letter epsilon in these equations is called the molar absorptivity - or sometimes the molar absorption coefficient. The larger the molar absorptivity, the more probable the electronic transition. In uv spectroscopy, the concentration of the sample solution is measured in molL^{-1} and the length of the light path in cm. Thus, given that absorbance is unitless, the units of molar absorptivity are L mol^{-1} cm^{-1}. However, since the units of molar absorptivity is always the above, it is customarily reported without units.

✓ Example 14.1.4

Guanosine has a maximum absorbance of 275 nm. $\epsilon_{275} = 8400 M^{-1} cm^{-1}$ and the path length is 1 cm. Using a spectrophotometer, you find the that $A_{275} = 0.70$. What is the concentration of guanosine?

Solution

To solve this problem, you must use Beer's Law.

$$A = \epsilon l c$$

$$0.70 = (8400\ \text{M}^{-1}\ \text{cm}^{-1})(1\ \text{cm})(c)$$

Next, divide both side by [(8400 M^{-1} cm^{-1})(1 cm)]

$$c = 8.33\text{x}10^{-5}\ \text{mol/L}$$

✓ Example 14.1.5

There is a substance in a solution (4 g/liter). The length of cuvette is 2 cm and only 50% of the certain light beam is transmitted. What is the extinction coefficient?

Solution

Using Beer-Lambert Law, we can compute the absorption coefficient. Thus,

$$-\log\left(\frac{I_t}{I_o}\right) = -\log(\frac{0.5}{1.0}) = A = 8\epsilon$$

Then we obtain that

$$\epsilon = 0.0376$$

✓ Example 14.1.6

In Example 3 above, what is the molar absorption coefficient if the molecular weight is 100?

Solution

It can simply obtained by multiplying the absorption coefficient by the molecular weight. Thus,

$$\epsilon = 0.0376 \text{ x } 100 = 3.76 \text{ L·mol}^{-1}\text{·cm}^{-1}$$

The proportion of the light absorbed will depend on how many molecules it interacts with. Suppose you have got a strongly colored organic dye. If it is in a reasonably concentrated solution, it will have a very high absorbance because there are lots of molecules to interact with the light. However, in an incredibly dilute solution, it may be very difficult to see that it is colored at all. The absorbance is going to be very low. Suppose then that you wanted to compare this dye with a different compound. Unless you took care to make allowance for the concentration, you couldn't make any sensible comparisons about which one absorbed the most light.

✓ Example 14.1.7

In Example $14.1.3$above, how much is the beam of light is transmitted when 8 g/liter ?

Solution

Since we know ϵ, we can calculate the transmission using Beer-Lambert Law. Thus,

$$log(1) - log(I_t) = 0 - log(I_t) \quad = 0.0376 \text{ x } 8 \text{ x } 2 = 0.6016$$

$$log(I_t) = -0.6016$$

Therefore, I_t = 0.2503 = 25%

✓ Example 14.1.7

The absorption coefficient of a glycogen-iodine complex is 0.20 at light of 450 nm. What is the concentration when the transmission is 40 % in a cuvette of 2 cm?

Solution

It can also be solved using Beer-Lambert Law. Therefore,

$$-\log(I_t) = -\log_{10}(0.4) = 0.20 \times c \times 2$$

Then c = 0.9948

The Beer-Lambert law Equation 14.1.16can be rearranged to obtain an expression for ϵ (the molar absorptivity):

$$\epsilon = \frac{A}{lc} \tag{14.1.18}$$

Remember that the absorbance of a solution will vary as the concentration or the size of the container varies. Molar absorptivity compensates for this by dividing by both the concentration and the length of the solution that the light passes through. Essentially, it works out a value for what the absorbance would be under a standard set of conditions - the light traveling 1 cm through a solution of 1 mol dm-3. That means that you can then make comparisons between one compound and another without having to worry about the concentration or solution length.

Values for molar absorptivity can vary hugely. For example, ethanal has two absorption peaks in its UV-visible spectrum - both in the ultra-violet. One of these corresponds to an electron being promoted from a lone pair on the oxygen into a pi anti-bonding orbital; the other from a π bonding orbital into a π anti-bonding orbital. Table 14.1.2 gives values for the molar absorptivity of a solution of ethanal in hexane. Notice that there are no units given for absorptivity. That's quite common since it assumes the length is in cm and the concentration is mol dm^{-3}, the units are mol^{-1} dm^{3} cm^{-1}.

Table 14.1.2:

electron jump	**wavelength of maximum absorption (nm)**	**molar absorptivity**
lone pair to π anti-bonding orbital	290	15
π bonding to π anti-bonding orbital	180	10,000

The ethanal obviously absorbs much more strongly at 180 nm than it does at 290 nm. (Although, in fact, the 180 nm absorption peak is outside the range of most spectrometers.) You may come across diagrams of absorption spectra plotting absorptivity on the vertical axis rather than absorbance. However, if you look at the figures above and the scales that are going to be involved, you are not really going to be able to spot the absorption at 290 nm. It will be a tiny little peak compared to the one at 180 nm. To get around this, you may also come across diagrams in which the vertical axis is plotted as $\log_{10}$(molar absorptivity). If you take the logs of the two numbers in the table, 15 becomes 1.18, while 10,000 becomes 4. That makes it possible to plot both values easily, but produces strangely squashed-looking spectra!

Table 14.1.3: Expected intensities of electronic transitions

Transition type	Typical values of ε /m^{2}mol^{-1}
Spin forbidden and Laporte forbidden	0.1
Spin allowed and Laporte forbidden	1 - 10
Spin allowed and Laporte allowed e.g. charge transfer bands	1,000 - 10^{6}

Contributors and Attributions

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14.2: Microwave Spectroscopy

Microwave rotational spectroscopy uses microwave radiation to measure the energies of rotational transitions for molecules in the gas phase. It accomplishes this through the interaction of the electric dipole moment of the molecules with the electromagnetic field of the exciting microwave photon.

Introduction

To probe the pure rotational transitions for molecules, scientists use microwave rotational spectroscopy. This spectroscopy utilizes photons in the microwave range to cause transitions between the quantum rotational energy levels of a gas molecule. The reason why the sample must be in the gas phase is due to intermolecular interactions hindering rotations in the liquid and solid phases of the molecule. For microwave spectroscopy, molecules can be broken down into 5 categories based on their shape and the inertia around their 3 orthogonal rotational axes. These 5 categories include diatomic molecules, linear molecules, spherical tops, symmetric tops and asymmetric tops.

Classical Mechanics

The **Hamiltonian solution** to the rigid rotor is

$$H = T \tag{14.2.1}$$

since,

$$H = T + V \tag{14.2.2}$$

Where T is kinetic energy and V is potential energy. Potential energy, V, is 0 because there is no resistance to the rotation (similar to a particle in a box model).

Since $H = T$, we can also say that:

$$T = \frac{1}{2}\sum m_i v_i^2 \tag{14.2.3}$$

However, we have to determine v_i in terms of rotation since we are dealing with rotation. Since,

$$\omega = \frac{v}{r} \tag{14.2.4}$$

where ω = angular velocity, we can say that:

$$v_i = \omega X r_i \tag{14.2.5}$$

Thus we can rewrite the T equation as:

$$T = \frac{1}{2}\sum m_i v_i \left(\omega X r_i\right) \tag{14.2.6}$$

Since ω is a scalar constant, we can rewrite the T equation as:

$$T = \frac{\omega}{2}\sum m_i \left(v_i X r_i\right) = \frac{\omega}{2}\sum l_i = \omega\frac{L}{2} \tag{14.2.7}$$

where l_i is the **angular momentum** of the *ith* particle, and **L** is the angular momentum of the *entire system*. Also, we know from physics that,

$$L = I\omega \tag{14.2.8}$$

where **I** is the moment of inertia of the rigid body relative to the axis of rotation. We can rewrite the T equation as,

$$T = \omega\frac{I\omega}{2} = \frac{1}{2}I\omega^2 \tag{14.2.9}$$

Quantum Mechanics

The internal Hamiltonian, H, is:

$$H = \frac{i^2\hbar^2}{2I} \tag{14.2.10}$$

and the Schrödinger Equation for rigid rotor is:

$$\frac{i^2\hbar^2}{2I}\psi = E\psi \tag{14.2.11}$$

Thus, we get:

$$E_n = \frac{J(J+1)h^2}{8\pi^2 I} \tag{14.2.12}$$

where J is a rotational quantum number and $\hbar$ is the reduced Planck's constant. However, if we let:

$$B = \frac{h}{8\pi^2 I} \tag{14.2.13}$$

where B is a rotational constant, then we can substitute it into the E_n equation and get:

$$E_n = J(J+1)Bh \tag{14.2.14}$$

Considering the transition energy between two energy levels, the difference is a multiple of 2. That is, from $J=0$ to $J=1$, the $\Delta E_{0\rightarrow 1}$ is 2Bh and from J = 1 to J = 2, the $\Delta E_{1\rightarrow 2}$ is 4Bh.

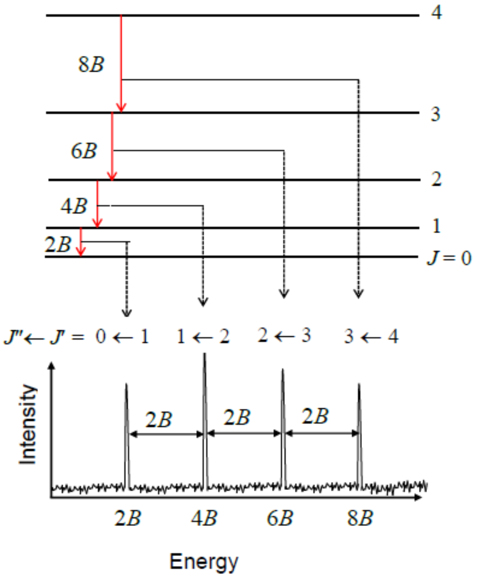


Figure 14.2.1: Energy levels and line positions calculated in the rigid rotor approximation. This diagram illustrates how transitions between the rotational energy levels of molecules map onto the energies at which these transitions are observed during laboratory experiments. (CC CS-BY 3.0; Nnrw).

Theory

When a gas molecule is irradiated with microwave radiation, a photon can be absorbed through the interaction of the photon’s electronic field with the electrons in the molecules. For the microwave region this energy absorption is in the range needed to cause transitions between rotational states of the molecule. However, only molecules with a permanent dipole that changes upon rotation can be investigated using microwave spectroscopy. This is due to the fact that their must be a charge difference across the molecule for the oscillating electric field of the photon to impart a torque upon the molecule around an axis that is perpendicular to this dipole and that passes through the molecules center of mass.

This interaction can be expressed by the transition dipole moment for the transition between two rotational states

$$\text{Probability of Transition} = \int \psi_{rot}(F)\hat{\mu}\psi_{rot}(I)d\tau \tag{14.2.15}$$

Where $\Psi_{rot(F)}$ is the complex conjugate of the wave function for the final rotational state, $\Psi_{rot(I)}$ is the wave function of the initial rotational state , and μ is the dipole moment operator with Cartesian coordinates of μ_x, μ_y, μ_z. For this integral to be nonzero the integrand must be an even function. This is due to the fact that any odd function integrated from negative infinity to positive infinity, or any other symmetric limits, is always zero.

In addition to the constraints imposed by the transition moment integral, transitions between rotational states are also limited by the nature of the photon itself. A photon contains one unit of angular momentum, so when it interacts with a molecule it can only impart one unit of angular momentum to the molecule. This leads to the selection rule that a transition can only occur between rotational energy levels that are only one quantum rotation level (J) away from another[1].

$$\Delta \mathrm{J} = \pm 1 \tag{14.2.16}$$

The transition moment integral and the selection rule for rotational transitions tell if a transition from one rotational state to another is allowed. However, what these do not take into account is whether or not the state being transitioned from is actually populated, meaning that the molecule is in that energy state. This leads to the concept of the Boltzmann distribution of states. The Boltzmann distribution is a statistical distribution of energy states for an ensemble of molecules based on the temperature of the sample[2].

$$\frac{n_J}{n_0} = \frac{e^{(-E_{rot}(J)/RT)}}{\sum_{J=1}^{J=n} e^{(-E_{rot}(J)/RT)}} \tag{14.2.17}$$

where $E_{rot(J)}$ is the molar energy of the J rotational energy state of the molecule,

- R is the gas constant,
- T is the temperature of the sample.
- n(J) is the number of molecules in the J rotational level, and
- n_0 is the total number of molecules in the sample.

This distribution of energy states is the main contributing factor for the observed absorption intensity distributions seen in the microwave spectrum. This distribution makes it so that the absorption peaks that correspond to the transition from the energy state with the largest population based on the Boltzmann equation will have the largest absorption peak, with the peaks on either side steadily decreasing.

Degrees of Freedom

A molecule can have three types of degrees of freedom and a total of 3N degrees of freedom, where N equals the number of atoms in the molecule. These degrees of freedom can be broken down into 3 categories[3].

- **Translational**: These are the simplest of the degrees of freedom. These entail the movement of the entire molecule's center of mass. This movement can be completely described by three orthogonal vectors and thus contains 3 degrees of freedom.
- **Rotational**: These are rotations around the center of mass of the molecule and like the translational movement they can be completely described by three orthogonal vectors. This again means that this category contains only 3 degrees of freedom. However, in the case of a linear molecule only two degrees of freedom are present due to the rotation along the bonds in the molecule having a negligible inertia.
- **Vibrational**: These are any other types of movement not assigned to rotational or translational movement and thus there are 3N – 6 degrees of vibrational freedom for a nonlinear molecule and 3N – 5 for a linear molecule. These vibrations include bending, stretching, wagging and many other aptly named internal movements of a molecule. These various vibrations arise due to the numerous combinations of different stretches, contractions, and bends that can occur between the bonds of atoms in the molecule.

Each of these degrees of freedom is able to store energy. However, In the case of rotational and vibrational degrees of freedom, energy can only be stored in discrete amounts. This is due to the quantized break down of energy levels in a molecule described by quantum mechanics. In the case of rotations the energy stored is dependent on the rotational inertia of the gas along with the corresponding quantum number describing the energy level.

Rotational Symmetries

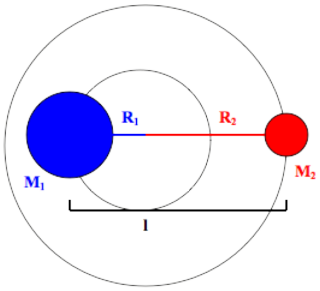
To analyze molecules for rotational spectroscopy, we can break molecules down into 5 categories based on their shapes and their moments of inertia around their 3 orthogonal rotational axes:[4]

1. Diatomic Molecules

2. Linear Molecules
3. Spherical Tops
4. Symmetrical Tops
5. Asymmetrical Tops

Diatomic Molecules

The rotations of a diatomic molecule can be modeled as a rigid rotor. This rigid rotor model has two masses attached to each other with a fixed distance between the two masses.



It has an inertia (I) that is equal to the square of the fixed distance between the two masses multiplied by the reduced mass of the rigid rotor.

$$I_e = \mu r_e^2 \tag{14.2.18}$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \tag{14.2.19}$$

Using quantum mechanical calculations it can be shown that the energy levels of the rigid rotator depend on the inertia of the rigid rotator and the quantum rotational number J[2].

$$E(J) = B_e J(J+1) \tag{14.2.20}$$

$$B_e = \frac{h}{8\pi^2 c I_e} \tag{14.2.21}$$

However, this rigid rotor model fails to take into account that bonds do not act like a rod with a fixed distance, but like a spring. This means that as the angular velocity of the molecule increases so does the distance between the atoms. This leads us to the **nonrigid rotor model** in which a centrifugal distortion term (D_e) is added to the energy equation to account for this stretching during rotation.

$$E(J)(cm^{-1}) = B_e J(J+1) - D_e J^2 (J+1)^2 \tag{14.2.22}$$

This means that for a diatomic molecule the transitional energy between two rotational states equals

$$E = B_e[J'(J'+1) - J''(J''+1)] - D_e[J'^2(J'+1)^2 - J''^2(J'+1)^2] \tag{14.2.23}$$

Where J' is the quantum number of the final rotational energy state and J'' is the quantum number of the initial rotational energy state. Using the selection rule of $\Delta J = \pm 1$ the spacing between peaks in the microwave absorption spectrum of a diatomic molecule will equal

$$E_R = (2B_e - 4D_e) + (2B_e - 12D_e)J'' - 4D_e J''^3 \tag{14.2.24}$$

Linear Molecules

Linear molecules behave in the same way as diatomic molecules when it comes to rotations. For this reason they can be modeled as a non-rigid rotor just like diatomic molecules. This means that linear molecule have the same equation for their rotational energy levels. The only difference is there are now more masses along the rotor. This means that the inertia is now the sum of the distance between each mass and the center of mass of the rotor multiplied by the square of the distance between them[2].

$$I_e = \sum_{j=1}^{n} m_j r_{ej}^2 \tag{14.2.25}$$

Where m_j is the mass of the jth mass on the rotor and r_{ej} is the equilibrium distance between the j^{th} mass and the center of mass of the rotor.

Spherical Tops

Spherical tops are molecules in which all three orthogonal rotations have equal inertia and they are highly symmetrical. This means that the molecule has no dipole and for this reason spherical tops do not give a microwave rotational spectrum.

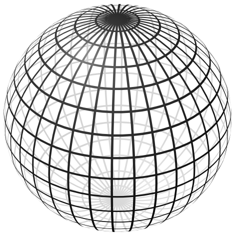
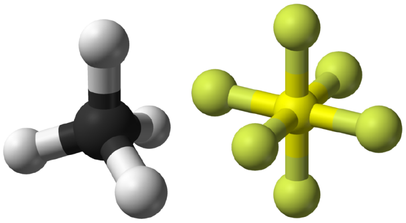


Figure 14.2.2: Geometrical example of a spherical top

Examples:



Symmetrical Tops

Symmetrical tops are molecules with two rotational axes that have the same inertia and one unique rotational axis with a different inertia. Symmetrical tops can be divided into two categories based on the relationship between the inertia of the unique axis and the inertia of the two axes with equivalent inertia. If the unique rotational axis has a greater inertia than the degenerate axes the molecule is called an oblate symmetrical top. If the unique rotational axis has a lower inertia than the degenerate axes the molecule is called a prolate symmetrical top. For simplification think of these two categories as either frisbees for oblate tops or footballs for prolate tops.

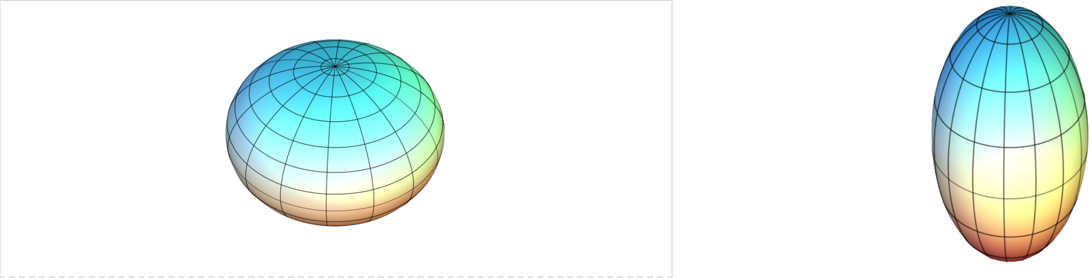


Figure* $14.2.3$*: *Symmetric Tops: (Left) Geometrical example of an oblate top and (right) a prolate top. Images used with permission from Wikipedia.com.*

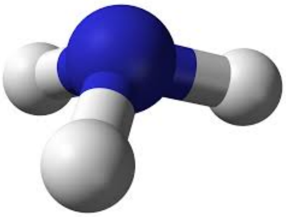


Figure 14.2.4: Examples of symmetric tops. Benzene (oblate) XeF_4 (oblate) $ClCH_3$ (prolate) NH_3 (prolate)

In the case of linear molecules there is one degenerate rotational axis which in turn has a single rotational constant. With symmetrical tops now there is one unique axis and two degenerate axes. This means an additional rotational constant is needed to describe the energy levels of a symmetrical top. In addition to the rotational constant an additional quantum number must be introduced to describe the rotational energy levels of the symmetric top. These two additions give us the following rotational energy levels of a prolate and oblate symmetric top

$$E_{(J,K)}(cm^{-1}) = B_e * J(J+1) + (A_e - B_e)K^2 \tag{14.2.26}$$

Where B_e is the rotational constant of the unique axis, A_e is the rotational constant of the degenerate axes, J is the total rotational angular momentum quantum number and K is the quantum number that represents the portion of the total angular momentum that lies along the unique rotational axis. This leads to the property that K is always equal to or less than J. Thus we get the two selection rules for symmetric tops

$$\Delta J = 0, \pm 1 \tag{14.2.27}$$

$$\Delta K = 0 \tag{14.2.28}$$

when $K \neq 0$

$$\Delta J = \pm 1 \tag{14.2.29}$$

$$\Delta K = 0 \tag{14.2.30}$$

when $K = 0$

However, like the rigid rotor approximation for linear molecules, we must also take into account the elasticity of the bonds in symmetric tops. Therefore, in a similar manner to the rigid rotor we add a centrifugal coupling term, but this time we have one for each quantum number and one for the coupling between the two.

$$E_{(J,K)}(cm^{-1}) = B_e J(J+1) - D_{eJ} J^2 (J+1)^2 + (A_e - B_e) * K^2 \tag{14.2.31}$$

$$-D_{ek} K^4 - D_{ejk} J(J+1) K^2 \tag{14.2.32}$$

Asymmetrical Tops

Asymmetrical tops have three orthogonal rotational axes that all have different moments of inertia and most molecules fall into this category. Unlike linear molecules and symmetric tops these types of molecules do not have a simplified energy equation to determine the energy levels of the rotations. These types of molecules do not follow a specific pattern and usually have very complex microwave spectra.

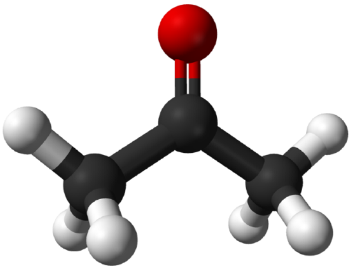


Figure 14.2.5: Molecular examples of asymmetrical tops. (left) water and (right) acetone

Additional Rotationally Sensitive Spectroscopies

In addition to microwave spectroscopy, IR spectroscopy can also be used to probe rotational transitions in a molecule. However, in the case of IR spectroscopy the rotational transitions are coupled to the vibrational transitions of the molecule. One other spectroscopy that can probe the rotational transitions in a molecule is Raman spectroscopy, which uses UV-visible light scattering to determine energy levels in a molecule. However, a very high sensitivity detector must be used to analyze rotational energy levels of a molecule.

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3. Shoemaker, D. P.; W., G. C.; W., N. J., *Experiments in Physical Chemistry*. 8th ed.; McGraw Hill: New York, 2009.
4. Hollas, M. J., *Basic Atomic and Molecular Spectroscopy*. Royal Society of Chemistry: Cambridge, 2002.

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SECTION OVERVIEW

14.3: Infrared Spectroscopy

Infrared Spectroscopy is the analysis of infrared light interacting with a molecule. This can be analyzed in three ways by measuring absorption, emission and reflection. The main use of this technique is in organic and inorganic chemistry. It is used by chemists to determine functional groups in molecules. IR Spectroscopy measures the vibrations of atoms, and based on this it is possible to determine the functional groups.5 Generally, stronger bonds and light atoms will vibrate at a high stretching frequency (wavenumber).

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14.4: Electronic Spectroscopy

This page explains what happens when organic compounds absorb UV or visible light, and why the wavelength of light absorbed varies from compound to compound.

Molecular Absorption of Light

When we were talking about the various sorts of molecular orbitals present in organic compounds earlier, you will have come across this diagram showing their relative energies:

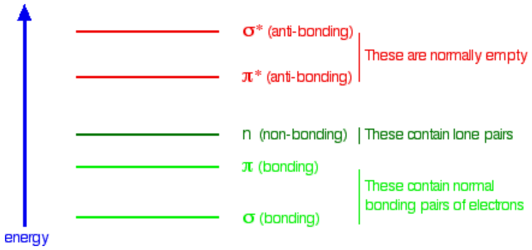


Figure 14.4.1: The diagram is not intended to be to scale - it just shows the relative placing of the different orbitals.

When light passes through the compound, energy from the light is used to promote an electron from a bonding or non-bonding orbital into one of the empty anti-bonding orbitals. The possible electron jumps that light might cause are:

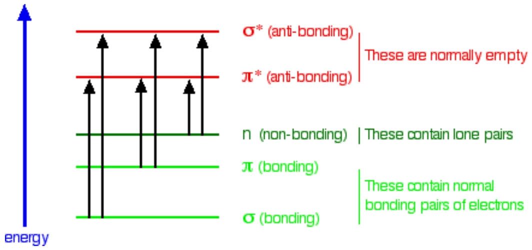


Figure 14.4.2: Promotion of an electron via different electron transitions

In each possible case, an electron is excited from a full orbital into an empty anti-bonding orbital. Each jump takes energy from the light, and a big jump obviously needs more energy than a small one. Each wavelength of light has a particular energy associated with it. If that particular amount of energy is just right for making one of these energy jumps, then that wavelength will be absorbed - its energy will have been used in promoting an electron.

An absorption spectrometer works in a range from about 200 nm (in the near ultra-violet) to about 800 nm (in the very near infra-red). Only a limited number of the possible electron jumps absorb light in that region. Look again at the possible jumps. This time, the important jumps are shown in black, and a less important one in grey. The grey dotted arrows show jumps which absorb light outside the region of the spectrum we are working in.

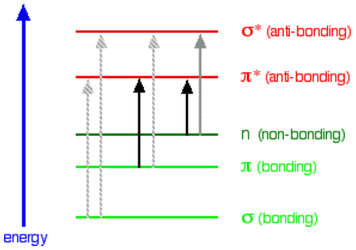


Figure 14.4.3: Promotion of an electron via different electron transitions scaled by energies.

Remember that bigger jumps need more energy and so absorb light with a shorter wavelength. The jumps shown with grey dotted arrows absorb UV light of wavelength less that 200 nm. The important jumps are:

- from π bonding orbitals to π anti-bonding orbitals;
- from non-bonding orbitals to π anti-bonding orbitals;
- from non-bonding orbitals to sigma anti-bonding orbitals.

That means that in order to absorb light in the region from 200 - 800 nm (which is where the spectra are measured), the molecule must contain either π bonds or atoms with non-bonding orbitals. Remember that a non-bonding orbital is a lone pair on, say, oxygen, nitrogen or a halogen. Groups in a molecule which absorb light are known as chromophores.

What does an absorption spectrum look like

The diagram below shows a simple UV-visible absorption spectrum for buta-1,3-diene - a molecule we will talk more about later. Absorbance (on the vertical axis) is just a measure of the amount of light absorbed. The higher the value, the more of a particular wavelength is being absorbed.

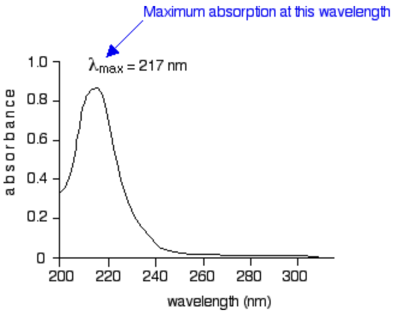


Figure 14.4.4: UV-visible absorption spectrum for buta-1,3-diene

You will see that absorption peaks at a value of 217 nm. This is in the ultra-violet and so there would be no visible sign of any light being absorbed - buta-1,3-diene is colorless. In buta-1,3-diene, CH_2=CH-CH=CH_2, there are no non-bonding electrons. That means that the only electron jumps taking place (within the range that the spectrometer can measure) are from π bonding to π anti-bonding orbitals.

A chromophore such as the carbon-oxygen double bond in ethanal, for example, obviously has π electrons as a part of the double bond, but also has lone pairs on the oxygen atom. That means that both of the important absorptions from the last energy diagram are possible. You can get an electron excited from a π bonding to a π anti-bonding orbital, or you can get one excited from an oxygen lone pair (a non-bonding orbital) into a π anti-bonding orbital.

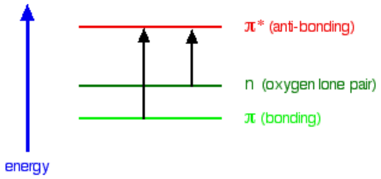


Figure 14.4.4: A simplified diagram showing $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions

The non-bonding orbital has a higher energy than a π bonding orbital. That means that the jump from an oxygen lone pair into a π anti-bonding orbital needs less energy. That means it absorbs light of a lower frequency and therefore a higher wavelength. For example, ethanal can therefore absorb light of two different wavelengths:

- the π bonding to π anti-bonding absorption peaks at 180 nm. These $n \rightarrow \pi^*$ transitions involve moving an electron from a nonbonding electron pair to a antibonding *pi^*\) orbital. They tend to have molar absorbtivities less than 2000
- the non-bonding to π anti-bonding absorption peaks at 290 nm. These $\pi \rightarrow \pi^*$ transitions involve moving an electron from a bonding $\pi*$ orbital to an antibonding π^* orbital. They tend to have molar absorptivities on the order of 10,000.

Both of these absorptions are in the ultra-violet, but most spectrometers will not pick up the one at 180 nm because they work in the range from 200 - 800 nm.

Conjugation and Delocalization

Consider these three molecules:

CH_2=CH_2	CH_2=CH-CH=CH_2	CH_2=CH-CH=CH-CH=CH_2
ethene	buta-1,3-diene	hexa-1,3,5-triene

Ethene contains a simple isolated carbon-carbon double bond, but the other two have conjugated double bonds. In these cases, there is delocalization of the π bonding orbitals over the whole molecule. Now look at the wavelengths of the light which each of these molecules absorbs.

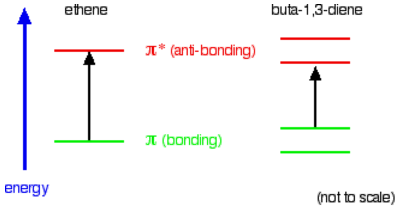
molecule	wavelength of maximum absorption (nm)
ethene	171
buta-1,3-diene	217
hexa-1,3,5-triene	258

All of the molecules give similar UV-visible absorption spectra - the only difference being that the absorptions move to longer and longer wavelengths as the amount of delocalization in the molecule increases. Why is this? You can actually work out what must be happening.

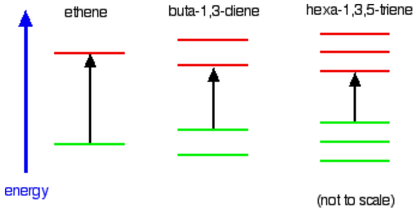
- The maximum absorption is moving to longer wavelengths as the amount of delocalization increases.
- Therefore maximum absorption is moving to shorter frequencies as the amount of delocalization increases.
- Therefore absorption needs less energy as the amount of delocalization increases.
- Therefore there must be less energy gap between the bonding and anti-bonding orbitals as the amount of delocalization increases.

. . . and that's what is happening.

Compare ethene with buta-1,3-diene. In ethene, there is one π bonding orbital and one π anti-bonding orbital. In buta-1,3-diene, there are two π bonding orbitals and two π anti-bonding orbitals. This is all discussed in detail on the introductory page that you should have read.



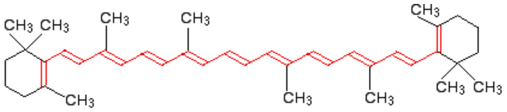
The highest occupied molecular orbital is often referred to as the HOMO - in these cases, it is a π bonding orbital. The lowest unoccupied molecular orbital (the LUMO) is a π anti-bonding orbital. Notice that the gap between these has fallen. It takes less energy to excite an electron in the buta-1,3-diene case than with ethene. In the hexa-1,3,5-triene case, it is less still.



If you extend this to compounds with really massive delocalization, the wavelength absorbed will eventually be high enough to be in the visible region of the spectrum, and the compound will then be seen as colored. A good example of this is the orange plant pigment, beta-carotene - present in carrots, for example.

Why is beta-carotene orange?

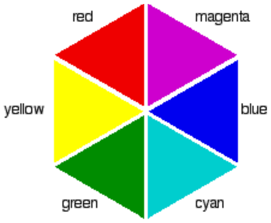
Beta-carotene has the sort of delocalization that we've just been looking at, but on a much greater scale with 11 carbon-carbon double bonds conjugated together. The diagram shows the structure of beta-carotene with the alternating double and single bonds shown in red.



The more delocalization there is, the smaller the gap between the highest energy π bonding orbital and the lowest energy π anti-bonding orbital. To promote an electron therefore takes less energy in beta-carotene than in the cases we've looked at so far - because the gap between the levels is less. Remember that less energy means a lower frequency of light gets absorbed - and that's equivalent to a longer wavelength. Beta-carotene absorbs throughout the ultra-violet region into the violet - but particularly strongly in the visible region between about 400 and 500 nm with a peak about 470 nm. The wavelengths associated with the various colors are approximately:

color region	wavelength (nm)
violet	380 - 435
blue	435 - 500
cyan	500 - 520
green	520 - 565
yellow	565 - 590
orange	590 - 625
red	625 - 740

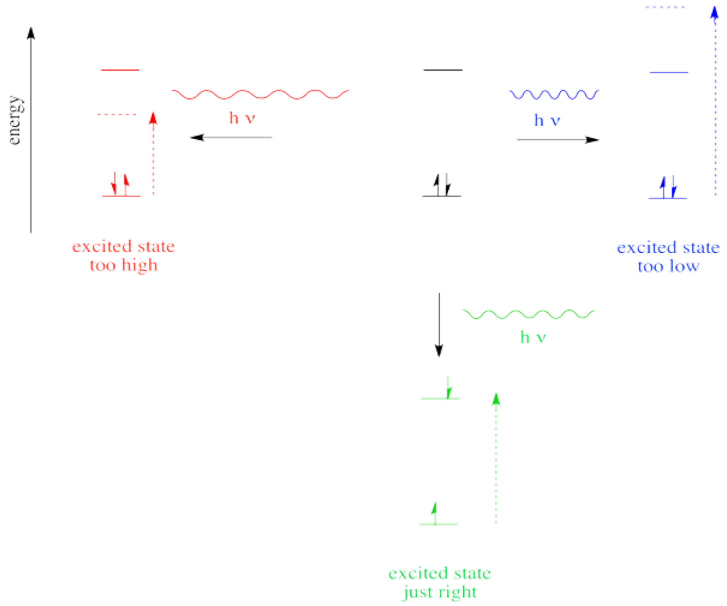
So if the absorption is strongest in the violet to cyan region, what color will you actually see? It is tempting to think that you can work it out from the colors that are left - and in this particular case, you wouldn't be far wrong. Unfortunately, it is not as simple as that! Sometimes what you actually see is quite unexpected. Mixing different wavelengths of light does not give you the same result as mixing paints or other pigments. You can, however, sometimes get some estimate of the color you would see using the idea of complementary colors. If you arrange some colors in a circle, you get a "color wheel". The diagram shows one possible version of this. An internet search will throw up many different versions!



colors directly opposite each other on the color wheel are said to be complementary colors. Blue and yellow are complementary colors; red and cyan are complementary; and so are green and magenta. Mixing together two complementary colors of light will give you white light. What this all means is that if a particular color is absorbed from white light, what your eye detects by mixing up all the other wavelengths of light is its complementary color. In the beta-carotene case, the situation is more confused because you are absorbing such a range of wavelengths. However, if you think of the peak absorption running from the blue into the cyan, it would be reasonable to think of the color you would see as being opposite that where yellow runs into red - in other words, orange.

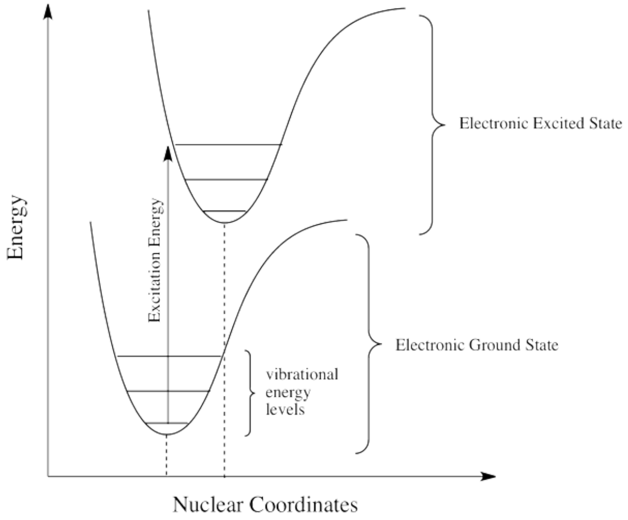
Franck-Condon: Electronic and Vibrational Coupling

So far, we have come across one big rule of photon absorbance. To be absorbed, a photon's energy has to match an energy difference within the compound that is absorbing it.



In the case of visible or ultraviolet light, the energy of a photon is roughly in the region that would be appropriate to promote an electron to a higher energy level. Different wavelengths would be able to promote different electrons, depending on the energy difference between an occupied electronic energy level and an unoccupied one. Other types of electromagnetic radiation would not be able to promote an electron, but they would be coupled to other events. For example, absorption of infrared light is tied to vibrational energy levels. Microwave radiation is tied to rotational energy levels in molecules. Thus, one reason a photon may or may not be absorbed has to do with whether its energy corresponds to the available energy differences within the molecule or ion that it encounters.

Photons face other limitations. One of these is a moderate variation on our main rule. It is called the Frank Condon Principle. According to this idea, when an electron is excited from its normal position, the ground state, to a higher energy level, the optimal positions of atoms in the molecule may need to shift. Because electronic motion is much faster than nuclear motion, however, any shifting of atoms needed to optimize positions as they should be in the excited state will have to wait until after the electron gets excited. In that case, when the electron lands and the atoms aren't yet in their lowest energy positions for the excited state, the molecule will find itself in an excited vibrational state as well as an excited electronic state.



That means the required energy for excitation does not just correspond to the difference in electronic energy levels; it is fine-tuned to reach a vibrational energy level, which is quantized as well.

- The Franck Condon Principle states that electronic transitions are vertical.
- A vertical transition is one in which non of the nuclei move while the electron journeys from one state to another.

- A vertical transition may begin in a vibrational ground state of an electronic ground state and end in a vibrational excited state of an electronic excited state.

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14.5: Nuclear Magnetic Resonance

Nuclear Magnetic Resonance (NMR) is a nuceli (Nuclear) specific spectroscopy that has far reaching applications throughout the physical sciences and industry. NMR uses a large magnet (Magnetic) to probe the intrinsic spin properties of atomic nuclei. Like all spectroscopies, NMR uses a component of electromagnetic radiation (radio frequency waves) to promote transitions between nuclear energy levels (Resonance). Most chemists use NMR for structure determination of small molecules.

Introduction

In 1946, NMR was co-discovered by Purcell, Pound and Torrey of Harvard University and Bloch, Hansen and Packard of Stanford University. The discovery first came about when it was noticed that magnetic nuclei, such as ^{1}H and ^{31}P (read: proton and Phosphorus 31) were able to absorb radio frequency energy when placed in a magnetic field of a strength that was specific to the nucleus. Upon absorption, the nuclei begin to resonate and different atoms within a molecule resonated at different frequencies. This observation allowed a detailed analysis of the structure of a molecule. Since then, NMR has been applied to solids, liquids and gasses, kinetic and structural studies, resulting in 6 Nobel prizes being awarded in the field of NMR. More information about the history of NMR can be found in the NMR History page. Here, the fundamental concepts of NMR are presented.

Spin and Magnetic Properties

The nucleus consists of elementary particles called neutrons and protons, which contain an intrinsic property called spin. Like electrons, the spin of a nucleus can be described using quantum numbers of I for the spin and m for the spin in a magnetic field. Atomic nuclei with even numbers of protons and neutrons have zero spin and all the other atoms with odd numbers have a non-zero spin. Furthermore, all molecules with a non-zero spin have a magnetic moment, μ, given by

$$\mu = \gamma I \tag{14.5.1}$$

where γ is the gyromagnetic ratio, a proportionality constant between the magnetic dipole moment and the angular momentum, specific to each nucleus (Table 14.5.1).

Table 14.5.1 : The gyromagnetic ratios for several common nuclei

Nuclei	Spin	Gyromagetic Ratio (MHz/T)	Natural Abundance (%)
^{1}H	1/2	42.576	99.9985
^{13}C	1/2	10.705	1.07
^{31}P	1/2	17.235	100
^{27}Al	5/2	11.103	100
^{23}Na	3/2	11.262	100
^{7}Li	3/2	16.546	92.41
^{29}Si	1/2	-8.465	4.68
^{17}O	5/2	5.772	0.038
^{15}N	1/2	-4.361	0.368

The magnetic moment of the nucleus forces the nucleus to behave as a tiny bar magnet. In the absence of an external magnetic field, each magnet is randomly oriented. During the NMR experiment the sample is placed in an external magnetic field, B_0, which forces the bar magnets to align with (low energy) or against (high energy) the B_0. During the NMR experiment, a spin flip of the magnets occurs, requiring an exact quanta of energy. To understand this rather abstract concept it is useful to consider the NMR experiment using the nuclear energy levels.

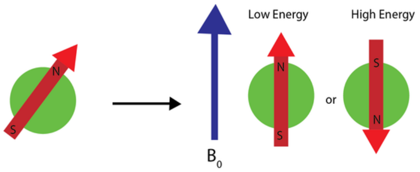

Figure **14.5.1 :** Application of a magnetic field to a randomly oriented bar magnet. The red arrow denotes magnetic moment of the nucleus. The application of the external magnetic field aligns the nuclear magnetic moments with or against the field.

Nuclear Energy Levels

As mentioned above, an exact quanta of energy must be used to induce the spin flip or transition. For any m, there are 2m+1 energy levels. For a spin 1/2 nucleus, there are only two energy levels, the low energy level occupied by the spins which aligned with B_0 and the high energy level occupied by spins aligned against B_0. Each energy level is given by

$$E = -m\hbar\gamma B_0 \tag{14.5.2}$$

where m is the magnetic quantum number, in this case +/- 1/2. The energy levels for $m > 1/2$, known as quadrupolar nuclei, are more complex and information regarding them can be found here.

The energy difference between the energy levels is then

$$\Delta E = \hbar\gamma B_0 \tag{14.5.3}$$

where $\hbar$ is Planks constant.

A schematic showing how the energy levels are arranged for a spin=1/2 nucleus is shown below. Note how the strength of the magnetic field plays a large role in the energy level difference. In the absence of an applied field the nuclear energy levels are degenerate. The splitting of the degenerate energy level due to the presence of a magnetic field in known as Zeeman Splitting.

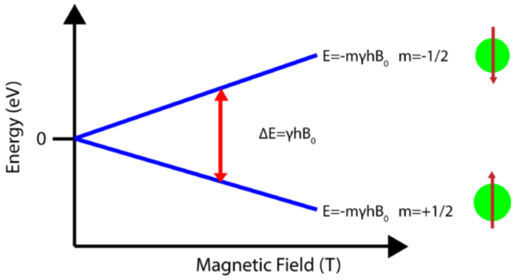

Figure **14.5.1:** The splitting of the degenerate nuclear energy levels under an applied magnetic field. The green spheres represent atomic nuclei which are either aligned with (low energy) or against (high energy) the magnetic field.

Energy Transitions (Spin Flip)

In order for the NMR experiment to work, a spin flip between the energy levels must occur. The energy difference between the two states corresponds to the energy of the electromagnetic radiation that causes the nuclei to change their energy levels. For most NMR spectrometers, B_0 is on the order of Tesla (T) while γ is on the order of 10^7. Consequently, the electromagnetic radiation required is on the order of Hz. The energy of a photon is represented by

$$E = h\nu \tag{14.5.4}$$

and thus the frequency necessary for absorption to occur is represented as:

$$\nu = \frac{\gamma B_0}{2\pi} \tag{14.5.5}$$

Hence, NMR experiment measures the resonant frequency that causes a spin flip. For the more advanced NMR users, the sections on NMR detection and Larmor frequency should be consulted.

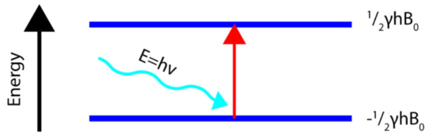

Figure **14.5.3 :** Absorption of radio frequency radiation to promote a transition between nuclear energy levels, called a spin flip.

Nuclear Shielding

The power of NMR is based on the concept of nuclear shielding, which allows for structural assignments. Every atom is surrounded by electrons, which orbit the nucleus. Charged particles moving in a loop will create a magnetic field which is felt by the nucleus. Therefore the local electronic environment surrounding the nucleus will slightly change the magnetic field experienced by the nucleus, which in turn will cause slight changes in the energy levels! This is known as shielding. Nuclei that experinece differnet magnetic fields due to the local electronic interactions are known as inequivalent nuclei. The change in the energy levels requires a different frequency to excite the spin flip, which as will be seen below, creates a new peak in the NMR spectrum. The shielding allows for structural determination of molecules.

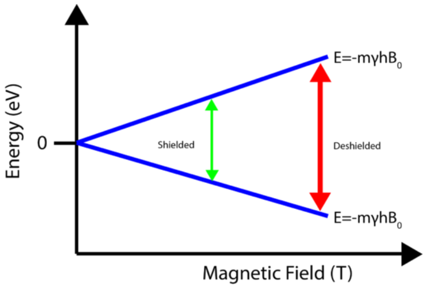

Figure **14.5.4** **:** *The effect that shielding from electrons has on the splitting of the nuclear energy levels. Electrons impart their own magnetic field which shields the nucleus from the externally applied magnetic field. This effect is greatly exaggerated in this illustration.*

The shielding of the nucleus allows for chemically inequivalent environments to be determined by Fourier Transforming the NMR signal. The result is a spectrum, shown below, that consists of a set of peaks in which each peak corresponds to a distinct chemical environment. The area underneath the peak is directly proportional to the number of nuclei in that chemical environment. Additional details about the structure manifest themselves in the form of different NMR interactions, each altering the NMR spectrum in a distinct manner. The x-axis of an NMR spectrum is given in parts per million (ppm) and the relation to shielding is explained here.

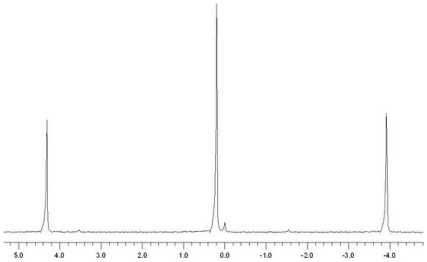

Figure **14.5.5** **:** ^{31}P spectrum of phosphinic acid. Each peak corresponds to a distinct chemical environment while the area under the peak is proportional to the number of nuclei in a given environment.

Relaxation

Relaxation refers to the phenomenon of nuclei returning to their thermodynamically stable states after being excited to higher energy levels (Figure 14.5.4). The energy absorbed when a transition from a lower energy level to a high energy level occurs is released when the opposite happens. This can be a fairly complex process based on different timescales of the relaxation. The two most common types of relaxation are spin lattice relaxation (T_1) and spin spin relaxation (T_2). A more complex treatment of relaxation is given elsewhere.

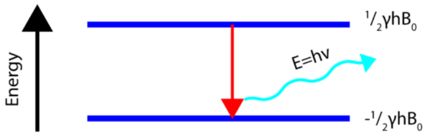

Figure **14.5.6** **:** The process of relaxation

To understand relaxation, the entire sample must be considered. By placing rhe nuclei in an external magnetic field, the nuclei create a bulk magnetization along the z-axis. The spins of the nuclei are also coherent. The NMR signal may be detected as long as the spins are coherent with one another. The NMR experiment moves the bulk magnetization from the z-axis to the x-y plane, where it is detected.

- **Spin-Lattice Relaxation** (T_1): T_1 is the time it takes for the 37% of bulk magnetization to recovery along Z-axis from the x-y plane. The more efficient the relaxation process, the smaller relaxation time (T_1) value you will get. In solids, since motions between molecules are limited, the relaxation time (T_1) values are large. Spin-lattice relaxation measurements are usually carried out by pulse methods.
- **Spin-Spin Relaxation** (T_2): T_2 is the time it takes for the spins to lose coherence with one another. T_2 can either be shorter or equal to T_1.

Applications

The two major areas where NMR has proven to be of critical importance is in the fields of medicine and chemistry, with new applications being developed daily

Nuclear magnetic resonance imaging, better known as magnetic resonance imaging (MRI) is an important medical diagnostic tool used to study the function and structure of the human body. It provides detailed images of any part of the body, especially soft tissue, in all possible planes and has been used in the areas of cardiovascular, neurological, musculoskeletal and oncological imaging. Unlike other alternatives, such as computed tomography (CT), it does not used ionized radiation and hence is very safe to administer.

Figure **14.5.7 :** ^{1}H MRI of a human head showing the soft tissue such as the brain and sinuses. The MRI also clearly shows the spinal column and skull. from Wikipedia

In many laboratories today, chemists use nuclear magnetic resonance to determine structures of important chemical and biological compounds. In NMR spectra, different peaks give information about different atoms in a molecule according specific chemical environments and bonding between atoms. The most common isotopes used to detect NMR signals are ^{1}H and ^{13}C but there are many others, such as ^{2}H, ^{3}He, ^{15}N, ^{19}F, etc., that are also in use.

NMR has also proven to be very useful in other area such as environmental testing, petroleum industry, process control, earth's field NMR and magnetometers. Non-destructive testing saves a lot of money for expensive biological samples and can be used again if more trials need to be run. The petroleum industry uses NMR equipment to measure porosity of different rocks and permeability of different underground fluids. Magnetometers are used to measure the various magnetic fields that are relevant to one's study.

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14.6: Electron Spin Resonance

Though less used than Nuclear Magnetic Resonance (NMR), Electron Paramagnetic Resonance (EPR) is a remarkably useful form of spectroscopy used to study molecules or atoms with an unpaired electron. It is less widely used than NMR because stable molecules often do not have unpaired electrons. However, EPR can be used analytically to observe labeled species in situ either biologically or in a chemical reaction.

Introduction

Electron Paramagnetic Resonance (EPR), also known as **Electron Spin Resonance (ESR).** The sample is held in a very strong magnetic field, while electromagnetic (EM) radiation is applied monochromatically (Figure 1).

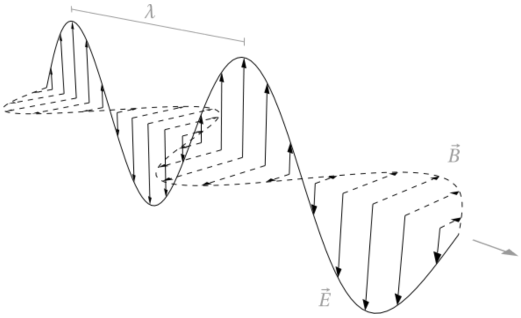

Figure 1(3)-monochromatic electromagnetic beam

This portion of EPR is analogous to simple spectroscopy, where absorbance by the sample of a single or range of wavelengths of EM radiation is monitored by the end user ie absorbance. The unpaired electrons can either occupy +1/2 or -1/2 m_s value (Figure 2). From here either the magnetic field "B_0" is varied or the incident light is varied. Today most researchers adjust the EM radiation in the microwave region, the theory is the find the exact point where the electrons can jump from the less energetic m_s=-1/2 to m_s=+1/2. More electrons occupy the lower m_s value (see Boltzmann Distribution).

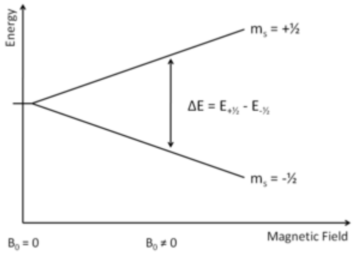

Figure 2: Resonance of a free electron.

Overall, there is an absorption of energy. This absorbance value, when paired with the associated wavelength can be used in the equation to generate a graph of showing how absorption relates to frequency or magnetic field.

$$\Delta E = h\nu = g_e \beta_B B_0 \tag{14.6.1}$$

where g_e equals to 2.0023193 for a free electron; β_B is the *Bohr magneton* and is equal to 9.2740 * 10 $^{-24}$ J T $^{-1}$; and B_0 indicates the external magnetic field.

Theory

Like NMR, EPR can be used to observe the geometry of a molecule through its magnetic moment and the difference in electron and nucleus mass. EPR has mainly been used for the detection and study of free radical species, either in testing or anylytical experimentation. "Spin labeling" species of chemicals can be a powerfull technique for both quantification and investigation of otherwise invisible factors.

The EPR spectrum of a free electron, there will be only one line (one peak) observed. But for the EPR spetrum of hydrogen, there will be two lines (2 peaks) observed due to the fact that there is interaction between the nucleus and the unpaired electron. This is also called *hyperfine splitting*. The distance between two lines (two peaks) are called ***hyperfine splitting constant (A)***.

By using (2NI+1), we can calculate the components or number of hyperfine lines of a multiplet of a EPR transtion, where N indicates number of spin, I indicates number of equivalent nuclei. For example, for nitroxide radicals, the nuclear spin of 14N is 1, N=1, I=1, we have 2 x 1 + 1 = 3, which means that for a spin 1 nucleus splits the EPR transition into a triplet.

To absorb microwave, there must be unpaired electrons in the system. no EPR signal will be observed if the system contains only paired electrons since there will be no resonant absorption of microwave energy. Molecules such as NO, NO_2, O_2 do have unpaired electrons in groud states. EPR can be also performed on proteins with paramagnetic ions such as Mn^{2+}, Fe^{3+} and Cu^{2+}. Additionally, molecules containing stable nitroxide radicals such as 2,2,6,6-tetramethyl-1-piperidinyloxyl (TEMPO, Figure 3) and di-*tert*-butyl nitroxide radical.

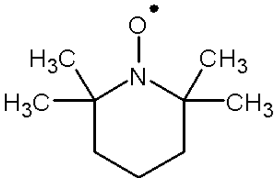

Figure 3-The nitroxide radical TEMPO

Examples of EPR spectra:

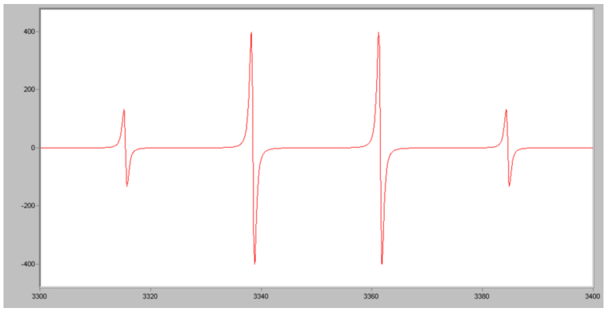

Figure 4 -Stimulated EPR spectrum of CH_3 radical

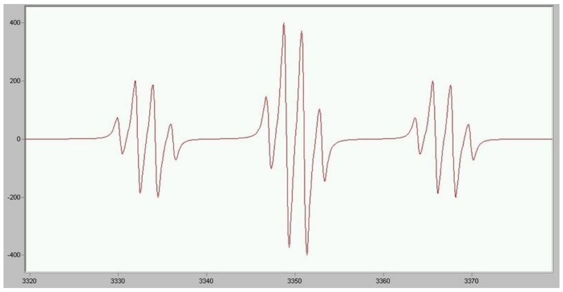

Figure 5 - Stimulated EPR spectrum of methoxymethl ($H_2C(OCH_3)$)radical

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14.7: Fluorescence and Phosphorescence

Singlet and Triplet Excited State

Understanding the difference between fluorescence and phosphorescence requires the knowledge of electron spin and the differences between singlet and triplet states. The Pauli Exclusion principle states that two electrons in an atom cannot have the same four quantum numbers (n, l, m_l, m_s) and only two electrons can occupy each orbital where they must have opposite spin states. These opposite spin states are called spin pairing. Because of this spin pairing, most molecules do not exhibit a magnetic field and are diamagnetic. In diamagnetic molecules, electrons are not attracted or repelled by the static electric field. Free radicals are paramagnetic because they contain unpaired electrons have magnetic moments that are attracted to the magnetic field.

A singlet state is defined as a state when all the electron spins are paired in the molecular electronic state and the electronic energy levels do not split when the molecule is exposed to a magnetic field. A doublet state occurs when there is an unpaired electron that can have two possible orientations when exposed to a magnetic field and imparts different energy to the system. A singlet or a triplet can form when one electron is excited to a higher energy level. In an excited singlet state, the electron is promoted with the same spin orientation as it had in the ground state (paired). In a triplet excited stated, the electron that is promoted has the same spin orientation (parallel) as the other unpaired electron. The difference between the spins of ground singlet, excited singlet, and excited triplet is shown in Figure 14.7.1. Singlet, doublet and triplet is derived using the equation for multiplicity, 2S+1, where S is the total spin angular momentum (sum of all the electron spins). Individual spins are denoted as spin up (s = +1/2) or spin down (s = -1/2). If we were to calculated the S for the excited singlet state, the equation would be 2(+1/2 + -1/2)+1 = 2(0)+1 = 1, therefore making the center orbital in the figure a singlet state. If the spin multiplicity for the excited triplet state was calculated, we obtain 2(+1/2 + +1/2)+1 = 2(1)+1 =3, which gives a triplet state as expected.

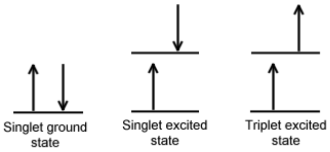


Figure 14.7.1: Spin in the ground and excited states

The difference between a molecule in the ground and triplet excited state is that the electrons are diamagnetic in the ground state and paramagnetic in the excited triplet state.This difference in spin state makes the transition from singlet to triplet (or triplet to singlet) more improbable than the singlet-to-singlet transitions because it involves a spin flip. This singlet to triplet (or reverse) transition involves a change in *electronic* state. For this reason, the lifetime of the triplet state is longer than that of the singlet state by an approximately 10^4 fold difference. Absorption of radiation inducing the transition from ground to excited triplet state has a low probability, thus their absorption bands are less intense than singlet-singlet state absorption. The excited triplet state can be populated from the excited singlet state of certain molecules which results in phosphorescence. These spin multiplicities in ground and excited states can be used to explain transition in photoluminescence molecules by the Jablonski diagram.

Jablonski Diagrams

The Jablonski diagram that drawn below is a partial energy diagram that represents the energy of photoluminescent molecule in its different energy states. The lowest and darkest horizontal line represents the ground-state electronic energy of the molecule which is the singlet state labeled as S_o. At room temperature, majority of the molecules in a solution are in this state.

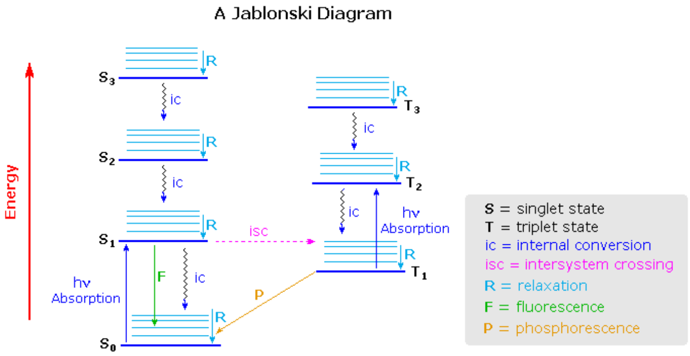


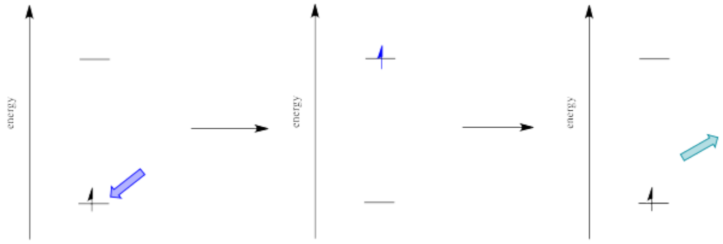
Figure 14.7.2: Partial Jablonski Diagram for Absorption, Fluorescence, and Phosphorescence. from Bill Reusch.

The upper lines represent the energy state of the three excited electronic states: S_1 and S_2 represent the electronic singlet state (left) and T_1 represents the first electronic triplet state (right). The upper darkest line represents the ground vibrational state of the three excited electronic state.The energy of the triplet state is lower than the energy of the corresponding singlet state.

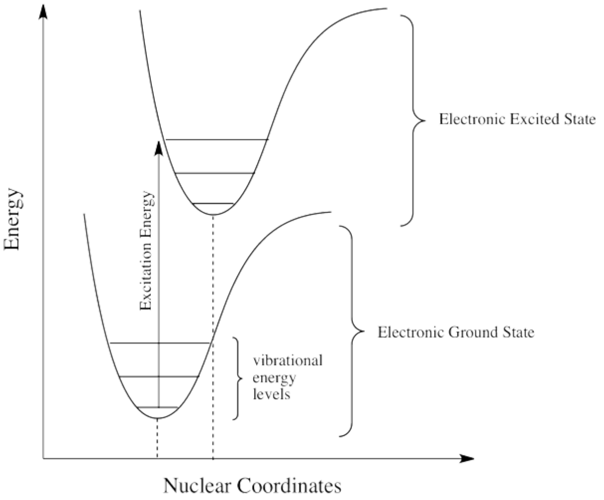
There are numerous vibrational levels that can be associated with each electronic state as denoted by the thinner lines. Absorption transitions (blues lines in Figure 14.7.2) can occur from the ground singlet electronic state (S_o) to various vibrational levels in the singlet excited vibrational states. It is unlikely that a transition from the ground singlet electronic state to the triplet electronic state because the electron spin is parallel to the spin in its ground state (Figure 14.7.1). This transition leads to a change in multiplicity and thus has a low probability of occurring thus it is a partially **forbidden transition.** Molecules also undergo vibrational relaxation to lose any excess vibrational energy that remains when excited to the electronic states (S_1 and S_2) as demonstrated in light blue arrows labelled R in Figure 14.7.2. The knowledge of forbidden transition is used to explain and compare the peaks of absorption and emission.

Relaxation and Fluorescence

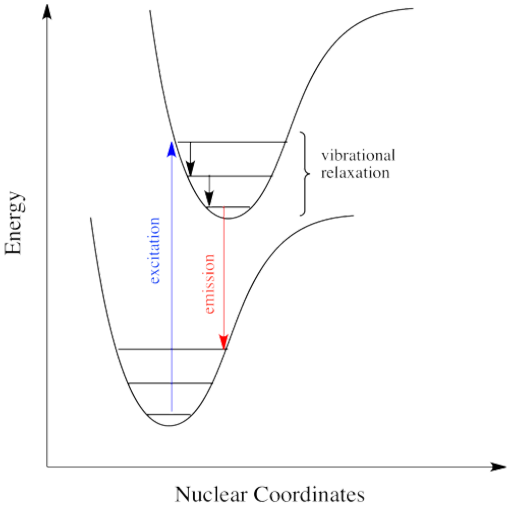
Sometimes, when an excited state species relaxes, giving off a photon, the wavelength of the photon is different from the one that initially led to excitation. When this happens, the photon is invariably red-shifted; its wavelength is longer than the initial one. This situation is called "fluorescence".



How can that be? Isn't energy quantized? How is the molecule suddenly taking a commission out of the energy the original photon brought with it? This discrepancy is related to the Franck-Condon principle from the previous page. When an electron is promoted to an electronic excited state, it often ends up in an excited vibrational state as well. Thus, some of the energy put into electronic excitation is immediately passed into vibrational energy. Vibrational energy, however, doesn't just travel in photons. It can be gained or lost through molecular collisions and heat transfer.



The electron might simply drop down again immediately; a photon would be emitted of exactly the same wavelength as the one that was previously absorbed. On the other hand, if the molecule relaxes into a lower vibrational state, some of that initial energy will have been lost as heat. When the electron relaxes, the distance back to the ground state is a little shorter. The photon that is emitted will have lower energy and longer wavelength than the initial one.



Just how does a molecule undergo vibrational relaxation? Vibrational energy is the energy used to lengthen or shorten bonds, or to widen or squeeze bond angles. Given a large enough molecule, some of this vibrational energy could be transferred into bond lengths and angles further away from the electronic transition. Otherwise, if the molecule is small, it may transfer some of its energy in collisions with other molecules.

Note

There are many examples of energy being transferred this way in everyday life. In a game of pool, one billiard ball can transfer its energy to another, sending it toward the pocket. Barry Bonds can transfer a considerable amount of energy through his bat into a baseball, sending it out of the park, just as Serena Williams can send a whole lot of energy whizzing back at her sister.

Exercise 1

How does the energy of an electronic absorption compare to other processes? To find out, you might consider the excitation of an entire mole of molecules, rather than a single molecule absorbing a single photon. Calculate the energy in kJ/mol for the following transitions.

a. absorbance at 180 nm (ultraviolet)

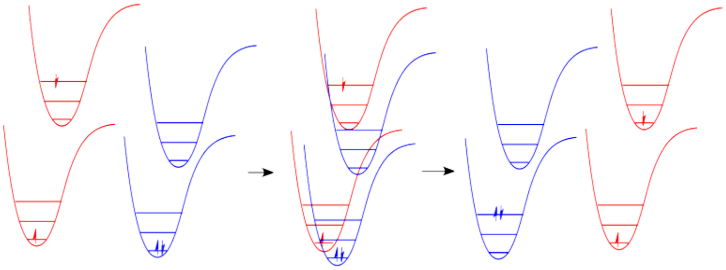
b. absorbance at 476 nm (blue)
c. absorbance at 645 nm (red)

? Exercise 2

How does the energy of an excitation between vibrational states compare to that of an electronic excitation? Typically, infrared absorptions are reported in cm^{-1}, which is simply what it looks like: the reciprocal of the wavelength in cm. Because wavelength and frequency are inversely related, wavenumbers are considered a frequency unit. Calculate the energy in kJ/mol for the following transitions.

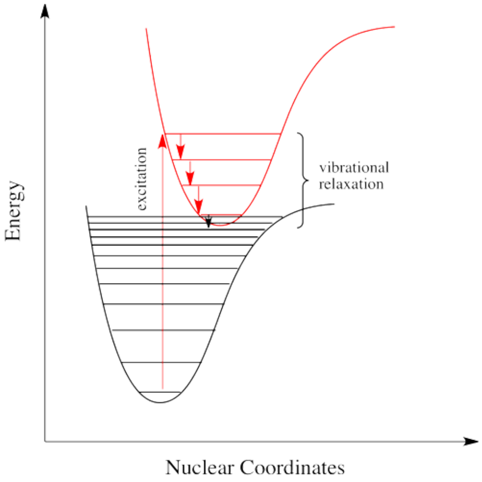
a. absorbance at 3105 cm^{-1}
b. absorbance at 1695 cm^{-1}
c. absorbance at 963 cm^{-1}

In molecules, as one molecule drops to a lower vibrational state, the other will hop up to a higher vibrational state with the energy it gains. In the drawing below, the red molecule is in an electronic excited and vibrational state. In a collision, it transfers some of its vibrational energy to the blue molecule. Energy can also be transferred from vibration to the kinetic energy of the molecules.



Radiationless Transitions: Internal Conversion

If electrons can get to a lower energy state, and give off a little energy at a time, by hopping down to lower and lower vibrational levels, do they need to give off a giant photon at all? Maybe they can relax all the way down to the ground state via vibrational relaxation. That is certainly the case. Given lots of vibrational energy levels, and an excited state that is low enough in energy so that some of its lower vibrational levels overlap with some of the higher vibrational levels of the ground state, the electron can hop over from one state to the other, without releasing a photon.



This event is called a "radiationless transition", because it occurs without release of a photon. The electron simply slides over from a low vibrational state of the excited electronic state to a high vibrational state of the electronic ground state. If the electron simply keeps dropping a vibrational level at a time back to the ground state, the process is called **"internal conversion"**.

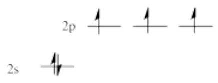
Internal conversion has an important consequence. Because the absorption of UV and visible light can result in energy transfer into vibrational states, much of the energy that is absorbed from these sources is converted into heat. That can be a good thing if you happen to be a marine iguana trying to warm up in the sun after a plunge in the icy Pacific. It can also be a tricky thing if you are a process chemist trying to scale up a photochemical reaction for commercial production of a pharmaceutical, because you have to make sure the system has adequate cooling available.

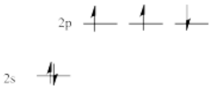
Radiationless Transitions: Intersystem Crossing

There is a very similar event, called "intersystem crossing", that leads to the electron getting caught between the excited state and the ground state. Just as, little by little, vibrational relaxation can lead the electron back onto the ground state energy surface, it can also lead the electron into states that are intermediate in energy.

For example, suppose an organic molecule undergoes electronic excitation. Generally, organic molecules have no unpaired electrons. Their ground states are singlet states. According to one of our selection rules for electronic excitation, the excited state must also have no unpaired electrons. In other words, the spin on the electron that gets excited is the same after excitation as it was before excitation.

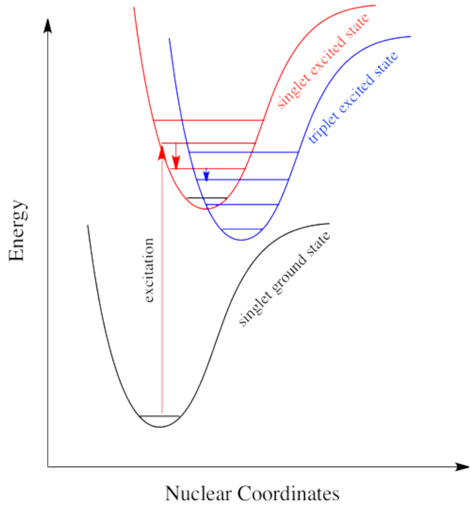
However, that's not the lowest possible energy state for that electron. When we think about atomic orbital filling, there is a rule that governs the spin on the electrons in degenerate orbitals: in the lowest energy state, **spin is maximized** (Hund's rule). In other words, when we draw a picture of the valence electron configuration of nitrogen, we show nitrogen's three p electrons each in its own orbital, with their spins parallel.





The picture with three unpaired electrons, all with parallel spins, shows a nitrogen in the quartet spin state. Having one of those spins point the other way would result in a different spin state. One pair of electrons in the p level would be spin-paired, one up and one down, even though they are in different p orbitals. That would leave one electron without an opposite partner. The nitrogen would be in a doublet spin state. That is not what happens. The spin state on the left is **lower** in energy than the state on the right. That's just one of the rules of quantum mechanics (**Hund's rule**): maximize spin when orbitals are singly occupied.

It's the same in a molecule with the triplet state lower in energy than the singlet state. Why didn't the electron get excited to the triplet state in the first place? That's against the rules. But sliding down vibrationally onto the triplet state from the singlet excited state is not, because it doesn't involve absorption of a photon.

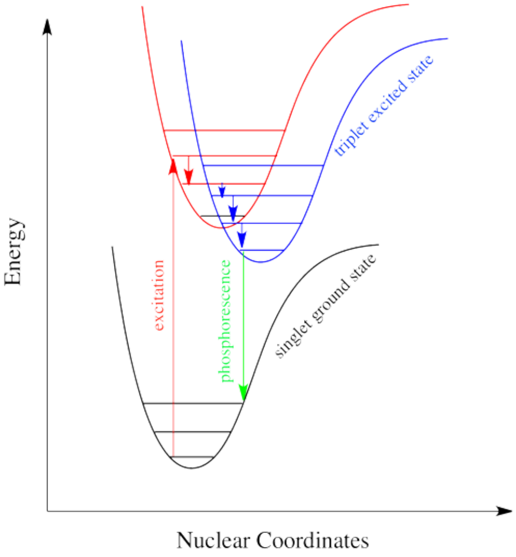


Intersystem crossing can have important consequences in reaction chemistry because it allows access to triplet states that are not normally available in many molecules. Because triplet states feature unpaired electrons, their reactivity is often high as would be typical for radicals. That means an added suite of reactions can be accessed via this process.

Phosphorescence: A Radiationless Transition Followed by Emission

Intersystem crossing is one way a system can end up in a triplet excited state. Even though this state is lower in energy than a singlet excited state, it cannot be accessed directly via electronic excitation because that would violate the spin selection rule

(\Delta S=0\). That's where the electron gets stuck, though. The quick way back down to the bottom is by emitting a photon, but because that would involve a change in spin state, it is not allowed. Realistically speaking, that means it takes a long time. By "a long time", we might mean a few seconds, several minutes, or possibly even hours. Eventually, the electron can drop back down, accompanied by the emission of a photon. This situation is called "phosphorescence".



Molecules that display phosphorescence are often incorporated into toys and shirts so that they will glow in the dark.

Contributors and Attributions

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14.8: Lasers

LASER is an acronym for Light Amplification by Stimulated Emission of Radiation. Laser is a type of light source which has the unique characteristics of directionality, brightness, and monochromaticity. The goal of this module is to explain how a laser operates (stimulated or spontaneous emission), describe important components, and give some examples of types of lasers and their applications.

Introduction

The word LASER is an acronym for Light Amplification by Stimulated Emission of Radiation. In 1916, Albert Einstein discovered the physical principle responsible for this amplification, and the foundation principle is called stimulated emission. It was widely accepted at that time that laser would represent a big leap in science and technology, even before Theodore H. Maiman built the first one in 1960. The 1951 Nobel Prize in physics was shared by Charles H. Townes, Nokolay Basov, and Aleksandr Prokhorov, in citation, “For Fundamental work in the field of quantum electronics, which has led to the construction of oscillator and amplifiers based on the maser-laser principle”.

The early lasers developed in the 1950s by Charles H. Townes and Arthur Shawlow were gas and solid-state lasers for use in spectroscopy. The principles of lasers were adapted from masers. MASER is an acronym that stands for Microwave Amplification by Stimulated Emission of Radiation. It uses the idea of stimulated emission and population inversion to produce a coherent amplified radiation of light in the microwave region. Stimulated emission is when an electron in an excited state falls back to ground state after absorbing energy from an incident photon. Amplified radiation or light is produced with the same direction and energy as the incident light. Population inversion is when you have a greater population of electrons in the excited state than in ground state. Population inversion is achieved through various pumping mechanisms. The laser uses these same ideas except that the electromagnetic wave created is in the visible light region. When emission begins the light oscillates within the resonant cavity and gains magnitude. Once enough light has been acquired, the laser beam is produced. This allows lasers to be used as a powerful light source. Three unique characteristics of a laser are its properties of monochromaticity, directionality, and brightness.

The monochromaticity of lasers is due to the fact that lasers are highly selective in the wavelength of light produced, which in itself is due to the resonant frequency inside the active material. Resonant frequency means that the light is oscillating in a single mode creating a monochromatic beam of light. The property of directionality depends on the angle of which the light propagates out of the source. Since lasers have large spatial and temporal coherence directionality is maximized. Temporal coherence is when there are small fluctuations in the phase. Spatial coherence has small changes in the amplitude of the emitted light. Like monochromaticity, directionality is dependent on the resonant cavity of the active material. The property of brightness is a result of the directionality and the coherence of the light. Due to these properties, lasers today are used in simple laser pointers, cutting devices, the development of military technologies, spectroscopy, and medical treatments. Their direct application to spectroscopy has allowed scientists to measure lifetimes of excited state molecules, structural analysis, probing far regions of the atmosphere, photochemistry and their use as ionization sources.

History

One of the most important characteristics of light is that it has wave-like properties and that it is an electromagnetic wave. Experiments on the blackbody radiation demonstrated a comprehensive idea of emission and absorption of electromagnetic waves. In 1900, Max Plank developed the theory that electromagnetic waves can only exist in distinct quantities of energy, which are directly proportional to a given frequency (ν). In 1905, Albert Einstein proposed the dual nature of light, having both wave-like and particle-like properties. He used the photoelectric effect to show that light acts as a particle, with energy inversely proportional to the wavelength of light. This is important, because the number of particles is directly related to how intense a light beam will be. In 1915, Einstein introduced the idea of stimulated emission- a key concept to lasers.

In 1957, Townes and Shawlow proposed the concept of lasers in the infrared and optical region by adapting the concept of masers to produce monochromatic and coherent radiation. In 1953, Townes was the first to build a maser with an ammonia gas source. Masers use stimulated emission to generate microwaves. Townes and other scientists wanted to develop the optical maser to generate light. Optical masers would soon adopt the name LASER: Light Amplification by Stimulated Emission of Radiation. An optical maser would need more energy than what can be provided by microwave frequencies and a resonant cavity of the order of 1μm or less. Townes and Shawlow proposed the use of a Fabry-Pérot interferometer equipped with parallel mirrors, where Interference of radiation which is traveling back and forth between parallel mirrors in the cavity allowed for selection of certain wavelengths. Townes built an optical maser with potassium gas. That failed because the mirrors degraded over time. In 1957, Gordon Gould improved upon Townes' and Shawlow's laser concept. It was Gould who renamed the optical maser to laser. In April 1959, Gould filed a patent for the laser and later in March 1960, Townes and Shawlow had also made a request for a patent. Since Gould's notebook was officially dated the idea was his first, but he did not receive the patent until 1977.

Components

A laser consists of three main components: a lasing medium, a resonant or optical cavity, and an output coupler. The lasing medium consists of a group of atoms, molecules , or ions in solid, liquid or gaseous form, which acts as an amplifier for light waves. For amplification, the medium has to achieve population inversion, which means in a state in which the number of atoms in the upper energy level is greater than the number of atoms in the lower energy level. The output coupler serves as energy source which provides for obtaining such a state of population inversion between a pair of energy levels of the atomic system. When the active medium is placed inside an optical resonator, the system acts as an oscillator.

Figure 1. Diagram of a typical laser, showing the three major parts.

Lasing Medium

The lasing medium is the component used to achieve lasing, such as chromium in the aluminum oxide crystal-found in a ruby laser. Helium and neon gas are two materials most commonly used in gas lasers. These are only a few examples of lasing mediums or materials that have been used in the past and present states of the laser. For further information about different types of lasing mediums please refer to the section where *Types of Lasers* is discussed.

Optical Cavity and Output Coupler

Rays of light moving along an optical path tend to diverge over time, because the energy of radiation has very high frequency. Therefore an optical cavity is needed to refocus the light. **Figure 1**, represents the basics of an optical cavity where the light inside moves back and forth between two mirrors. These redirect and focus the light each time it hits the surface of the mirrors. There are two types of cavities: stable cavities and unstable cavities. A stable cavity is when the ray of light does not diverge far from the optical axis. An unstable cavity is when the ray of light bounces off and away from a mirrors surface. The importance of the cavities is that it allows for the laser to have properties of directionality, monochromaticity and brightness.

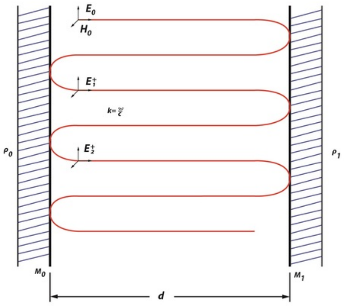

Figure 2. an optical cavity where the light inside moves back and forth between two mirrors

Light oscillating between the first mirror (M_o) and the second mirror (M_1) separated by distance, d, will have a round-trip phase shift (RTPS) of 2θ=2kd=q2π- ϕ. In **Figure 1**, a round-trip can be described as the beam traveling from M_o to M_1back to M_o. Resonance occurs in the cavity because the light propagating between the two mirrors is uniform. The ABCD law describes that an optical cavity has a field distribution, because it reproduces itself as it is making these round-trips between the two parallel mirrors. The ABCD law was first applied to a Gaussian beam with a beam parameter, q, which is described as

$$q_2 = \frac{(Aq_1 + B)}{(Cq_1 + D)}$$

This law states that the beam, which is oscillating through an optical system, will experience some changing as it moves in the cavity. Fields that are created in an optical cavity have analogous shape and phase as they make each trip back and forth. However, the one thing that changes is the size of the field because the electromagnetic wave is unrestricted, unlike a wave in a short-circuited coaxial cable used to build a resonator or a microwave cavity mode. Since there is a field distribution of $E_o$at the surface of $M_{o,}$ it can be said that there is a field distribution at the surface of M_1. Since there will be a change in size of the field this means that the electromagnetic wave will have change in amplitude by ρ_0*ρ_1 and a phase factor of e^-jk2d, creating additional fields.

This is an example of a phasorial addition of all fields between M_o and $M_{1,}$ creating a total field E_T (**Figure 2**). Phasorial addition is described by RTPS, where each additional E_n will have a delay of angle ϕ which is related to kd.

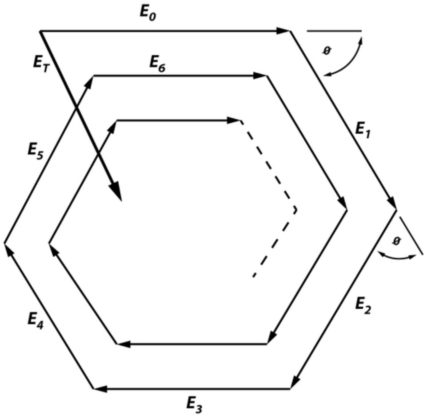

Figure 3. Totle field E_T

E_T will always be greater than $E_o$only if ρ_0 and $\rho_1$are not greater than 1 and ϕ=0. In this case, when ϕ=0 resonance is enhanced because all factors such as E_T travelling between M_o and M_1, the intensity of the electromagnetic waves, number of photons traveling between $M_o$and $M_{1,}$ and the amount of energy that is stored are maximized. The resonant wavelength can also be determined by using the relationship between RTPS, and because

$$k = \frac{\omega n}{c} = \frac{2\pi}{\lambda}$$

Using $2\theta = 2kd = q2\pi$

$$\frac{2\pi 2d}{\lambda} = q2\pi$$

$$d = \frac{q\lambda}{2}$$

Where the wavelength of interest is given by $\lambda = \lambda_0/n$, where n is the index of refraction and λ_0 is the free-space wavelength .

Since we are dealing with light as a wave, the light in the resonant cavity can be described in terms of frequency, ν. Where

$$k2d = \omega \frac{2nd}{c} = 2\pi\nu \frac{2nd}{c} = q(2\pi)$$

$$\nu = q\frac{c}{2nd}$$

A Fabry-Pérot interferometer is a prime example of an optical cavity used in a laser. The Fabry-Pérot is equipped with two parallel mirrors, one that is completely reflective and the other that is partially reflective. As light is accumulating in the cavity after taking several round trips between the two mirrors, some light is transmitted through the partially reflective mirror and a laser beam is produced. The beam can be in pulsed mode or continuous-wave (CW) mode. To increase the performance of the resonant cavity, the length of the cavity (d) must be considered as a way to avoid a decrease in the laser beam intensity due to any diffraction losses. The size of the aperture of the cavity is also important because it determines the strength or the intensity of the laser beam. In fact, determining the best length of a resonant cavity will enhance the coupling conditions of the output coupler by producing a frequency that is stable, which ultimately generates a laser beam that is coherent and has high power.

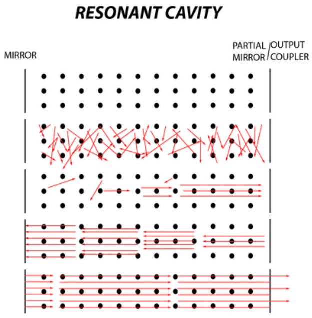

Figure 4. The first stage shows that all molecules present are in the ground state since there is no excitation energy present in the cavity. In the second stage, molecules become excited causing spontaneous emission of photons. In the third stage, photons collide with excited molecules causing an amplification of the light. This results in stimulated emission where the photon that is released has the same energy and direction of the photon that created it. Last is the fourth stage, where stimulated emission causes amplification of the light, and those photons that are traveling parallel to the cavities axis will hit one of the parallel mirrors and will be reflected back along the same axis. As the light is building up from the back and forth movement from one mirror to another, some of the light will pass through the partial mirror or the output coupler as a beam of rays. The remaining light in the cavity will continue producing more photons as long as there is a population inversion.

There are essentially six stages in the lasing process. First is the ground state where there is no excitation of the lasing medium. Second is pumping, which is applied to the medium where spontaneous emission occurs. Then the third stage is when emitted photons collide with an excited molecule where stimulated emission occurs. In the fourth stage the photons are produced in multiples, however those moving parallel in the cavity will hit a mirror and then hit the second mirror. During the fifth stage this process continues until there is an accumulation of light that is coherent and of a specific frequency. Finally, the sixth stage is when the light or laser beam exits the partially reflective mirror which is also known as the output coupler. An output coupler is the last important component of a laser because it must be efficient to produce an output of light with maximum intensity. If the output coupler is too transparent than there is much more loss of electromagnetic waves and this will decrease lasing significantly because population inversion will no longer be maintained. If the output coupler or partially reflective mirror is too reflective, then all the accumulated light that is built up in the resonant cavity will be trapped in the cavity. The beam will not pass through the output coupler, producing little to no light making the laser ineffective.

Emission

Lasers create a high energy beam of light by stimulated emission or spontaneous emission. Within in a molecule there are discrete energy levels. A simple molecular description has a low energy ground state (E_1) and a high energy excited state (E_2). When an electromagnetic wave, referred to as the incident light, irradiates a molecule there are two processes that can occur: absorption and stimulated emission.

Absorption occurs when the energy of the incident light matches the energy difference between the ground and excited state, causing the population in the ground state to be promoted to the excited state. The rate of absorption is given by the equation:

$$\frac{dN_1}{dt} = -W_{12}N_1$$

Where N_1 is the population in $E_{1,}$ and W_{12} is the probability of this transition. The probability of the transition can also be related to the photon flux (intensity of incident light):

$$W_{12} = \sigma_{12}F$$

Where F is the photon flux and σ_{12} is the cross section of the transition with units of area. When absorption occurs photons are removed from the incident light and the intensity of the light is decreased.

Stimulated emission is the reverse of absorption. Stimulated emission has two main requirements: there must be population in the excited state and the energy of the incident light must match the difference between the excited and ground state. When these two requirements are met, population from the excited state will move to the ground energy level. During this process a photon is emitted with the same energy and direction as the incident light. Unlike absorption, stimulated emission adds to the intensity of the incident light. The rate for stimulated emission is similar to the rate of absorption, except that it uses the population of the higher energy level:

$$W_{21} = \sigma_{21}F$$

Like absorption the probability of the transition is related to the photon flux of the incident light through the equation:

$$\frac{dN_2}{dt} = -W_{21}N_2$$

When absorption and stimulated emission occur simultaneously in a system the photon flux of the incident light can increase or decrease. The change in the photon flux is a combination of the rate equations for absorption and stimulated emission. This is given by the equation:

$$dF = \sigma F(N_2 - N_1)d\tau$$

Spontaneous emission has the same characteristics as stimulated emission except that no incident light is required to cause the transition from the excited to ground state. Population in the excited state is unstable and will decay to the ground state through several processes. Most decays involve non-radiative vibrational relaxation, but some molecules will decay while emitting a photon matching the energy of the energy difference between the two states. The rate of spontaneous emission is given by:

$$\frac{dN_2}{dt} = -AN_2$$

Where A is the spontaneous emission probability which depends on the transition involved. The coefficient A is an Einstein coefficient obtained from the spontaneous emission lifetime. Since spontaneous emission is not competing with absorption, the photon flux is based solely on the rate of spontaneous emission.

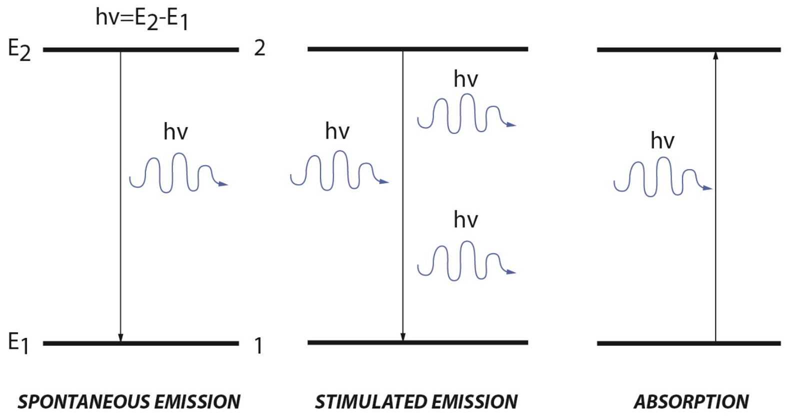

Figure 5. Diagram of spontaneous emission, stimulated emission and absorption in a two energy level system

The population ratio of a molecule or atom is found using the Boltzmann distribution and the energy of the ground state (E_1) and the excited state (E_2):

$$\frac{N_2}{N_1} = e^{\frac{-(E_2 - E_1)}{kT}}$$

Under normal conditions, the majority, if not all, of the population is in the lower energy level (E_1). This is because the energy of the excited is greater than the ground state. Normal thermal energy available (kT) is not enough to overcome the difference, and the ratio of population favors the ground state. For example, if the difference in energy between two states absorbes light at 500nm, the ratio of N_1 to N_2 is $5.1\text{x}10^{41}$:1. The photon flux of the incident light is directly proportional to the difference in populations. Since the ground state has more populations, the photon flux decreases: there is more absorption occurring than stimulated emission. In order to increase the photon flux there must be more population in the excited state than in the ground state, generally known as a population inversion.

In a two level energy system it is impossible to create the population inversion needed for a laser. Instead three or four level energy systems are generally used (**Figure 5**).

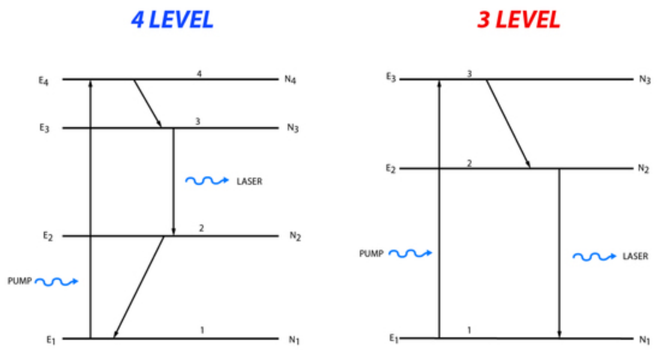

Figure 6. Three and four level energy system

Three level processes involve pumping of population from the lowest energy level to the highest, third energy state. The population can then decay down to the second energy level or back down to the first energy level. The population that makes it to the second energy level is available for stimulated emission. Light matching the energy difference between the second and first energy level will cause a stimulated emission. Four level systems follow roughly the same process except that population is moved from the lowest state to the highest fourth level. Then it decays to the third level and lasing happens when the incident light matches the energy between the third and second level. After lasing there is decay to the first level.

Pumping Process

Pumping is the movement of population from the ground state to a higher excited state. The general rate at which this is done is given by:

$$(\frac{dN_g}{dt})_p = W_p N_g$$

Where N_g is the population in the ground level and W_p is the pump rate. Pumping can be done optically, electronically, chemically (see chemical laser), using gases at high flow rates, and nuclear fission. Only optical and electrical pumping will be discussed in detail.

Optical Pumping

Optical pumping uses light to create the necessary population inversion for a laser. Usually high pressure xenon or krypton lamps are used to excite solid or liquid laser systems. The active material in the laser absorbs the light from the pump lamp, promoting the population from the ground state to the higher energy state. The material used in the laser can be continuously exposed to the pumping light which creates a continuous wave laser (CW). A pulsed laser can be created by using flashes of pumping light.

In optical pumping there are three types of efficiency: transfer, lamp radiative, and pump quantum efficiency. Transfer efficiency is the ratio of the energy created by the lamp and the power of the light emitted by the laser. The lamp radiative efficiency is the measure of how much electrical power is converted into light in the optical lamp. Pump quantum efficiency accounts for the ratio of population that decays to the correct energy level and population that decays either back to the ground state or another incorrect energy level. For example, the overall pumping rate of the first ruby laser was around 1.1%.

The average pump rate for optical pumping depends on the total efficiency of the pump (η_p), volume of the laser material (V), ground state population (N_g), power input (P), and frequency of the lasing transition (ν_0):

$$\langle W_p \rangle = \eta_p (P/(V N_g \hbar \upsilon_0))$$

Electrical Pumping

Electrical pumping is a much more complicated process than optical pumping. Usually used for gas and semiconducting lasers, electrical pumping uses electrical current to excite and promote the ground state population. In a simple gas laser that contains only one species (A), current passes through the gas medium and creates electrons that collide with the gas molecules to produce excited state molecules (A^*):

$$A + e \longrightarrow A^* + e$$

During electron impact either an ion or an excited state can be created. The ability to make the excited state depends mostly on the material used in the laser and not the electrical pumping source making it difficult to describe the efficiency of the pumping. Total efficiencies have been calculated and tabulated for most active materials used in electrical pumping. Where eficiencies range from a < 0.1% N_2 gas laser to 70% for some CO_2 gas lasers.

Like the pumping rate of optical pumps, the rate of electrical pumping is found using the overall efficiency of the pump, power applied, and population of the ground state. However instead of using the frequency of the ground to upper state transition, electrical pumping uses the energy of the upper state ($\hbar\omega_p$) and the volume of the electron discharge (V):

$$\langle W_p \rangle = \eta_p (P/(V N_g \hbar\omega_p))$$

Pulsed operation

Q-Switching

The technique of Q switching allows the generation of laser pulses of short duration from a few nanoseconds to a few tens of nanoseconds and high peak power from a few megawatts to a few tens of megawatts.

Suggest we put a shutter into the laser cavity. If the shutter is closed, laser action cannot occur and the population inversion can be very high. If the shutter is opened suddenly, the stored energy will be released in a short and intense light pulse. This technique is known as Q-switching. Q here denotes the ratio of the energy stored to the energy dissipated in the cavity. This technique is used in many types of solid-stat lasers and CO_2 lasers to get a high-power pulsed output.

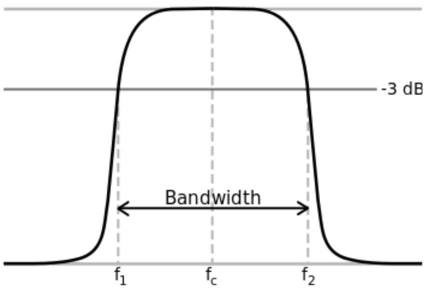

Figure 7. The bandwidth, Δf , or f1 to f2, of a damped oscillator is shown on a graph of energy versus frequency. The Q factor of the damped oscillator, or filter, is $f_c/\Delta f$. The higher the Q, the narrower and 'sharper' the peak is.

To produce high inversion required for Q-switching, four requirements must be satisfied.

1. The lifetime of the upper level must be longer than cavity buildup time.
2. The pumping flux duration must be longer than the cavity build up time.
3. The initial cavity losses must be high enough during the pumping duration to prevent oscillation occurring.
4. The cavity losses must be reduced instantaneously.

Mode-Locking

The technique of mode locking allows the generation of laser pulses of ultrashort duration from less than a picosecond to femtoseconds and very high peak, a few gigawatts.

Mode-locking is achieved by inducing the different longitudinal modes of a laser to a locked mode. When combining the electromagnetic waves modes with different frequencies and random phases, they produce a random and average output. When the modes are added in phase, they combine to produce a total amplitude and intensity output with a repeated pulse.

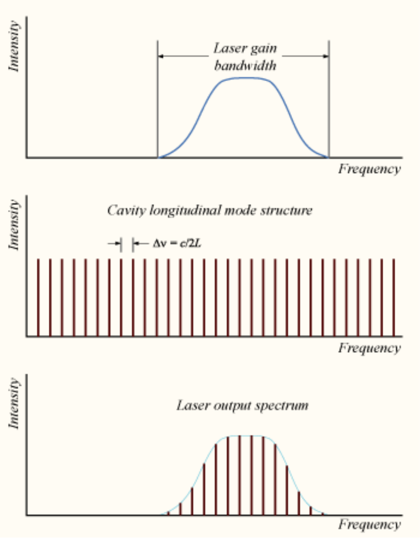

FIgure 8:Laser mode structure

Types of Lasers

There are many different types of lasers with a wide range applications, and below is a brief description of some of the main types.

Solid State Lasers

A solid-state laser is one that uses a solid active medium generally in a rod shape. Inside the active material is a dopant that acts as the light emitting source. Optical pumping is used to create population inversion of the active material. Solid-state lasers generally use stimulated emission as the mechanism for creating the high energy beam.

Ruby Laser

The ruby laser was the first operating laser and was built in 1960. It has a three-level (**Figure 6**) energy system that uses aluminum oxide with some of the aluminum atom replaced with chromium as its active material. The chromium in the aluminum oxide crystal is the active part of the laser. Electrons in the ground state of chromium absorb the incident light and become promoted to higher energy states. The short lived excited state relaxes down to a metastable state with a longer lifetime. Laser emission happens when there is relaxation from the metastable state back to the ground state.

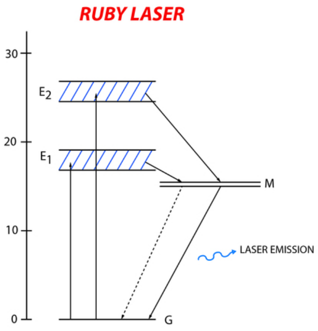

Figure 9. Schematic of Ruby laser

A xenon flash lamp emitting light at wavelengths of 6600Å and 4000Å (matching the energy needed to excite the chromium atoms). In order to create resonance of the incident light in the active material silver platting was put at both ends of the ruby rod. One end was completely covered while the other end was partially covered so lasing light could exit the system.

Nd: YAG Laser

Nd: YAG laser are the most popular type of solid state laser. The laser medium is a crystal of $Y_3Al_5O_{12}$ which are commonly called YAG, an acronym for yttrium aluminum garnet. A simplified energy-level scheme for Nd:YAG is shown in Fig. 9. The λ=1.06 μm laser transition is the strongest of the $4F_{3/2} \rightarrow 4I_{11/2}$ transitions.

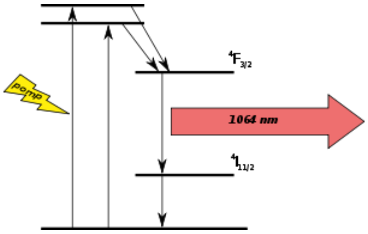

Figure 10. Simplified energy level diagram of the$^4F_{3/2}$---4I$_{11/2}$ laser transition in Nd:YAG showing the four- level nature of the system

The major application of the Nd laser is in various form of material processing: drilling, spot welding, and laser marking. Because they can be focused to a very small spot, the laser are also used in resistor trimming and in circuit mask , memory repair and also in cutting out specialized circuits. Medical applications include many types of surgeries. Many medical applications take advantage of low-loss optical fiber delivery systems that can be inserted into the body to wherever is needed. Nd lasers are also used in military applications such as range finding and target designation. High power pilsed versions are also used for X-ray spectral regions. In addition, Nd lasers are used in scientific lab as good sources for pumping dye laser and other types of lasers.

Semiconductor Laser

The semiconductor laser is another type of solid state laser that uses a semiconducting material like germanium or silicon. When the temperature of the semiconducting material is increased, electrons move from the valence band to the conducting band creating holes in the valence band (**Figure 7**). In between the conducting band and valence band is a region where there are no energy levels, called the band gap. Applying a voltage to the semiconductor causes electrons to move to the conduction band creating a population inversion. Irradiating a semiconductor with incident light matching the energy of the forbidden area causes a large transition from the conduction band to the valence band, increasing and amplifying the incident light.

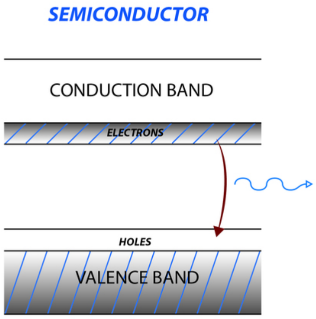

Figure 11. Schematic of semicondecor laser

Gas Lasers

A gas laser contains active material composed of a mixture of gases with similar energy states inside a small gas chamber. Electrical pumping is used to create the population inversion where one gas is excited through collisions with electrons and in turn excites the other gas through collisions.

Helium-Neon Laser

The helium-neon laser was the first gas laser. It consists of a long narrow tube that contains He and Ne gas. Mirrors are placed at both ends of the gas tube to form the resonant cavity with one of the mirrors partially reflecting the incident light. Stimulated emission of the gas mixture is carried out by first exciting the He gas to a higher energy state through electron collision with electrons from the electronic pumping source (electrical pumping). Then the excited He atoms collide with the Ne atoms transferring their energy and exciting them to a higher energy level. The Ne atoms in the higher energy level will then relax to a lower metastable energy state. Lasing occurs when there is relaxation from the metastable state to a lower energy state causing spontaneous emission. The Ne gas then returns to the ground state when it collides with the outer walls of the gas tube (**Figure 8**).

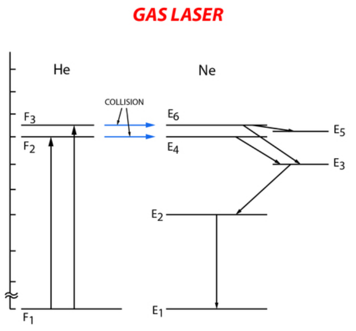

Figure 12. Schematic of gas laser

Carbon Dioxide Laser

The carbon dioxide laser is a gas laser that uses the energy difference between rotational-vibrational energy levels. Within the vibrational levels of CO_2 there are rotational sub-energy levels. A mixture of N_2 and CO_2 gas are placed inside a chamber. The N_2 atoms are excited through an electrical pumping mechanism. The excited atoms then collide with the CO_2 atoms transfer energy. This transfer of energy causes the CO_2 to go into a higher vibrational level. The excited CO_2 molecules then go through spontaneous emission when they are relaxed to lower rotational-vibrational levels increasing the signal of the incident light (**Figure 9**). Carbon dioxide lasers are extremely efficient, around 70%, and powerful compared to other gas lasers making them useful for welding and cutting.

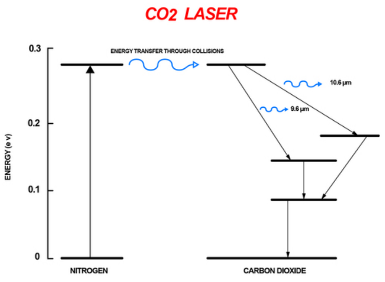

Figure 13. Schematic of carbondioxide laser

Liquid Lasers

Liquid lasers consist of a liquid active material usually composed of an organic dye compound. The most common type of liquid laser uses rhodamine 6G (**Figure 10**) dye mixed with alcohol and is excited by different types of lasers, such as an argon-ion laser or a nitrogen laser. Organic dyes are large compounds that have absorption bands in the UV or visible region with a strong intense fluorescence spectrum. The free π electrons of the dye are excited using an optical pumping source and the transition from the S_1 to the S_0 state creates the lasing light (see Jablonski diagrams). Liquids are generally used because they can easily be tuned to emit a certain wavelength by changing the resonant frequency within the cavity. Wavelengths from the visible to the infrared can be covered. There are many benefits of liquid lasers, some include that they can be cooled in a relative amount of time, they cannot be damaged unlike a solid-laser, and their production is cost-effective. The efficiency of liquid lasers is low because the lifetime of the excited state is relatively short; there are many non-radiative decay processes, and the material degrades over time. Liquid lasers tend to be used only as a pulse laser when tunability is required. Liquid lasers can be used for high-resolution spectroscopy since they are easily tuned over a wide range of wavelengths. They can also be used because they have concentrations which are manageable when dissolved in solids or other liquids.

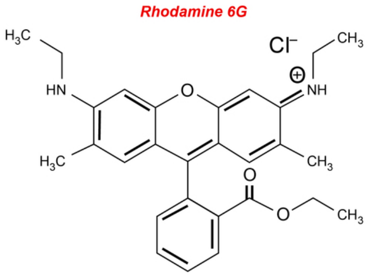

Figure 14. Rhodamine 6G molecule

Chemical Lasers

Chemical lasers are different from other lasers because the population inversion is the direct product of a chemical reaction when energy is released as a result of an exothermic reaction. Usually reactions involve gases where the energy created is used to make vibrationally excited molecules. Light used for lasing is then created from vibrational-rotational relaxation like in the CO_2 gas laser. An example of a chemical laser is the HF gas laser. Inside the gas chamber fluorine and hydrogen react to form an excited HF molecule:

$F + H_2 \rightarrow HF + H$

The excess energy from the reaction allows HF to stay in its excited state. As it relaxes, light is emitted through spontaneous emission. Deuterium can also be used in place of hydrogen. Deterium fluoride is useds for applications that require high-power. For example, MIRACL was built for military research and was known to produce 2.2 megawatts of power. The uniqueness of a chemical laser is that the power required for lasing is produced in the reaction itself.

Laser Applications

The applications of lasers are numerous and cover scientific and technological fields. In general, these applications are a direct consequence of the special characteristics of lasers. Below are a few examples of the laser applications, for a complete list please go to en.Wikipedia.org/wiki/List_of...ons_for_lasers

Lidar

Lidar is short for light detection and ranging which is an optical remote sensing technology can be used for monitoring the environment. A typical lidar system involves a transmitter of laser radiation and a receiver for the detection and analysis of backscattered light. A beam expander is usually used at transmitter to reduce divergence of the laser beam before it propagates into the atmosphere. The receiver includes a wavelength filter, a photo detector, and computers and electronics for data acquisition and analysis.

Lidar system dates back to the 1930, because of the laser, it has become one of the primary tools in atmospheric and environmental research. Other than that, Lidar has been put into various uses. In agriculture, lidar can be used to create topographic map to help farmer to decide appropriate amount of fertilizing to achieve a better crop yield. In Archaeology, lidar can be used to create a geographic information system to help archaeologists to find sites. In transportation, lidar has been used in autonomous cruise control system to prevent road accident and policemen are also using lidar speed gun to enforce the speed limit regulation.

Laser in Material Processing

The beam of a laser is usually a few millimeters in diagram. For most material processing applications, lenses are used to increase the intensity of the beam. The beam from a laser is either plane or spherical. After passing through a lens, the beam should get focused to a point. But in actual practice, diffraction effects have to be taken into consideration, the incoming will focus into a region of radius. If λ is the wavelength of the laser light, a is the radius of the beam, and f is the focal length of the lens, then the radius of the region is

$$b = \frac{\lambda f}{a}$$

If P represents the power of the laser beam, the intensity I, obtained at the focused region would be given by,

$$I=\frac{P}{\pi b^2}=\frac{Pa^2}{\pi\pi\lambda^2 f^2}$$

The high-power (P>100w) laser are widely used in material processing such as welding, drilling, cutting, surface treatment, and alloying. The main advantage of the laser beam can be summarized as follow: (1) The heating produced by the laser is less than that in conventional process. Material distortion is considerably reduced. (2) Possibility of working in inaccessible region. Any region which can be seen can be processed by a laser. (3) The process can be better controlled and easily automatized. However, against all these advantages, the disadvantages are: (1) high cost of the laser system. (2) Reliability and reproducibility problems of the laser system. (3) Safety problems.

Laser in Medicine

In field of medicine, the major use of lasers is for surgery such as laser eye surgery commonly known as LASIK. Besides that, there are also a few diagnosetic applications such as clinical use of flow microfluormeters, Doppler velocimetry to measure the blood velocity, laser fluorescence bronchoscope to detect tumors in their early phase.

For surgery, the laser beams are used instead of a conventional scalpel. The infrared beam from the CO^2 laser is strongly absorbed by water molecules in the tissue. It produces a rapid evaporation of these molecules, consequently cutting the tissue. The main advantage of laser beam surgery can be summarized as follows: (1) High precision. The incision can be made with a high precision particularly when the beam is directed by means of a microscope. (2) Possibility of operating in inaccessible region. Laser surgery can be operated in any region of the body which can be observed by means of an optical system. (4) Limited damage to blood vessel and adjacent tissue. However, the disadvantages are: (1) considerable cost. (2) Smaller velocity of the laser scalpel. (3) Reliability and safety problems associated with the laser procedure.

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Outside Links

- http://en.Wikipedia.org/wiki/Laser
- en.Wikipedia.org/wiki/List_of_laser_types
- en.Wikipedia.org/wiki/Q_factor
- en.Wikipedia.org/wiki/Mode-locking

Problems

1. Determine the free-space wavelength (λ_0) in Å, and frequency of the resonant cavity for a beam parameter q_1 that is 632,110 and q_2 that is 632,111 in a helium-neon gas laser at 1 atm. The index of refraction n is 1.00, the length of the resonant cavity is 20 cm and the wavelength region of interest is 6328Å.
2. What wavelength of light will be released by the spontaneous emission of Ne gas, where the the energy difference between the excited and ground state is 9.9×10^{-19} J.
3. What is the population ratio of the above question at 300K.

Answers

1. For q_1 $\lambda_0 = 6328.0125$\angstromÅ, q_2 $\lambda_0 = 6328.0025$\angstromÅ, and v=474 THz for both q values
2. 200 nm
3. N_2/N_1=1.9 x 10^{-105}

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14.9: Optical Rotatory Dispersion and Circular Dichroism

Circular Dichroism, an absorption spectroscopy, uses circularly polarized light to investigate structural aspects of optically active chiral media. It is mostly used to study biological molecules, their structure, and interactions with metals and other molecules.

Introduction

Circular Dichroism (CD) is an absorption spectroscopy method based on the differential absorption of left and right circularly polarized light. Optically active chiral molecules will preferentially absorb one direction of the circularly polarized light. The difference in absorption of the left and right circularly polarized light can be measured and quantified. UV CD is used to determine aspects of protein secondary structure. Vibrational CD, IR CD, is used to study the structure of small organic molecules, proteins and DNA. UV/Vis CD investigates charge transfer transitions in metal-protein complexes.

Circular Polarization of Light

Electromagnetic radiation consists of oscillating electric and magnetic fields perpendicular to each other and the direction of propagation. Most light sources emit waves where these fields oscillate in all directions perpendicular to the propagation vector. Linear polarized light occurs when the electric field vector oscillates in only one plane. In circularly polarized light, the electric field vector rotates around the propagation axis maintaining a constant magnitude. When looked at down the axis of propagation the vector appears to trace a circle over the period of one wave frequency (one full rotation occurs in the distance equal to the wavelength). In linear polarized light the direction of the vector stays constant and the magnitude oscillates. In circularly polarized light the magnitude stays constant while the direction oscillates.

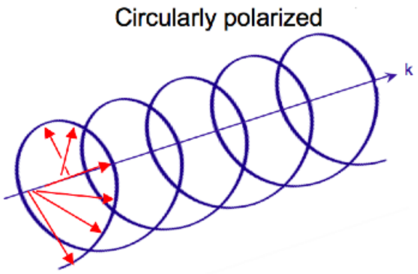

Figure 1: Diagram of linearly polarized and circularly polarized light

As the radiation propagates the electric field vector traces out a helix. The magnetic field vector is out of phase with the electric field vector by a quarter turn. When traced together the vectors form a double helix.

Light can be circularly polarized in two directions: left and right. If the vector rotates counterclockwise when the observer looks down the axis of propagation, the light is left circularly polarized (LCP). If it rotates clockwise, it is right circularly polarized (RCP). If LCP and RCP of the same amplitude, they are superimposed on one another and the resulting wave will be linearly polarized.

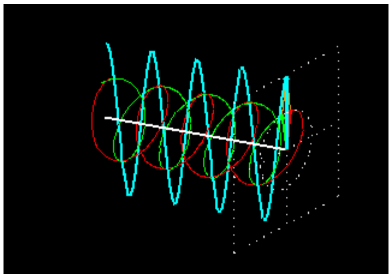

Figure 2: The superposition of LCP and RCP light of the same amplitude produces linearly polarized light

Interaction with Matter

As with linear polarized light, circularly polarized light can be absorbed by a medium. An optically active chiral compound will absorb the two directions of circularly polarized light by different amounts

$$\Delta A = A_l - A_r \tag{14.9.1}$$

This can be extended to the Beer-Lambert Law. The molar absorpitivty of a medium will be different for LCP and RCP. The Beer-Lambert Law can be rewritten as

$$A = (\varepsilon_l - \varepsilon_r)cl \tag{14.9.2}$$

The difference in molar absorptivity is also known as the molar circular dichroism

$$\Delta\varepsilon = \varepsilon_l - \varepsilon_r \tag{14.9.3}$$

The molar circular dichroism is not only wavelength dependent but also depends on the absorbing molecules conformation, which can make it a function of concentration, temperature, and chemical environment.

Any absorption of light results in a change in amplitude of the incident wave; absorption changes the intensity of the light and intensity of the square of the amplitude. In a chiral medium the molar absorptivities of LCP and RCP light are different so they will be absorbed by the medium in different amounts. This differential absorption results in the LCP and RCP having different amplitudes which means the superimposed light is no longer linearly polarized. The resulting wave is elliptically polarized.

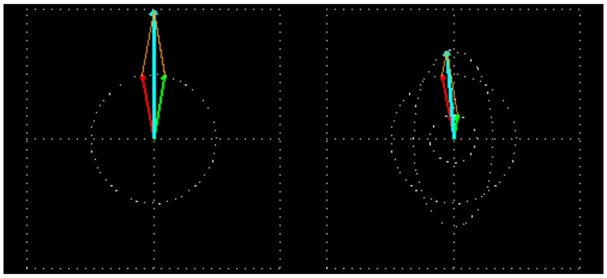

Figure 3: The diagrams of the superposition of LCP and RCP light when viewed down the axis of propagation. On the left the two circular waves (red and green) have the same amplitude which produces linearly polarized light (blue). On the right the LCP (red) has a larger amplitude than the RCP (green), the superposition of the two waves (blue) forms an ellipse.

Molar Ellipticity

The CD spectrum is often reported in degrees of ellipticity, θ, which is a measure of the ellipticity of the polarization given by:

$$tan\theta = \frac{E_l - E_r}{E_l + E_r} \tag{14.9.4}$$

where E is the magnitude of the electric field vector.

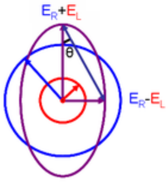

Figure 4: Elliptically polarized light (purple) is the superposition of LCP (red) and RCP (blue) light. θ is the angle between the magnitude of the electric field vector at its maximum and its minimum

The change in polarization is usually small and the signal is often measured in radians where $\theta = \frac{2.303}{4}(A_l - A_r)$ and is a function of wavelength. θ can be converted to degrees by multiplying by $\frac{180}{\pi}$ which gives $\theta = 32.98\Delta A$

The historical reported unit of CD experiments is molar ellipticity, $[\theta]$, which removes the dependence on concentration and path length

$$[\theta] = 3298\Delta\varepsilon \tag{14.9.5}$$

where the 3298 converts from the units of molar absorptivity to the historical units of degrees· cm^2·dmol^{-1}.

Applications

Instrumentation

Most commercial CD instruments are based on the modulation techniques introduced by Grosjean and Legrand. Light is linearly polarized and passed through a monochromator. The single wavelength light is then passed through a modulating device, usually a photoelastic modulator (PEM), which transforms the linear light to circular polarized light. The incident light on the sample switches between LCP and RCP light. As the incident light swtches direction of polarization the absorption changes and the differention molar absorptivity can be calculated.

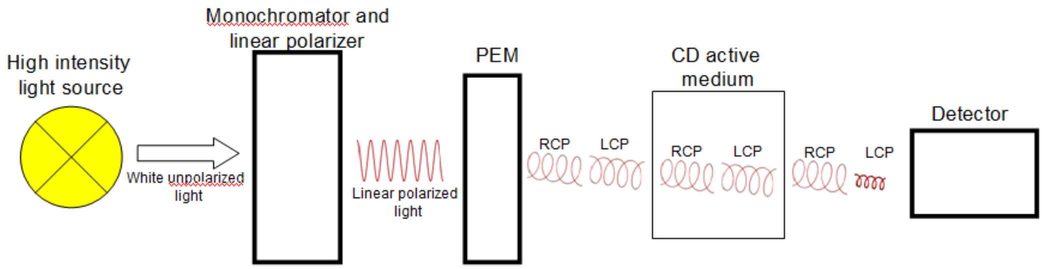

Figure 5: The instrumentation for a common CD spectrometer showing the polarization of light and the differential absorption of LCP and RCP light.

Biological molecules

The most widely used application of CD spectroscopy is identifying structural aspects of proteins and DNA. The peptide bonds in proteins are optically active and the ellipticity they exhibit changes based on the local conformation of the molecule. Secondary structures of proteins can be analyzed using the far-UV (190-250 nm) region of light. The ordered α-helices, β-sheets, β-turn, and random coil conformations all have characteristic spectra. These unique spectra form the basis for protein secondary structure analysis. It should be noted that in CD only the relative fractions of residues in each conformation can be determined but not specifically where each structural feature lies in the molecule. In reporting CD data for large biomolecules it is necessary to convert the data into a normalized value that is independent of molecular length. To do this the molar ellipticity is divided by the number of residues or monomer units in the molecule.

The real value in CD comes from the ability to show conformational changes in molecules. It can be used to determine how similar a wild type protein is to mutant or show the extent of denaturation with a change in temperature or chemical environment. It can also provide information about structural changes upon ligand binding. In order to interpret any of this information the spectrum of the native conformation must be determined.

Some information about the tertiary structure of proteins can be determined using near-UV spectroscopy. Absorptions between 250-300 nm are due to the dipole orientation and surrounding environment of the aromatic amino acids, phenylalanine, tyrosine, and tryptophan, and cysteine residues which can form disulfide bonds. Near-UV techniques can also be used to provide structural information about the binding of prosthetic groups in proteins.

Metal containing proteins can be studied by visible CD spectroscopy. Visible CD light excites the d-d transitions of metals in chiral environments. Free ions in solution will not absorb CD light so the pH dependence of the metal binding and the stoichiometry can be determined.

Vibrational CD (VCD) spectroscopy uses IR light to determine 3D structures of short peptides, nucleic acids, and carbohydrates. VCD has been used to show the shape and number of helices in A-, B-, and Z-DNA. VCD is still a relatively new technique and has the potential to be a very powerful tool. Resolving the spectra requires extensive *ab initio* calculations, as well as, high concentrations and must be performed in water, which may force the molecule into a nonnative conformation.

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14.E: Spectroscopy (Exercises)

14.1: Vocabulary

Q14.2

Find the wave number and frequency of light with a wavelength of 700 nm (to three significant figures).

S14.2

1. Wave number is equal to the reciprocal of wavelength. Its units are inverse centimeters.

$$ \tilde \nu = \dfrac{1}{\lambda} \]

$$ \tilde \nu = \dfrac{1}{700\ nm} \times \dfrac{10^9\ nm}{100\ cm} \]

$$ \tilde \nu = 1.43\ \times 10^4\ cm^{-1} \]

2. Use the relationship between frequency, speed, and wavelength to solve for frequency.

$$ \nu = \dfrac{c}{\lambda} \]

$$ \nu = \dfrac{2.998\ \times 10^8\ m/s}{700\ nm \times \dfrac{m}{10^9\ nm}} \]

$$ \nu = 4.28 \times 10^{14}\ s^{-1} \]

Q14.2a

Convert $3 \times 10^4\ cm^{-1}$ to wavelength. Identify what kind of spectroscopy?

Q14.2a

What is the frequency and wavenumber of a 740 nm photon?

Q14.2b

The wavelength of the red line in the Hydrogen spectrum is 656 nm $(656 \times 10^{-9}\ m)$. What is the wavenumber and frequency of it?

S14.2b

The wave number =1/λ = 1/656 x10^{-9} m = 1.5x10^{6} m^{-1}

Q14.2c

Convert 533 nm to wavenumber and frequency.

Q14.4a

Convert the following absorbance to percent transmittance: (a) 0.56, (b) 1.5, (c) 6.8.

Q14.4b

Calculate percent transmittance from the following values of absorbance:

a. 4.0
b. 0.23
c. 1.6

S14.4b

Solve, using the relationship between transmittance and absorbance.

$$ -\log){10}T = A \]

$$ T = 10^{-A} \]

For percent transmittance, multiply T by 100%

(a)

$$ T = 10^{-4.0} \times 100\% \]

$$ T = 0.010\% \]

(b)

$$T = 10^{-0.23} \times 100\%$$

$$T = 59\%$$

(c)

$$T = 10^{-1.6} \times 100\%$$

$$T = 2.5\%$$

Answers: 0.010%, 59%, 2.5%

Q14.4c

Convert the following from percent transmittance to absorbance.

a. 0.10%
b. 23%
c. 84%

Q14.4c

What is the percent transmitter of the following absorbance

a. 0.4
b. 1.2

S14.4c

We have A = 2- log %T

a. 0.4 = 2-log%T -->%T= $10^{(2-0.4)}$

%T= 39.8

b. 1.2 = 2-log%T ---> %T = 6.3%

Q14.6a

When molecules are exposed to radiation with frequency, v, such that $\Delta E = hv$, do they travel through a transition from a higher to lower state, or lower to higher state?

Q14.6b

Find the uncertainty of simultaneously measuring the frequency and wavelength of an emission, if the wavelength is 430 nm and the excited state lifetime is 0.50 nanoseconds.

S14.6b

1. Use Heisenberg's uncertainty principle and the relationship between energy and frequency to find the uncertainty of frequency.

$$\Delta E \Delta t \geq \dfrac{h}{4 \pi}$$

$$\Delta E = h \Delta \nu$$

$$h \Delta \nu \Delta t \geq \dfrac{h}{4 \pi}$$

$$\Delta \nu \geq \dfrac{1}{4 \pi \Delta t}$$

The maximum value for Δt is the lifetime of the excited state.

$$\Delta \nu \geq \dfrac{1}{4 \pi 0.50 ns \times \dfrac{s}{10^9\ ns}}$$

$$\Delta \nu \geq 1.6 \times 10^8\ s^{-1}$$

2. Use the uncertainty of frequency and the relationship between frequency and wavelength to find the uncertainty of the wavelength.

$$\lambda = \dfrac{c}{\nu}$$

$$| \Delta \lambda | = \dfrac{c}{\nu^2} | \Delta \nu |$$

$$ | \Delta \lambda | = \dfrac{\lambda ^2 | \Delta \nu | }{c} \]

$$ | \Delta \lambda | = \dfrac{(430\ nm)^2 \times 1.6 \times 10^8\ s^{-1}}{2.998 \times 10^8\ m/s} \times \dfrac{m}{10^9\ nm} \]

$$ | \Delta \lambda | = 2.3 \times 10^{-7}\ nm \]

Q14.6c

Calculate the wavelength emission of an electronically excited molecule with uncertainties in frequency (Δv) is 5.6x10^6 s^{-1}and the wavelength (Δλ) 4x10^{-6} nm? c= 3x10^{8}ms^{-1}=3x10^{17}nms^{-1}

S14.6c

We have:

$$|\,\Delta\,\lambda| = \frac{\lambda|\,\Delta\,v|}{v} \tag{14.E.1}$$

Since

$$\nu = \frac{c/}{\lambda} \tag{14.E.2}$$

then

$$|\,\Delta\,\lambda| = \frac{\lambda^2|\,\Delta\,v|}{c} \tag{14.E.3}$$

=> 4x10^{-6}nm = (λ^2 x 5.6x10^6 $\cancel{s^{-1})}$/ 3x10^{17}nm$\cancel{s^{-1}}$

=> λ = 463 nm

Q14.8a

In the gas phase, using electronic spectroscopy, what is observed on the electronic spectra of diatomic molecules at high resolution in terms of structure and bands?

Q14.8b

Explain why the decreasing of temperature will increase the resolution of visible and UV spectra?

S14.8b

Decreasing temperature will lower the kinetic energy of molecules. Thus the effect of Doppler and collisional broadening decrease, making the resolution enhances.

Q14.8c

Measuring the spectrum of the UV light at low temperature is a good way to enhance the resolution of the UV light. Explain. Give one more example.

Q14.10

In a 5.0 mM solution, a solute absorbs 90% of a visible light as the beam passes through a 80 mm cell. Calculate the molar absorptivity of this solute.

S14.10

We can calculate the transmittance:

$$T = 1.00 - 0.9 = 0.10 \tag{14.E.4}$$

Also, the absorbance is

$$A = -\log T = -\log(0.10) = 1.0 \tag{14.E.5}$$

Next step, use Beer-Lambert law to determine the molar absorptivity,

$$\epsilon = \frac{A}{bc} \tag{14.E.6}$$

$$\epsilon = \frac{1}{(8.0\,cm)(5.0\,mM)} = 2.5 \times 10^{-2} L\,mol^{-1}\,cm^{-1} \tag{14.E.7}$$

Q14.10

Calculate the absorbance (A) with the molar absorptivity= 6.17$Lmol^{-1}cm^{-1}$, c= 0.52 M when a certain wavelength passes through 2.3-cm cell.

S14.10

$$A = \epsilon bc = (6.17)(2.3)(0.52) = 7.38 \tag{14.E.8}$$

Q14.12

Calculate E_{vib} for a harmonic oscillator if $v = 2$ and $\nu = 3.24 \times 10^{13}\ Hz$

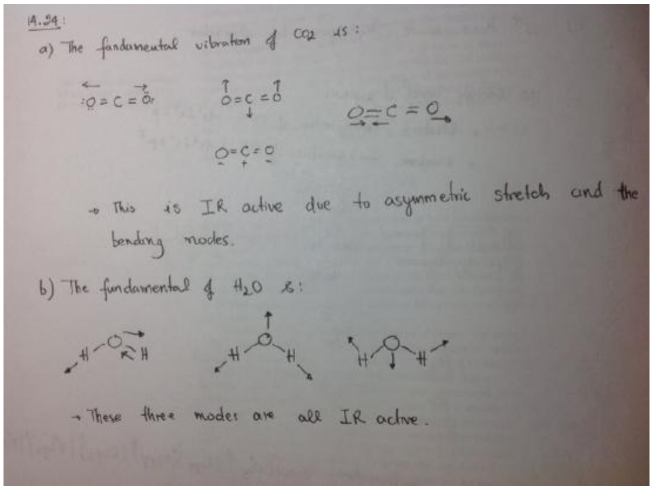
S14.12

$$E_{vib} = (v + \frac{1}{2})h\nu = (2 + \frac{1}{2})6.626 \times 10^{-34} \times 3.24 \times 10^{13} = 5.37 * 10^{-20} Hz \tag{14.E.9}$$

Q14.24

Given the following molecules: CO_2, H_2O. Show the fundamental vibration modes for each of the molecule and explain which one are IR active or both.

S14.24



14.24:

a) The fandamental vibration of CO_2 is:

→ This is IR active due to asymmetric stretch and the bending modes.

b) The fundamental of H_2O is:

→ These three modes are all IR active.

Q14.26

Given the following molecules: He_2, F_2, H_2, O_2 and Li_2. Rank these molecules from lowest to highest fundamental frequency of vibration? Show works.

S14.26

This can be determined by looking at the mass of the molecules. The one with the lowest mass will have the highest fundamental frequency of vibration and vice versa. $\mu_{He2} = \frac{(4.003amu)(4.003amu)}{(4.003amu)+(4.003amu)} = 2.0015$ and the similar calculation can be applied for other molecules, and the rank is as the following: Lowest --- $F_2 < O_2 < Li_2 < He_2 < H_2$ ---- highest

14.5: Nuclear Magnetic Resonance

Q14.12

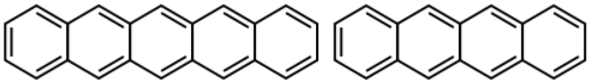
A chemist used the NMR machine to scan his sample and he obtained a signal-to-noise (S/N) ratio of 2.0. How long would it takes the chemist to generate a spectrum with a S/N ratio of 40? Assumed he spent 5 minutes per scan.

S14.12

We are looking at the $\left(\frac{S}{N}\right)_n$. This mean the ratio of signal to noise would change according to the number of n scans Thus, $\left(\frac{S}{N}\right)_n = \frac{nS}{\sqrt{nN}} = \sqrt{n}\left(\frac{S}{N}\right)_1 \sqrt{n} = \left(\frac{S}{N}\right)_n \div \left(\frac{S}{N}\right)_1 = 40 \div 2 = 20$ $n = 400$ Since 400 scans at the interval of 5 mins, it would take 400 × 5min = 2000min (1h/60min) = 33.3 h to generate this spectrum

Q14.28

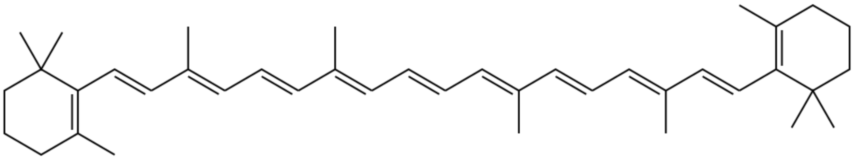
Explain why pentacene crystals are blue in color, but tetracene crystals are orange.



pentacene tetracene

Q14.29

Use the particle in a one-dimensional-box model to calculate the longest wavelength peak in the absorption spectrum of ß-carotene (structure shown below).



Q14.32a

What does chemical shift measure? What can influence chemical shift?

S14.32a

Chemical shift measures the difference in resonance frequencies between a nucleus of interest and a reference nucleus. It is influenced by electron shielding; the more electrons are pulled away from a proton of interest (the smaller the electron density around the nucleus of interest), the greater the chemical shift.

Q14.32b

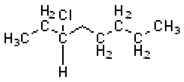
Assume you are doing an NMR spectroscopy. You operate the spectrometer at 100 Hz, but you find a signal of a compound at an unknown frequency downfield from TMS peak. However, you know its chemical shift is 6.5 ppm. Calculate the unknown frequency for your lab report.

Q14.34b

Assuming the precession frequency is 100 MHz and $\gamma = 10.0\text{x}10^5\ T^{-1}s^{-1}$, calculate the Larmor frequency for ^{17}O .

Q14.32c

Identify the most shielded and deshielded hydrogen for this compound:



S14.32c

The hydrogen groups on the far right end are the most shielded and the hydrogen group on the carbon with the chlorine group is the most deshielded.

Q14.32d

The NMR signal of coumpound is 280 Hz downfield from TMS is 70 MHZ. find its chemical shifl in ppm.

S14.32d

$$\delta = \frac{\nu - \nu_{ref}}{\nu_{spec}} \times 10^6 \tag{14.E.10}$$

$$\delta = \frac{280\ Hz}{70 \times 10^6} \times 10^6 = 4.0\ ppm \tag{14.E.11}$$

Q14.34

a. Calculate the magnetic field, B_0 that corresponds to a precession frequency of 600 MHz for ^{1}H.
b. What is the field strength (in tesla) needed to generate a ^{1}H frequency of 500 MHz?
c. How do spin-spin relaxation and spin-lattice relaxation differ from each other?
d. The ^{1}H NMR spectrum of toluene shows that it has two peaks because of methyl and aromatic protons recorded at 60 MHz and 1.41 T. Given this information, what would be the magnetic field at 400 MHz?
e. What is the difference between ^{13}C and ^{1}H NMR?

S14.34

a. B_0= 14.1 T.
b. Using the equation used in problem 1 and solving it for B_0we get a field strength of 11.74 T.
c. Look under relaxation.
d. Since we know that the NMR frequency is directly proportional to the magnetic strength, we calculate the magnetic field at 400 MHz: B_0 = (400 MHz/60MHz) x 1.41 T = 9.40 T
e. Look under applications.

Q14.34

calculate the field strength in tesla to generate ^{1}H frequency of 300 MHz?

S14.34

$$B_0 = 2\pi v/ɣ = 2\pi(300 \text{ x } 10^6\ s^{-1})/\ 26.75 \text{ x } 10^7\ T^{-1}s^{-1}$$

$$B_0 = 7.04\ T$$

Q14.36

Given 4.7 T, calculate the diference in frequency for 2 protons whose § value differ 1.25 and 400 MHz

S14.36

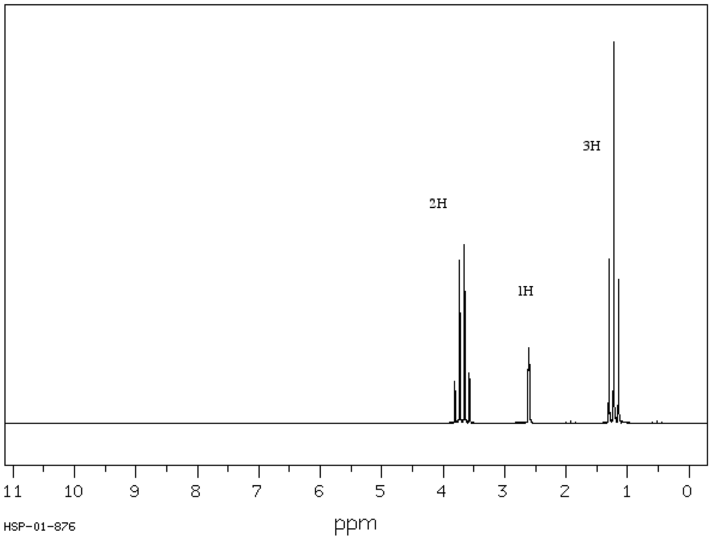
$$B_0 = (\Delta\delta \text{ x } v_{spec})\ /\ 10^6 = (1.25\ (200 \text{ x } 10^6\ Hz))\ /\ 10^6$$

$$B_0 = 2.5 \text{ x } 10^2\ Hz$$

Q14.38

Draw the NMR spectrum of isobutyl alcohol with chemical shift -CH 0.90 ppm, -A-H 1.68ppm, -CH2 3.26 ppm, O-H 4.49 ppm

S14.38



14.6: Electron Spin Resonance

Q14.42

You performed an electron spin resonance (ESR) experiment with di-*tert*-butyl nitroxide radical and get 3 lines of equal intensity. Then, you combine di-*tert*-butyl nitroxide radical with ascorbic acid and was about to run another ESR experiment but Jill stopped you. Why did Jill stop you?

14.7: Fluorescence and Phosphorescence

Q14.43

Someone has handed you data of the luminescence of a material as a function of time. How can you decide whether the luminescence process was fluorescence or phosphorescence?

14.8: Lasers

14.9: Optical Rotatory Dispersion and Circular Dichroism

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CHAPTER OVERVIEW

15: Photochemistry and Photobiology

Photochemistry is the branch of chemistry concerned with the chemical effects of light. Generally, this term is used to describe a chemical reaction caused by absorption of high energy light. Photobiology is the scientific study of the interactions of the photochemistry of living organisms and includes the study of photosynthesis, visual processing, circadian rhythms, bioluminescence, and ultraviolet radiation effects.

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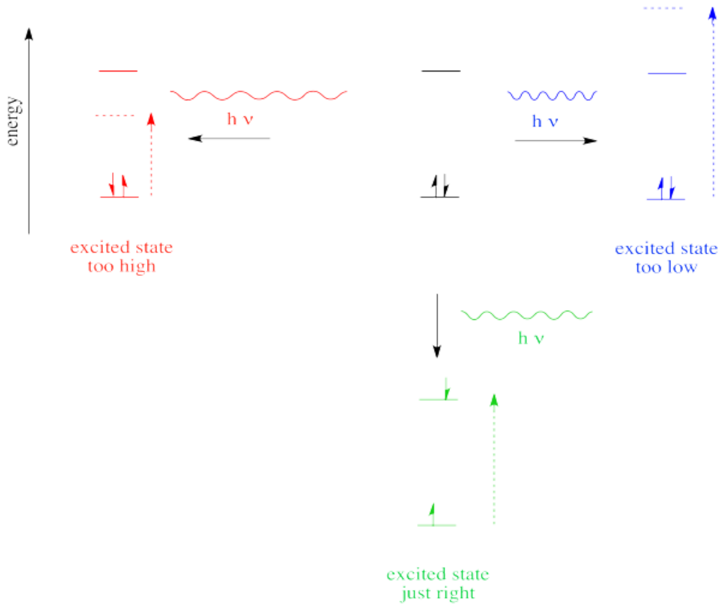
15.1: Introduction to Photochemistry

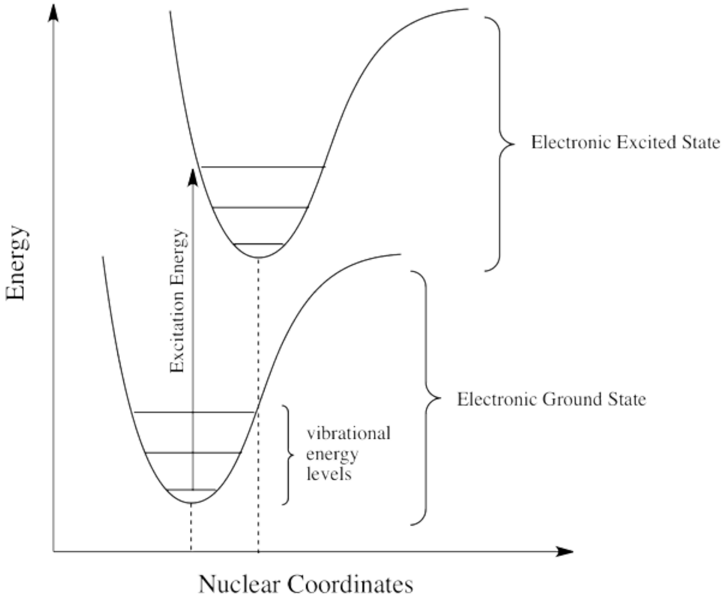
So far, we have come across one big rule of photon absorbance. In order to be absorbed, a photon's energy has to match an energy difference within the compound that is absorbing it.



In the case of visible or ultraviolet light, the energy of a photon is roughly in the region that would be appropriate to promote an electron to a higher energy level. Different wavelengths would be able to promote different electrons, depending on the energy difference between an occupied electronic energy level and an unoccupied one. Other types of electromagnetic radiation would not be able to promote an electron, but they would be coupled to other events. For example, absorption of infrared light is tied to vibrational energy levels. Microwave radiation is tied to rotational energy levels in molecules. Thus, one reason a photon may or may not be absorbed has to do with whether its energy corresponds to the available energy differences within the molecule or ion that it encounters.

Franck-Condon: Electronic and Vibrational Coupling

Photons face other limitations. One of these is a moderate variation on our main rule. It is called the Frank Condon Principle. According to this idea, when an electron is excited from its normal position, the ground state, to a higher energy level, the optimal positions of atoms in the molecule may need to shift. Because electronic motion is much faster than nuclear motion, however, any shifting of atoms needed to optimize positions as they should be in the excited state will have to wait until after the electron gets excited. In that case, when the electron lands and the atoms aren't yet in their lowest energy positions for the excited state, the molecule will find itself in an excited vibrational state as well as an excited electronic state.



That means the required energy for excitation doesn't just correspond to the difference in electronic energy levels; it is fine-tuned to reach a vibrational energy level, which is quantized as well.

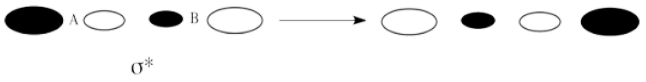
- The Franck Condon Principle states that electronic transitions are vertical.
- A vertical transition is one in which non of the nuclei move while the electron journeys from one state to another.
- A vertical transition may begin in a vibrational ground state of an electronic ground state and end in a vibrational excited state of an electronic excited state.

LaPorte: Orbital Symmetry

There are other restrictions on electronic excitation. Symmetry selection rules, for instance, state that the donor orbital (from which the electron comes) and the acceptor orbital (to which the electron is promoted) must have different symmetry. The reasons for this rule are based in the mathematics of quantum mechanics. What constitutes the same symmetry vs. different symmetry is a little more complicated than we will get into here. Briefly, let's just look at one "symmetry element" and compare how two orbitals might differ with respect to that element.

If an orbital is centrosymmetric, one can imagine each point on the orbital reflecting through the very centre of the orbital to a point on the other side. At the end of the operation, the orbital appears unchanged. That means the orbital is symmetric with respect to a centre of inversion..

If we do the same thing with a sigma antibonding orbital, things turn out differently.



In the drawing, the locations of the atoms are labelled A and B, but the symmetry of the orbital itself doesn't depend on that. If we imagine sending each point on this orbital through the very centre to the other side, we arrive at a picture that looks exactly the opposite of what we started with. These two orbitals have different symmetry. A transition from one to the other is allowed by symmetry.

Problem RO2.1.

Decide whether each of the following orbitals is centrosymmetric.

a) an s orbital b) a p orbital c) a d orbital d) a π orbital e) a π* orbital

Problem RO2.2.

Decide whether each of the following transitions would be allowed by symmetry.

a) π → π* b) p → π* c) p → σ* d) d → d

Symmetry selection rules are in reality more like "strong suggestions." They depend on the symmetry of the molecule remaining strictly static, but all kinds of distortions occur through molecular vibrations. Nevertheless, these rules influence the likelihood of a given transition. The likelihood of a transition, similarly, has an influence upon the extinction coefficient, ε.

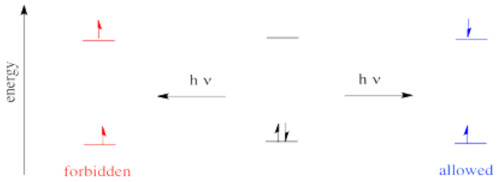
transition	**ε, extinction coefficient**
π → π*	3,000 - 25,000 M^{-1} cm^{-1}
p → π*	20 - 150 M^{-1} cm^{-1}
p → σ*	100 - 7,000
d → d	5 - 400 M^{-1} cm^{-1}

Spin State

Let's take a quick look at one last rule about electronic emissions. This rule concerns the spin of the excited electron, or more correctly, the "spin state" of the excited species. The spin state describes the number of unpaired electrons in the molecule or ion.

number of unpaired electrons	**spin state**
0	singlet
1	doublet
2	triplet
3	quartet

The rule says that in an electronic transition, the spin state of the molecule must be preserved. That means if there are no unpaired electrons before the transition, then the excited species must also have no unpaired electrons. If there are two unpaired electrons before the transition, the excited state must also have two unpaired electrons.



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15.2: Photosynthesis

Learning Objectives

1. Define the following:
    - photoautotrophenic a. oxyg
    - photoautotroph anoxygenicb.
    - c. photon
2. Name the two stages of photosynthesis.
3. State how all radiations in the electromagnetic spectrum travel.
4. State what constitutes visible light.
5. Define photon and describe what happens when photons of visible light energy strike certain atoms of pigments during photosynthesis and how this can lead to the generation of ATP.
6. Describe the structure of a chloroplast and list the pigments it may contain.
7. Give the overall reaction for photosynthesis.
8. State the reactants and the products for photosynthesis and indicate which are oxidized and which are reduced.

1. Briefly describe the overall function of the light-dependent reactions in photosynthesis and state where in the chloroplast they occur.

- 2. State the reactants and the products for the light-dependent reactions.
- 3. Describe an antenna complex and state the function of the reaction center.
- 4. Briefly describe the overall function of Photosystem II in the light-dependent reactions of photosynthesis.
- 5. Briefly describe how ATP is generated by chemiosmosis during the light-dependent reactions of photosynthesis.
- 6. Briefly describe the overall function of Photosystem I in the light-dependent reactions of photosynthesis.
- 7. Compare noncyclic photophosphorylation and cyclic photophosphorylation in terms of Photosystems involved and products produced.

1. Briefly describe the overall function of the light-independent reactions in photosynthesis and state where in the chloroplast they occur.

1. State how the light-dependent and light-independent reactions are linked during photosynthesis.
2. State the reactants and the products for the light-independent reactions.
3. Briefly describe the following stages of the Calvin cycle:
    - CO2 fixation
    - production of G3P
    - regeneration of RuBP
4. State the significance of glyceraldehyde-3-phosphate (G3P) in the Calvin cycle.

Autotrophs are organisms that are able to synthesize organic molecules from inorganic materials. Photoautotrophs absorb and convert light energy into the stored energy of chemical bonds in organic molecules through a process called photosynthesis. Plants, algae, and bacteria known as cyanobacteria are known as oxygenic photoautotrophs because they synthesize organic molecules from inorganic materials, convert light energy into chemical energy, use water as an electron source, and generate oxygen as an end product of photosynthesis. Some bacteria, such as the green and purple bacteria, are known as anoxygenic phototrophs. Unlike the oxygenic plants, algae, and cyanobacteria, anoxygenic phototrophs do not use water as an electron source and, therefore, do not evolve oxygen during photosynthesis. The electrons come from compounds such as hydrogen gas, hydrogen sulfide, and reduced organic molecules. In this section on photosynthesis, we be concerned with the oxygenic phototrophs.

Photosynthesis is composed of two stages: the light-dependent reactions and the light-independent reactions. The light-dependent reactions convert light energy into chemical energy, producing ATP and NADPH. The light-independent reactions use the ATP and NADPH from the light-dependent reactions to reduce carbon dioxide and convert the energy to the chemical bond energy in carbohydrates such as glucose. Before we get to these photosynthetic reactions however, we need to understand a little about the electromagnetic spectrum and chloroplasts.

The Electromagnetic Spectrum

Visible light constitutes a very small portion of a spectrum of radiation known as the **electromagnetic spectrum**. All radiations in the electromagnetic spectrum travel in **waves** and different portions of the spectrum are catagorized by their wavelength. A **wavelength** is the distance from the peak of one wave to that of the next. At one end of the spectrum are television and radio waves with longer wavelengths and low energy. At the other end of the spectrum are gamma rays with a very short wavelength and a great deal of energy. **Visible light** is the range of wavelengths of the electromagnetic spectrum that humans can see, a mixture of wavelengths ranging from 380 nanometers to 760 nanometers. It is this light that is used in photosynthesis.

Light and other types of radiation are composed of individual packets of energy called **photons**. The shorter the wavelength of the radiation, the greater the energy per photon. As will be seen shortly, when photons of visible light energy strike certain atoms of pigments during photosynthesis, that energy may push an electron from that atom to a higher energy level where it can be picked up by an electron acceptor in an electron transport chain (see Fig. 15.2.1). ATP can then be generated by chemiosmosis.

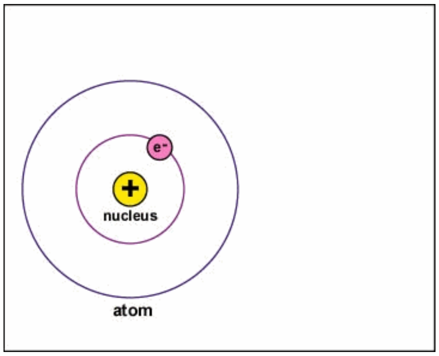

***Fig. 15.2.1**: Interaction Between a Photon and an Atom. When photons of visible light energy strike certain atoms of pigments during photosynthesis, that energy may push an electron from that atom to a higher energy level where it can be picked up by an electron acceptor in an electron transport chain.*

Chloroplasts

In eukaryotic cells, photosynthesis takes place in organelles called **chloroplasts**.

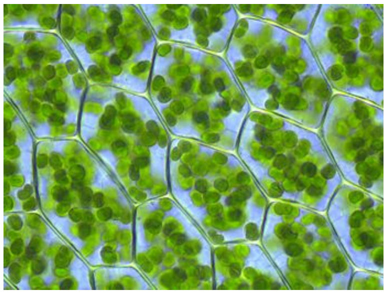

Figure: Chloroplasts visible in the cells of Plagiomnium affine, the many-fruited thyme moss. (GFDL , credit: Kristian Peters)

Like mitochondria, chloroplasts are surrounded by an inner and an outer membrane. The **inner membrane** encloses a fluid-filled region called the **stroma** that contains enzymes for the light-independent reactions of photosynthesis. Infolding of this inner membrane forms interconnected stacks of disk-like sacs called **thylakoids**, often arranged in stacks called **grana**. The thylakoid membrane, which encloses a fluid-filled thylakoid interior space, contains chlorophyll and other photosynthetic pigments as well as electron transport chains. The light-dependent reactions of photosynthesis occur in the thylakoids. The outer membrane of the chloroplast encloses the intermembrane space between the inner and outer chloroplast membranes (see Fig. 2).

The thylakoid membranes contain several pigments capable of absorbing visible light. **Chlorophyll** is the primary pigment of photosynthesis. Chlorophyll absorbs light in the blue and red region of the visible light spectrum and reflects green light. There are two major types of chlorophyll, chlorophyll *a* that initiates the light-dependent reactions of photosynthesis, and chlorophyll *b*, an accessory pigment that also participates in photosynthesis. The thylakoid membranes also contain other accessory pigments. **Carotenoids** are pigments that absorb blue and green light and reflect yellow, orange, or red. **Phycocyanins** absorb green and yellow light and reflect blue or purple. These accessory pigments absorb light energy and transfer it to chlorophyll.

Photosynthetic prokaryotic cells do not possess chloroplasts. Instead, thylakoid membranes are usually arranged around the periphery of the bacterium as infoldings of the cytoplasmic membrane.

Photosynthesis

As mentioned above, photoautotrophs use sunlight as a source of energy and through the process of photosynthesis, reduce carbon dioxide to form carbohydrates such as glucose. The radient energy is converted to the chemical bond energy within glucose and other organic molecules. The **overall reaction for photosynthesis** is as follows:

$$6CO_2 + 12H_2O \text{in the presence of light and chlorophyll yields} C_6H_{12}O_6 + 6O_2 + 6H2O \tag{15.2.1}$$

Note that carbon dioxide (CO_2) is reduced to produce glucose ($C_6H_{12}O_6$), while water (H_2O) is oxidized to produce oxygen (O_2). Photosynthesis is composed of two stages: the light-dependent reactions and the light independent reactions. We will now look at the role of each in the next two sections.

Light-Dependent Reactions

The exergonic light-dependent reactions of photosynthesis convert light energy into chemical energy, producing ATP and NADPH. These reactions occur in the thylakoids of the chloroplasts. The products of the light-dependent reactions, ATP and NADPH, are both required for the endergonic light-independent reactions.

The light-dependent reactions can be summarized as follows:

12 H_2O + 12 $NADP^+$ + 18 ADP + 18 P_i + light and chlorophyll yields 6 O_2 + 12 NADPH + 18 ATP

The light-dependent reactions involve two photosystems called **Photosystem I and Photosystem II**. These photosystems include units called **antenna complexes** composed of chlorophyll molecules and accessory pigments located in the thylakoid membrane. **Photosystem I contain chlorophyll *a* molecules called P700** because they have an absorption peak of 700 nanometers. **Photosystem II contains chlorophyll *a* molecules referred to as P680** because they have an absorption peak of 680 nanometers.

Each antenna complex is able to trap light and transfer energy to a complex of chlorophyll molecules and proteins called the **reaction center** (see Fig. 3). As photons are absorbed by chlorophyll and accessory pigments, that energy is eventually transfered to the reaction center where, when absorbed by an excitable electron, moves it to a higher energy level. Here the electron may be accepted by an electron acceptor molecule of an electron transport chain (see Fig. 3) where the light energy is converted to chemical energy by chemiosmosis.

The most common light-dependent reaction in photosynthesis is called noncyclic photophosphorylation. Noncyclic photophosphorylation involves both Photosystem I and Photosystem II and produces ATP and $NADPH$. During noncyclic photophosphorylation, the generation of ATP is coupled to a one-way flow of electrons from H_2O to $NADP^+$. We will now look at Photosystems I and II and their roles in noncyclic photophosphorylation.

1. **As photons are absorbed by pigment molecules in the antenna complexes of Photosystem II, excited electrons from the reaction center are picked up by the primary electron acceptor of the Photosystem II electron transport chain. During this process, Photosystem II splits molecules of H_2O into 1/2 O_2, $2H^{+,}$ and 2 electrons**. These electrons continuously replace the electrons being lost by the P680 chlorophyll *a* molecules in the reaction centers of the Photosystem II antenna complexes (see Fig. 4).

During this process, ATP is generated by the Photosystem II electron transport chain and chemiosmosis. According to the **chemiosmosis theory**, as the electrons are transported down the electron transport chain, some of the energy released is used to pump protons across the thylakoid membrane from the stroma of the chloroplast to the thylakoid interior space **producing a proton gradient or proton motive force**. As the accumulating protons in the thylakoid interior space pass back across the thylakoid membrane to the stroma through **ATP synthetase** complexes, this proton motive force is used to **generate ATP** from ADP and P*i* (see Fig. 4 and Fig. 5).

Flash animation illustrating the development of proton motive force as a result of chemiosmosis and ATP production by ATPsynthase.

2. Meanwhile, **photons are also being absorbed by pigment molecules in the antenna complex of Photosystem I and excited electrons from the reaction center are picked up by the primary electron acceptor of the Photosystem I electron transport chain.** The electrons being lost by the P700 chlorophyll *a* molecules in the reaction centers of Photosystem I are replaced by the electrons traveling down the Photosystem II electron transport chain. **The electrons transported down the Photosystem I electron transport chain combine with 2H$^+$ from the surrounding medium and NADP$^+$ to produce NADPH + H$^+$** (see Fig. 4).

McGraw-Hill Flash animation illustrating photosynthetic electran transport and ATP production by ATPsynthase.

Cyclic photophosphorylation occurs less commonly in plants than noncyclic photophosphorylation, most likely occurring when there is too little NADP$^+$ available. It is also seen in certain photosynthetic bacteria. Cyclic photophosphorylation involves only Photosystem I and generates ATP but not NADPH. As the electrons from the reaction center of Photosystem I are picked up by the electron transport chain, they are transported back to the reaction center chlorophyll. As the electrons are transported down the electron transport chain, some of the energy released is used to pump protons across the thylakoid membrane from the stroma of the chloroplast to the thylakoid interior space producing a proton gradient or proton motive force. As the accumulating protons in the thylakoid interior space pass back across the thylakoid membrane to the stroma through ATP synthetase complexes, this energy is used to generate ATP from ADP and P*i* (see Fig. 6).

McGraw-Hill Flash animation illustrating cyclic and non-cyclic photophosphorylation.

Light Independent Reactions

The endergonic light-independent reactions of photosynthesis use the ATP and NADPH synthesized during the exergonic light-dependent reactions to provide the energy for the synthesis of glucose and other organic molecules from inorganic carbon dioxide and water. This is done by "fixing" carbon atoms from CO_2 to the carbon skeletons of existing organic molecules. These reactions occur in the stroma of the chloroplasts.

The *light-independent reactions* can be summarized as follows:

$$\mathbf{12\ NADPH + 18\ ATP + 6\ CO_2\ yields\ C_6H_{12}O_6\ (glucose) + 12\ NADP^+ + 18\ ADP + 18\ P_{\mathit{i}} + 6\ H_2O}$$

Most plants use the Calvin (C_3) cycle to fix carbon dioxide. C_3 refers to the importance of 3-carbon molecules in the cycle. Some plants, known as C_4 plants and CAM plants, differ in their initial carbon fixation step.

> ### *1. The Calvin (C_3) Cycle*
>
> *There are three stages to the Calvin cycle: 1) CO_2 fixation; 2) production of G3P; and 3) regeneration of RuBP. We will now look at each stage.*
>
> > #### *stage 1: CO_2 fixation*
> >
> > *To begin the Calvin cycle, **a molecule of CO_2 reacts with a five-carbon compound called***

ribulose bisphosphate (RuBP) producing an unstable six-carbon intermediate which immediately breaks down into two molecules of the three-carbon compound phosphoglycerate (PGA) *(see Fig. 7). The carbon that was a part of inorganic* CO_2 *is now part of the carbon skeleton of an organic molecule. The enzyme for this reaction is ribulose bisphosphate carboxylase or Rubisco. A total of six molecules of* CO_2 *must be fixed this way in order to produce one molecule of the six-carbon sugar glucose.*

stage 2: Production of G3P from PGA

The energy from ATP and the reducing power of NADPH (both produced during the light-dependent reactions) is now used to convert the molecules of PGA to glyceraldehyde-3-phosphate (G3P), another three-carbon compound *(see Fig. 7). For every six molecules of* CO_2 *that enter the Calvin cycle, two molecules of G3P are produced. Most of the G3P produced during the Calvin cycle - 10 of every 12 G3P produced - are used to regenerate the RuBP in order for the cycle to continue (see Fig. 7).* ***Some of the molecules of G3P, however, are used to synthesize glucose and other organic molecules****. As can be seen in Fig. 7, two molecules of the three-carbon G3P can be used to synthesize one molecule of the six-carbon sugar glucose. The G3P is also used to synthesize the other organic molecules required by photoautotrophs (see Fig. 8).*

stage 3: Regeneration of RuBP from G3P

> > *As mentioned in the previous step, most of the G3P produced during the Calvin cycle - 10 of every 12 G3P produced - are used to regenerate the RuBP so that the cycle may continue (see Fig. 7).* ***Ten molecules of the three-carbon compound G3P eventually form six molecules of the four-carbon compound ribulose phosphate (RP)*** *(see Fig. 7).* ***Each molecule of RP then becomes phosphorylated by the hydrolysis of ATP to produce ribulose bisphosphate (RuBP)****, the starting compound for the Calvin cycle (see Fig. 7).*

Contributors and Attributions

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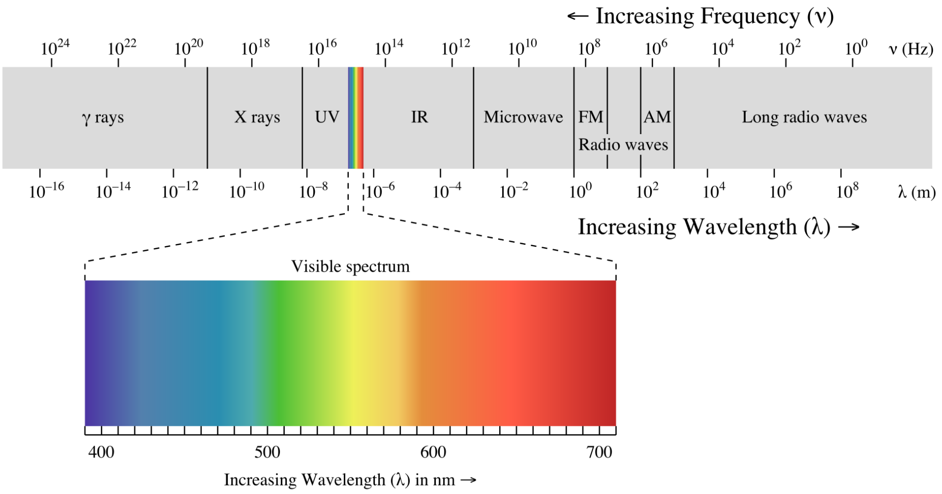
15.3: Vision

Vision is such an everyday occurrence that we seldom stop to think and wonder how we are able to see the objects that surround us. Yet the vision process is a fascinating example of how light can produce molecular changes. The retina contain the molecules that undergo a chemical change upon absorbing light, but it is the brain that actually makes sense of the visual information to create an image.

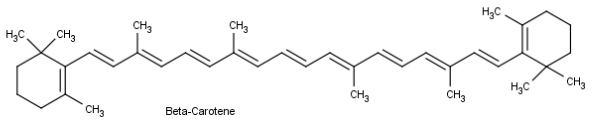
Introduction

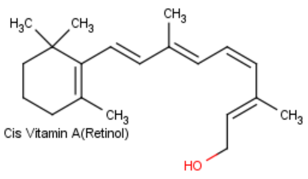
Light is one of the most important resources for civilization, it provides energy as it pass along by the sun. Light influence our everyday live. Living organisms sense light from the environment by photoreceptors. Light, as waves carry energy, contains energy by different wavelength. In vision, light is the stimulus input. Light energy goes into eyes stimulate photoreceptor in eyes. However, as an energy wave, energy is passed on through light at different wavelength.

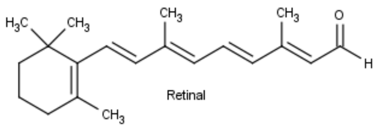


Light, as waves carry energy, contains energy by different wavelength. From long wavelength to short wavelength, energy increase. 400 nm to 700 nm is visible spectrum.

Light energy can convert chemical to other forms. Vitamin A, also known as retinol, anti-dry eye vitamins, is a required nutrition for human health. The predecessor of vitamin A is present in the variety of plant carotene. Vitamin A is critical for vision because it is needed by the retina of eye. Retinol can be convert to retinal, and retinal is a chemical necessary for rhodopsin. As light enters the eye, the 11-*cis*-retinal is isomerized to the all-"trans" form.

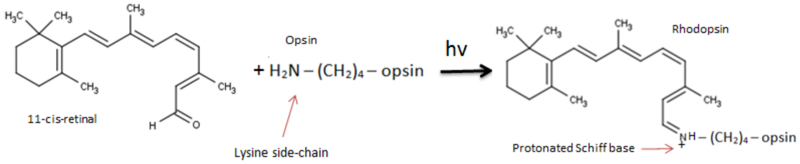






Mechanism of Vision

The molecule cis-retinal can absorb light at a specific wavelength. When visible light hits the cis-retinal, the cis-retinal undergoes an isomerization, or change in molecular arrangement, to all-trans-retinal. The new form of trans-retinal does not fit as well into the protein, and so a series of geometry changes in the protein begins. The resulting complex is referred to a bathrhodopsin (there are other intermediates in this process, but we'll ignore them for now).



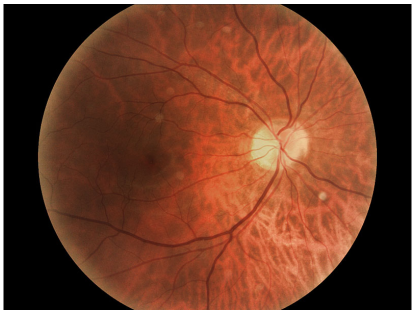
The reaction above shows Lysine side-chain from the opsin react with 11-cis-retinal when stimulated. By removing the oxygen atom from the retinal and two hydrogen atom from the free amino group of the lysine, the linkage show on the picture above is formed, and it is called Schiff base.

Signal Transduction Pathway

As the protein changes its geometry, it initiates a cascade of biochemical reactions that results in changes in charge so that a large potential difference builds up across the plasma membrane. This potential difference is passed along to an adjoining nerve cell as an electrical impulse. The nerve cell carries this impulse to the brain, where the visual information is interpreted.

The light image is mapped on the surface of the retina by activating a series of light-sensitive cells known as rods and cones or photoreceptors. The rods and cones convert the light into electrical impulses which are transmitted to the brain via nerve fibers. The brain then determines, which nerve fibers carried the electrical impulse activate by light at certain photoreceptors, and then creates an image.

The retina is lined with many millions of photoreceptor cells that consist of two types: 7 million cones provide color information and sharpness of images, and 120 million rods are extremely sensitive detectors of white light to provide night vision. The tops of the rods and cones contain a region filled with membrane-bound discs, which contain the molecule cis-retinal bound to a protein called opsin. The resulting complex is called rhodopsin or "visual purple".



In human eyes, rod and cones react to light stimulation, and a series of chemical reactions happen in cells. These cells receive light, and pass on signals to other receiver cells. This chain of process is class signal transduction pathway. Signal transduction pathway is a mechanism that describe the ways cells react and response to stimulation.

References

1. Biochemistry, L. Stryer (W.H. Freeman and Co, San Francisco, 1975).
2. *The Cambridge Guide to the Material World*, Rodney Cotterill (Cambridge University Press, Cambridge, 1985)

Contributors

- {{template.ContribOphardt()}}

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15.4: Biological Effects of Radiation

Learning Objectives

- Describe the biological impact of ionizing radiation.
- Define units for measuring radiation exposure.
- Explain the operation of common tools for detecting radioactivity.
- List common sources of radiation exposure in the US.

The increased use of radioisotopes has led to increased concerns over the effects of these materials on biological systems (such as humans). All radioactive nuclides emit high-energy particles or electromagnetic waves. When this radiation encounters living cells, it can cause heating, break chemical bonds, or ionize molecules. The most serious biological damage results when these radioactive emissions fragment or ionize molecules. For example, alpha and beta particles emitted from nuclear decay reactions possess much higher energies than ordinary chemical bond energies. When these particles strike and penetrate matter, they produce ions and molecular fragments that are extremely reactive. The damage this does to biomolecules in living organisms can cause serious malfunctions in normal cell processes, taxing the organism's repair mechanisms and possibly causing illness or even death (Figure 15.4.1).

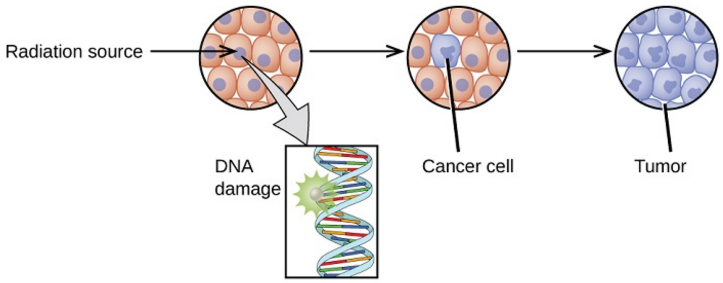

Figure 15.4.1: Radiation can harm biological systems by damaging the DNA of cells. If this damage is not properly repaired, the cells may divide in an uncontrolled manner and cause cancer.

A diagram is shown which has a white sphere followed by a right-facing arrow and a large sphere composed of many smaller white and green spheres. The single sphere has impacted the larger sphere. A right-facing arrow leads from the larger sphere to a pair of smaller spheres which are collections of the same white and green spheres. A starburst pattern lies between these two spheres and has three right-facing arrows leading from it to two white spheres and a circle full of ten smaller, peach-colored circles with purple dots in their centers. An arrow leads downward from this circle to a box that contains a helical shape with a starburst near its top left side and is labeled "D N A damage." A right-facing arrow leads from this circle to a second circle, with nine smaller, peach-colored circles with purple dots in their centers and one fully purple small circle labeled "Cancer cell." A right-facing arrow leads to a final circle, this time full of the purple cells, that is labeled "Tumor."

Ionizing vs. Nonionizing Radiation

There is a large difference in the magnitude of the biological effects of nonionizing radiation (for example, light and microwaves) and ionizing radiation, emissions energetic enough to knock electrons out of molecules (for example, α and β particles, γ rays, X-rays, and high-energy ultraviolet radiation) (Figure 15.4.2).

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Figure 15.4.2: Lower frequency, lower-energy electromagnetic radiation is nonionizing, and higher frequency, higher-energy electromagnetic radiation is ionizing.

Energy absorbed from nonionizing radiation speeds up the movement of atoms and molecules, which is equivalent to heating the sample. Although biological systems are sensitive to heat (as we might know from touching a hot stove or spending a day at the beach in the sun), a large amount of nonionizing radiation is necessary before dangerous levels are reached. Ionizing radiation, however, may cause much more severe damage by breaking bonds or removing electrons in biological molecules, disrupting their structure and function. The damage can also be done indirectly, by first ionizing H_2O (the most abundant molecule in living organisms), which forms a H_2O^+ ion that reacts with water, forming a hydronium ion and a hydroxyl radical:

$$H_2O + \text{radiation} \xrightarrow{e^-} H_2O^+ + H_2O \longrightarrow H_3O^+ + OH^\bullet$$

Figure 15.4.3.

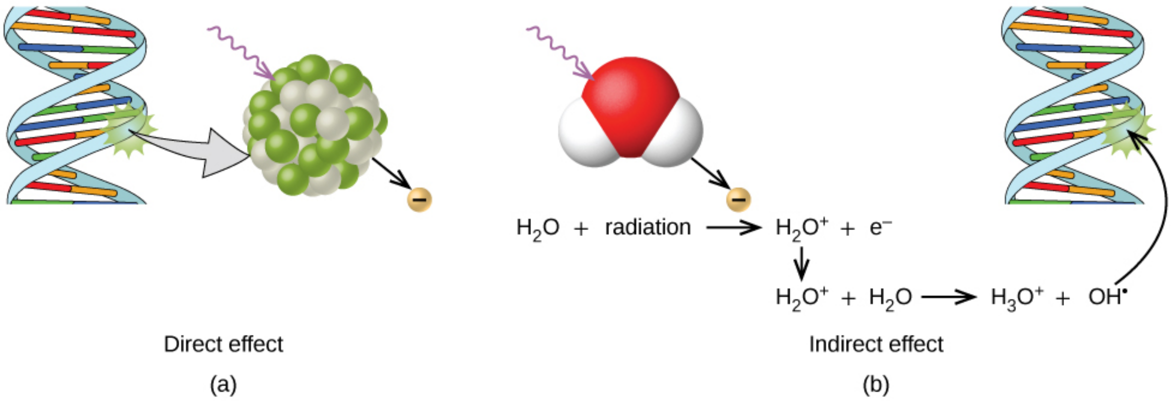


Figure 15.4.3: Ionizing radiation can (a) directly damage a biomolecule by ionizing it or breaking its bonds, or (b) create an H_2O^+ ion, which reacts with H_2O to form a hydroxyl radical, which in turn reacts with the biomolecule, causing damage indirectly.

Biological Effects of Exposure to Radiation

Radiation can harm either the whole body (somatic damage) or eggs and sperm (genetic damage). Its effects are more pronounced in cells that reproduce rapidly, such as the stomach lining, hair follicles, bone marrow, and embryos. This is why patients undergoing radiation therapy often feel nauseous or sick to their stomach, lose hair, have bone aches, and so on, and why particular care must be taken when undergoing radiation therapy during pregnancy.

Different types of radiation have differing abilities to pass through material (Figure 15.4.4). A very thin barrier, such as a sheet or two of paper, or the top layer of skin cells, usually stops alpha particles. Because of this, alpha particle sources are usually not dangerous if outside the body, but are quite hazardous if ingested or inhaled (see the Chemistry in Everyday Life feature on Radon Exposure). Beta particles will pass through a hand, or a thin layer of material like paper or wood, but are stopped by a thin layer of metal. Gamma radiation is very penetrating and can pass through a thick layer of most materials. Some high-energy gamma radiation is able to pass through a few feet of concrete. Certain dense, high atomic number elements (such as lead) can effectively attenuate gamma radiation with thinner material and are used for shielding. The ability of various kinds of emissions to cause ionization varies greatly, and some particles have almost no tendency to produce ionization. Alpha particles have about twice the ionizing power of fast-moving neutrons, about 10 times that of β particles, and about 20 times that of γ rays and X-rays.

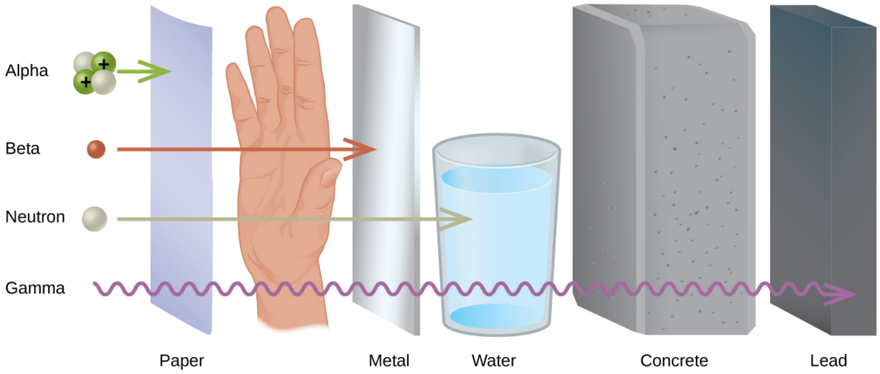


Figure 15.4.4: The ability of different types of radiation to pass through material is shown. From least to most penetrating, they are alpha < beta < neutron < gamma.

A diagram shows four particles in a vertical column on the left, followed by an upright sheet of paper, a person’s hand, an upright sheet of metal, a glass of water, a thick block of concrete and an upright, thick piece of lead. The top particle listed is made up of two white spheres and two green spheres that are labeled with positive signs and is labeled “Alpha.” A right-facing arrow leads from this to the paper. The second particle is a red sphere labeled “Beta” and is followed by a right-facing arrow that passes through the paper and stops at the hand. The third particle is a white sphere labeled “Neutron” and is followed by a right-facing arrow that passes through the paper, hand and metal but is stopped at the glass of water. The fourth particle is shown by a squiggly arrow and it passes through all of the substances but stops at the lead. Terms at the bottom read, from left to right, “Paper,” “Metal,” “Water,” “Concrete” and “Lead.”

For many people, one of the largest sources of exposure to radiation is from radon gas (Rn-222). Radon-222 is an α emitter with a half–life of 3.82 days. It is one of the products of the radioactive decay series of U-238, which is found in trace amounts in soil and rocks. The radon gas that is produced slowly escapes from the ground and gradually seeps into homes and other structures above.

Since it is about eight times more dense than air, radon gas accumulates in basements and lower floors, and slowly diffuses throughout buildings (Figure 15.4.5).

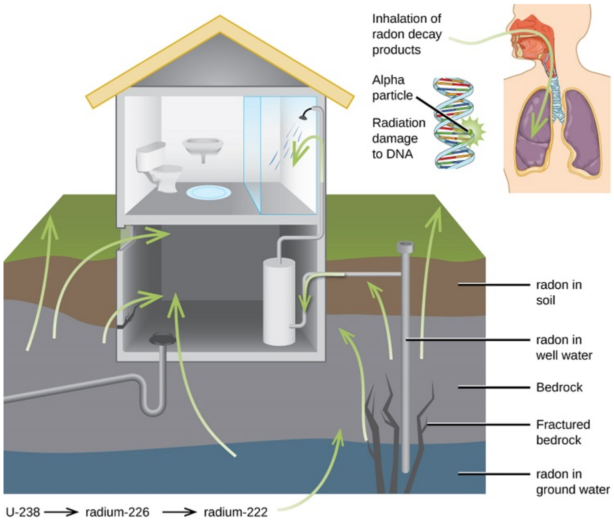


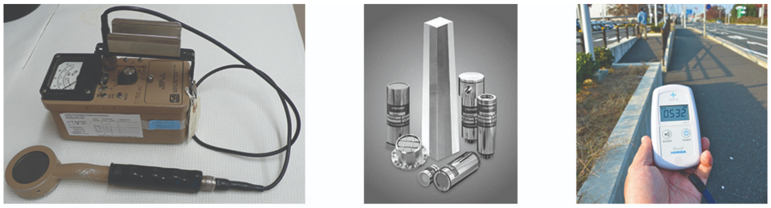
Figure 15.4.5: Radon-222 seeps into houses and other buildings from rocks that contain uranium-238, a radon emitter. The radon enters through cracks in concrete foundations and basement floors, stone or porous cinderblock foundations, and openings for water and gas pipes.

A cut-away image of the side of a house and four layers of the ground it rests on is shown, as well as a second cut-away image of a person's head and chest cavity. The house is shown with a restroom on the second floor and a basement with a water heater as the first floor. Green arrows lead from the lowest ground layer, labeled "radon in ground water," from the third ground layer, labeled "Bedrock" and "Fractured bedrock," from the second layer, labeled "radon in well water," and from the top layer, labeled "radon in soil to the inside of the basement area. In the smaller image of the torso, a green arrow is shown to enter the person's nasal passage and travel to the lungs. This is labeled "Inhalation of radon decay products." A small coiled, helical structure next to the torso is labeled "alpha particle" on one section where it has a starburst pattern and "Radiation damage to D N A" on another segment.

Radon is found in buildings across the country, with amounts dependent on location. The average concentration of radon inside houses in the US (1.25 pCi/L) is about three times the level found in outside air, and about one in six houses have radon levels high enough that remediation efforts to reduce the radon concentration are recommended. Exposure to radon increases one's risk of getting cancer (especially lung cancer), and high radon levels can be as bad for health as smoking a carton of cigarettes a day. Radon is the number one cause of lung cancer in nonsmokers and the second leading cause of lung cancer overall. Radon exposure is believed to cause over 20,000 deaths in the US per year.

Measuring Radiation Exposure

Several different devices are used to detect and measure radiation, including Geiger counters, scintillation counters (scintillators), and radiation dosimeters (Figure 15.4.6). Probably the best-known radiation instrument, the Geiger counter (also called the Geiger-Müller counter) detects and measures radiation. Radiation causes the ionization of the gas in a Geiger-Müller tube. The rate of ionization is proportional to the amount of radiation. A scintillation counter contains a scintillator—a material that emits light (luminesces) when excited by ionizing radiation—and a sensor that converts the light into an electric signal. Radiation dosimeters also measure ionizing radiation and are often used to determine personal radiation exposure. Commonly used types are electronic, film badge, thermoluminescent, and quartz fiber dosimeters.



(a) (b) (c)

Figure 15.4.6: Devices such as (a) Geiger counters, (b) scintillators, and (c) dosimeters can be used to measure radiation. (Credit c: modification of work by “osaMu”/Wikimedia commons.)

Three photographs are shown and labeled “a,” “b” and “c.” Photo a shows a Geiger counter sitting on a table. It is made up of a metal box with a read-out screen and a wire leading away from the box connected to a sensor wand. Photograph b shows a collection of tall and short vertical tubes arranged in a grouping while photograph c shows a person’s hand holding a small machine with a digital readout while standing on the edge of a roadway.

A variety of units are used to measure various aspects of radiation (Table 15.4.1). The SI unit for rate of radioactive decay is the becquerel (Bq), with 1 Bq = 1 disintegration per second. The curie (Ci) and millicurie (mCi) are much larger units and are frequently used in medicine (1 curie = 1 Ci = 3.7×10^{10} disintegrations per second). The SI unit for measuring radiation dose is the gray (Gy), with 1 Gy = 1 J of energy absorbed per kilogram of tissue. In medical applications, the radiation absorbed dose (rad) is more often used (1 rad = 0.01 Gy; 1 rad results in the absorption of 0.01 J/kg of tissue). The SI unit measuring tissue damage caused by radiation is the sievert (Sv). This takes into account both the energy and the biological effects of the type of radiation involved in the radiation dose.

Table 15.4.1: Units Used for Measuring Radiation

Measurement Purpose	Unit	Quantity Measured	Description
activity of source	becquerel (Bq)	radioactive decays or emissions	amount of sample that undergoes 1 decay/second
	curie (Ci)		amount of sample that undergoes 3.7×10^{10} decays/second
absorbed dose	gray (Gy)	energy absorbed per kg of tissue	1 Gy = 1 J/kg tissue
	radiation absorbed dose (rad)		1 rad = 0.01 J/kg tissue
biologically effective dose	sievert (Sv)	tissue damage	Sv = RBE × Gy
	roentgen equivalent for man (rem)		Rem = RBE × rad

The roentgen equivalent for man (rem) is the unit for radiation damage that is used most frequently in medicine (1 rem = 1 Sv). Note that the tissue damage units (rem or Sv) includes the energy of the radiation dose (rad or Gy), along with a biological factor referred to as the RBE (for relative biological effectiveness), that is an approximate measure of the relative damage done by the radiation. These are related by:

$$\text{number of rems} = \text{RBE} \times \text{number of rads} \tag{15.4.1}$$

with RBE approximately 10 for α radiation, 2(+) for protons and neutrons, and 1 for β and γ radiation.

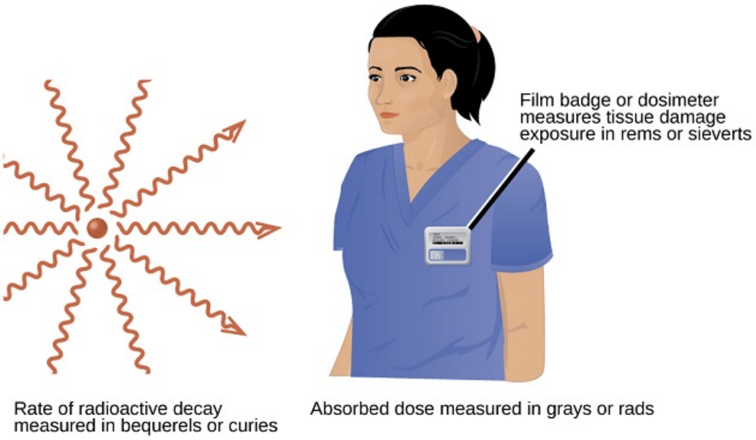


Figure 15.4.7: Different units are used to measure the rate of emission from a radioactive source, the energy that is absorbed from the source, and the amount of damage the absorbed radiation does. (CC by 4.0; OpenStax)

Two images are shown. The first, labeled "Rate of radioactive decay measured in becquerels or curies," shows a red sphere with ten red squiggly arrows facing away from it in a 360 degree circle. The second image shows the head and torso of a woman wearing medical scrubs with a badge on her chest. The caption to the badge reads "Film badge or dosimeter measures tissue damage exposure in rems or sieverts" while a phrase under this image states "Absorbed dose measured in grays or rads."

✓ Example 15.4.1: Amount of Radiation

Cobalt-60 ($t_{1/2}$ = 5.26 y) is used in cancer therapy since the γ rays it emits can be focused in small areas where the cancer is located. A 5.00-g sample of Co-60 is available for cancer treatment.

a. What is its activity in Bq?
b. What is its activity in Ci?

Solution

The activity is given by:

$$\text{Activity} = \lambda N = \left(\frac{\ln 2}{t_{1/2}}\right) N = \left(\frac{\ln 2}{5.26\text{ y}}\right) \times 5.00\text{ g} = 0.659\ \frac{\text{g}}{\text{y}}\text{ of }^{60}\text{Co that decay}$$

And to convert this to decays per second:

$$0.659\ \frac{\text{g}}{\text{y}} \times \frac{\text{y}}{365\text{ day}} \times \frac{1\text{ day}}{24\text{ hours}} \times \frac{1\text{ h}}{3,600\text{ s}} \times \frac{1\text{ mol}}{59.9\text{ g}} \times \frac{6.02\times10^{23}\text{ atoms}}{1\text{ mol}} \times \frac{1\text{ decay}}{1\text{ atom}}$$

$$= 2.10\times10^{14}\ \frac{\text{decay}}{\text{s}}$$

(a) Since $1\text{ Bq} = 1\ \frac{\text{decay}}{\text{s}}$, the activity in Becquerel (Bq) is:

$$2.10\times10^{14}\frac{\text{decay}}{\text{s}} \times \left(\frac{1\text{ Bq}}{1\ \frac{\text{decay}}{\text{s}}}\right) = 2.10\times10^{14}\text{ Bq}$$

(b) Since $1\text{ Ci} = 3.7\times10^{11}\ \frac{\text{decay}}{\text{s}}$, the activity in curie (Ci) is:

$$2.10\times10^{14}\frac{\text{decay}}{\text{s}} \times \left(\frac{1\text{ Ci}}{3.7\times10^{11}\frac{\text{decay}}{\text{s}}}\right) = 5.7\times10^{2}\text{ Ci}$$

? Exercise 15.4.1

Tritium is a radioactive isotope of hydrogen ($t_{1/2} = 12.32$ years) that has several uses, including self-powered lighting, in which electrons emitted in tritium radioactive decay cause phosphorus to glow. Its nucleus contains one proton and two neutrons, and the atomic mass of tritium is 3.016 amu. What is the activity of a sample containing 1.00mg of tritium (a) in Bq and (b) in Ci?

Answer a

$3.56 \times 10^{11}\text{Bq}$

Answer b

$0.962\ \text{Ci}$

Effects of Long-term Radiation Exposure on the Human Body

The effects of radiation depend on the type, energy, and location of the radiation source, and the length of exposure. As shown in Figure $15.4.8$, the average person is exposed to background radiation, including cosmic rays from the sun and radon from uranium in the ground (see the Chemistry in Everyday Life feature on Radon Exposure); radiation from medical exposure, including CAT scans, radioisotope tests, X-rays, and so on; and small amounts of radiation from other human activities, such as airplane flights (which are bombarded by increased numbers of cosmic rays in the upper atmosphere), radioactivity from consumer products, and a variety of radionuclides that enter our bodies when we breathe (for example, carbon-14) or through the food chain (for example, potassium-40, strontium-90, and iodine-131).

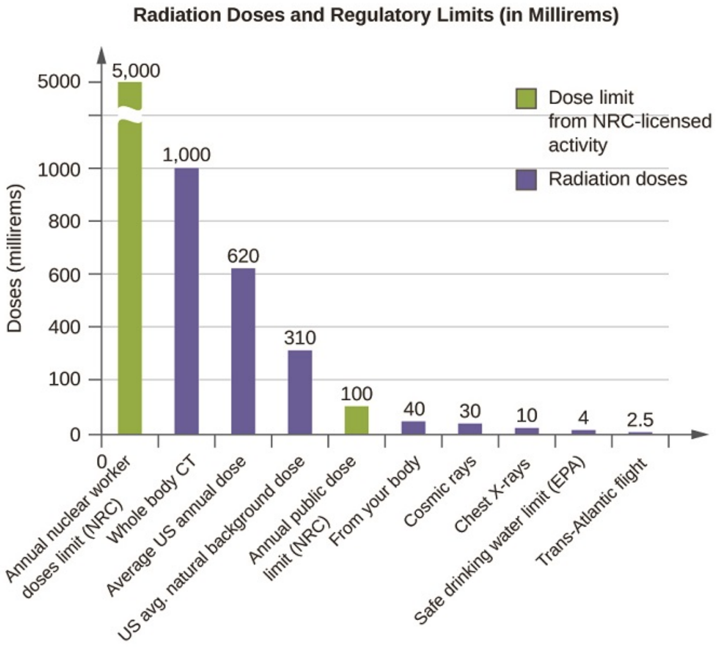


Figure $15.4.8$: The total annual radiation exposure for a person in the US is about 620 mrem. The various sources and their relative amounts are shown in this bar graph. (source: U.S. Nuclear Regulatory Commission).

A bar graph titled “Radiation Doses and Regulatory Limits, open parenthesis, in Millirems, close parenthesis” is shown. The y-axis is labeled “Doses in Millirems” and has values from 0 to 5000 with a break between 1000 and 5000 to indicate a different scale to the top of the graph. The y-axis is labeled corresponding to each bar. The first bar, measured to 5000 on the y-axis, is drawn in red and is labeled “Annual Nuclear Worker Doses Limit, open parenthesis, N R C, close parenthesis.” The second bar, measured to 1000 on the y-axis, is drawn in blue and is labeled “Whole Body C T” while the third bar, measured to 620 on the y-axis, is drawn in blue and is labeled “Average U period S period Annual Dose.” The fourth bar, measured to 310 on the y-axis, is drawn in blue and is labeled “U period S period Natural Background Dose” while the fifth bar, measured to 100 on the y-axis and drawn in red reads “Annual Public Dose Limit, open parenthesis, N R C, close parenthesis.” The sixth bar, measured to 40 on the y-axis, is drawn in blue and is labeled “From Your Body” while the seventh bar, measured to 30 on the y-axis and drawn in blue reads “Cosmic rays.” The eighth bar, measured to 4 on the y-axis, is drawn in blue and is labeled “Safe Drinking Water Limit, open parenthesis, E P A, close parenthesis” while the ninth bar, measured to 2.5 on the y-axis and drawn in red reads “Trans Atlantic Flight.” A legend on the graph shows that red means “Dose Limit From N R C dash licensed activity” while blue means “Radiation Doses.”

A short-term, sudden dose of a large amount of radiation can cause a wide range of health effects, from changes in blood chemistry to death. Short-term exposure to tens of rems of radiation will likely cause very noticeable symptoms or illness; a dose of about 500 rems is estimated to have a 50% probability of causing the death of the victim within 30 days of exposure. Exposure to radioactive emissions has a cumulative effect on the body during a person’s lifetime, which is another reason why it is important to avoid any unnecessary exposure to radiation. Health effects of short-term exposure to radiation are shown in Table $15.4.2$.

Table 15.4.2: Health Effects of Radiation

Exposure (rem)	Health Effect	Time to Onset (Without Treatment)
5–10	changes in blood chemistry	—
50	nausea	hours
55	fatigue	—
70	vomiting	—
75	hair loss	2–3 weeks
90	diarrhea	—
100	hemorrhage	—
400	possible death	within 2 months
1000	destruction of intestinal lining	—
	internal bleeding	—
	death	1–2 weeks
2000	damage to central nervous system	—
	loss of consciousness	minutes
	death	hours to days

It is impossible to avoid some exposure to ionizing radiation. We are constantly exposed to background radiation from a variety of natural sources, including cosmic radiation, rocks, medical procedures, consumer products, and even our own atoms. We can minimize our exposure by blocking or shielding the radiation, moving farther from the source, and limiting the time of exposure.

Summary

We are constantly exposed to radiation from a variety of naturally occurring and human-produced sources. This radiation can affect living organisms. Ionizing radiation is the most harmful because it can ionize molecules or break chemical bonds, which damages the molecule and causes malfunctions in cell processes. It can also create reactive hydroxyl radicals that damage biological molecules and disrupt physiological processes. Radiation can cause somatic or genetic damage, and is most harmful to rapidly reproducing cells. Types of radiation differ in their ability to penetrate material and damage tissue, with alpha particles the least penetrating, but potentially most damaging, and gamma rays the most penetrating.

Various devices, including Geiger counters, scintillators, and dosimeters, are used to detect and measure radiation, and monitor radiation exposure. We use several units to measure radiation: becquerels or curies for rates of radioactive decay; gray or rads for energy absorbed; and rems or sieverts for biological effects of radiation. Exposure to radiation can cause a wide range of health effects, from minor to severe, including death. We can minimize the effects of radiation by shielding with dense materials such as lead, moving away from the source of radiation, and limiting time of exposure.

Footnotes

1. 1 Source: US Environmental Protection Agency

Glossary

becquerel (Bq)

SI unit for rate of radioactive decay; 1 Bq = 1 disintegration/s.

curie (Ci)

Larger unit for rate of radioactive decay frequently used in medicine; 1 Ci = 3.7×10^{10} disintegrations/s.

Geiger counter

Instrument that detects and measures radiation via the ionization produced in a Geiger-Müller tube.

gray (Gy)

SI unit for measuring radiation dose; 1 Gy = 1 J absorbed/kg tissue.

ionizing radiation

Radiation that can cause a molecule to lose an electron and form an ion.

millicurie (mCi)

Larger unit for rate of radioactive decay frequently used in medicine; 1 Ci = 3.7×10^{10} disintegrations/s.

nonionizing radiation

Radiation that speeds up the movement of atoms and molecules; it is equivalent to heating a sample, but is not energetic enough to cause the ionization of molecules.

radiation absorbed dose (rad)

SI unit for measuring radiation dose, frequently used in medical applications; 1 rad = 0.01 Gy.

radiation dosimeter

Device that measures ionizing radiation and is used to determine personal radiation exposure.

relative biological effectiveness (RBE)

Measure of the relative damage done by radiation.

roentgen equivalent man (rem)

Unit for radiation damage, frequently used in medicine; 1 rem = 1 Sv.

scintillation counter

Instrument that uses a scintillator—a material that emits light when excited by ionizing radiation—to detect and measure radiation.

sievert (Sv)

SI unit measuring tissue damage caused by radiation; takes energy and biological effects of radiation into account.

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CHAPTER OVERVIEW

16: Macromolecules

Macromolecules are a very large molecules, such as protein, commonly created by polymerization of smaller subunits (monomers). They are typically composed of thousands or more atoms.

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