CH 215: CHEMISTRY OF THE ELEMENTS, FALL 2023



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CH 215: Chemistry of the Elements, Fall 2023

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1.1: Quantum Mechanics and Wavefunctions

Estimated Time to Read: 6 min

Quantum Mechanics

Electrons and other subatomic particles behave as both particles and waves. An individual particle like an electron has mass, but it is spread out, not located in one position, and it has a wavelength. The wavelike nature of electrons and other subatomic particles, as well as the paradox described by Heisenberg's uncertainty principle, made it impossible to use the equations of classical physics to describe the motion of electrons in atoms. Scientists needed a new approach that took the wave behavior of the electron into account.

In 1926, an Austrian physicist, Erwin Schrödinger (1887–1961; Nobel Prize in Physics, 1933), developed *wave mechanics*, a mathematical technique that describes the relationship between the motion of a particle that exhibits wavelike properties and its allowed energies. Schrödinger's wave equation allowed scientists to make predictions about the electronic structure of atoms. Where are the electrons found? What is their energy?

Although quantum mechanics uses sophisticated mathematics, you do not need to understand the mathematical details to follow our discussion of its general conclusions. We focus on the properties of the *wavefunctions* that are the solutions of Schrödinger's equations.

Erwin Schrödinger (1887–1961)

Schrödinger's unconventional approach to atomic theory was typical of his unconventional approach to life. He was notorious for his intense dislike of memorizing data and learning from books. When Hitler came to power in Germany, Schrödinger escaped to Italy. He then worked at Princeton University in the United States but eventually moved to the Institute for Advanced Studies in Dublin, Ireland, where he remained until his retirement in 1955.

Wavefunctions

A wavefunction (Ψ) is a mathematical function that relates the location of an electron and the energy of the electron. A wavefunction uses three variables to describe the position of an electron in space (as with the Cartesian coordinates *x*, *y*, and *z*). A fourth variable specifies the time at which the electron is at the specified location.

By analogy, if you were the captain of a ship trying to intercept an enemy submarine, you would need to know its latitude, longitude, and depth, as well as the time at which it was going to be at this position (Figure **1.1.1**). For electrons, we can ignore the time dependence because we will be using standing waves, which by definition do not change with time, to describe the position of an electron.

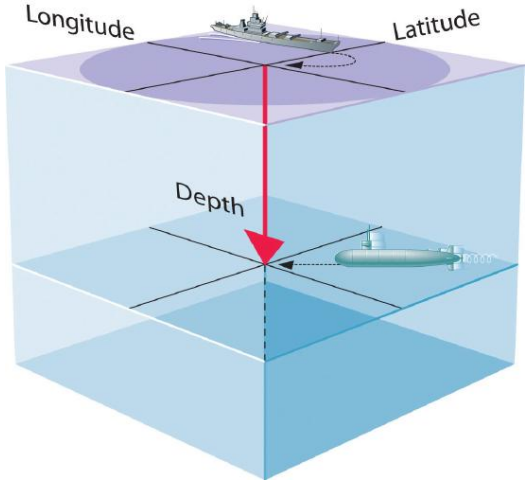


Figure 1.1.1: The Four Variables (Latitude, Longitude, Depth, and Time) required to precisely locate an object

The magnitude of the wavefunction at a particular point in space is proportional to the amplitude of the wavefunction at that point. Many wavefunctions are complex functions, which means that they contain $\sqrt{-1}$, represented as i. Hence the amplitude of the wave has no real physical significance.

In contrast, the sign of the wavefunction (either positive or negative) corresponds to the phase of the wave, which will be important in our discussion of chemical bonding. The sign of the wavefunction should *not* be confused with a positive or negative electrical charge.

The square of the wavefunction at a given point in space is proportional to the probability of finding an electron at that point in space. (The square of the wavefunction (Ψ^2) is always a real quantity [recall that that $\sqrt{-1}^2 = -1$]) The probability of finding an electron at any point in space depends on several factors, including the distance from the nucleus and, in many cases, the atomic equivalent of latitude and longitude. One way of graphically representing the probability distribution is demonstrated in Figure **1.1.2** for a hydrogen atom. The probability of finding an electron is indicated by the density of colored dots.

Schrödinger's approach treats electrons as three-dimensional standing waves. It is a requirement of standing waves that they be in phase with one another to avoid cancellation; this results in a limited number of solutions (wavefunctions), each of which is associated with a particular energy. As in Bohr's model, the energy of an electron in an atom is quantized; it can have only certain allowed values, which are specified by the quantum numbers. Quantum numbers define solutions to the Schrödinger equation. The major difference between Bohr's model and Schrödinger's approach is that Bohr had to impose the idea of quantization arbitrarily, whereas in Schrödinger's approach, quantization is a natural consequence of describing an electron as a standing wave.

Adrien Legendre (1752–1783)

As you might expect, the patterns of three-dimensional standing waves are complicated. However, in the 18th century a French mathematician, Adrien Legendre (1752–1783), developed a set of equations to describe the motion of tidal waves on the surface of a flooded planet. Schrödinger incorporated Legendre's equations into his wavefunctions.

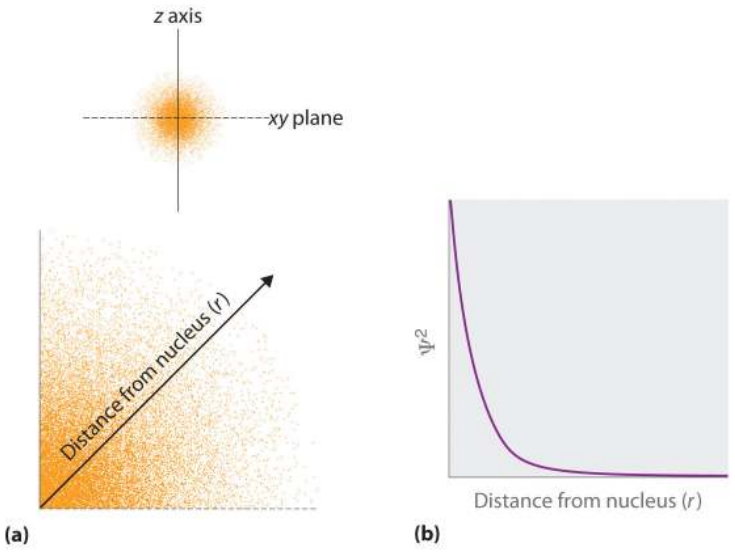


Figure 1.1.2: Probability of Finding the Electron in the Ground State of the Hydrogen Atom at Different Points in Space. (a) The density of the dots shows electron probability. (b) In this plot of Ψ^2 versus r for the ground state of the hydrogen atom, the electron probability density is greatest at $r = 0$ (the nucleus) and falls off with increasing r. Because the line never actually reaches the horizontal axis, the probability of finding the electron at very large values of r is very small but *not* zero.

The *wavefunction* is a mathematical expression that describes the electron. It can be plotted as a three-dimensionional graph. The three-dimensional plot of the wavefunction is sometimes called an *orbital*. Often, chemists find it useful to look at pictures of orbitals in order to gain some sense of where electrons may be and how they may behave. In another sense, orbitals are probability maps that reveal the probability of an electron being located at a particular position in space.

Suppose you could take a series of photos of an electron and superimpose all of those pictures, like time-lapse photography. The result might look something like the drawing in Figure **1.1.2**, in which every dot represents where the electron showed up in one of the photos. It's impossible to predict exactly where the electron would show up in the next photo, but it would be a pretty good guess that it would show up somewhere in the same rough circle as it did all of the other times.



1s

Figure 1.1.3: Probability map, or orbital, of a wavefunction. Each dots represents the probability of an electron being located at that point in space at a moment in time. (https://employees.csbsju.edu/cschall...tomnumbers.htm; Chris Schaller)

In three-dimensional space, the probability map (or *orbital)* shown in Figure **1.1.3** would be a sphere instead of a circle. The probability map shown can be interpreted as a thin slice through the middle of the probability sphere. The orbital shown is specifically an s orbital. In the very center of the sphere, is the nucleus of the atom. The electron is found within a certain distance of the nucleus, but it can be found in any direction. Other electrons will have different distributions about the nucleus of the atom, resulting in other orbital shapes in three-dimensional space. Quantum numbers will be used to describe the various orbitals, the probability of finding an electron at a point in space and roughly how much energy the electron has.

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1.2: Quantum Numbers

Estimated Time to Read: 7 min

Quantum Numbers

Schrödinger's approach uses four quantum numbers (n, l, m_l, and m_s) to specify any wavefunction. The first three quantum numbers (n, l, and m_l) provide information about the spatial distribution of an electron. Although n can be any positive integer, only certain values of l, m_l, and m_s are allowed for a given value of n.

The Principal Quantum Number

The **principal quantum number** (n) tells the average relative distance of an electron from the nucleus. Its value can be any positive integer:

$$n = 1, 2, 3, 4, \ldots \tag{1.2.1}$$

As n 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 wavefunctions that have the same value of n are said to constitute a principal shell because those electrons have similar average distances from the nucleus. 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 Angular Momentum (or Azimuthal) Quantum Number

The **angular momentum quantum number** (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 $n - 1$:

$$l = 0, 1, 2, \ldots, n - 1 \tag{1.2.2}$$

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 wavefunctions that have the same values of both n and l form a subshell. The regions of space occupied by electrons in the same subshell usually have the same shape, but they are oriented differently in space.



Principal quantum number (n) and angular momentum (l): The Orbital Subshell: Principal quantum number (n) and angular momentum (l): The Orbital Subshell [youtu.be]

The Magnetic Quantum Number

The **magnetic quantum number** (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:

$$m_l = -l, -l + 1, \ldots, 0, \ldots, l - 1, l \tag{1.2.3}$$

For example, if $l = 0$, then m_l 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 wavefunction with an allowed combination of n, l, and m_l values describes an atomic *orbital*, 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.

The Spin Quantum Number

Scientists analyzed the emission and absorption spectra of the elements closely and saw that for elements having more than one electron, nearly all the lines in the spectra were actually *pairs* of very closely spaced lines. Each line in the spectra represents an energy level available to electrons in the atom; pairs of lines resulted in twice as many energy levels as would be predicted solely based on the quantum numbers n, l, and m_l. Scientists also discovered that applying a magnetic field caused the lines in the pairs to split farther apart. In 1925, two graduate students in physics in the Netherlands, 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**.

In an external magnetic field, the electron has two possible orientations (Figure Figure **1.2.1**). It can align with the magnetic field or against it. These orientations are described by the **spin quantum number**, m_s, which can have a value of +½ (spin up) and −½ (spin down) to indicate that the two orientations are opposites. The value of m_s does not depend on the other three quantum numbers. Spin is significant in that it allows two electrons to occupy the same orbital. Two electrons can have the same values for n, l, and m_l but opposite spin values that allow them to occupy the same orbital. Thus, each orbital can hold one pair of electrons, each with a different spin quantum number value. Every electron in an atom must have a unique set of quantum number. If n, m, and l are the same for two electrons, then m_s must be different.

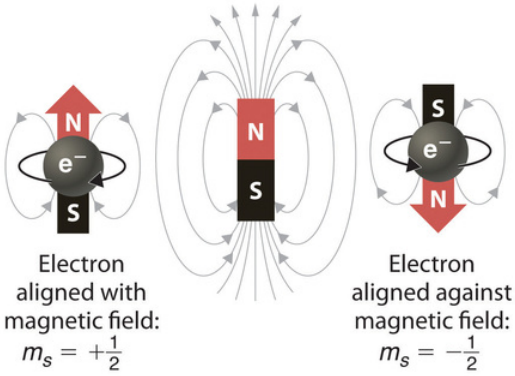


Figure 1.2.1: Electron Spin. In a magnetic field, an electron has two possible orientations with different energies, one with spin up, aligned with the magnetic field, and one with spin down, aligned against it. All other orientations are forbidden.



Magnetic Quantum Number (m_l) & Spin Quantum Number (m_s): Magnetic Quantum Number (ml) & Spin Quantum Number (ms) [youtu.be]

Exercise 1.2.1: n = 3 Shell Structure

How many subshells are contained within the principal shell with $n = 3$?

Hint

Given $n = 3$, calculate the allowed values of l. From these allowed values, count the number of subshells.

Answer

If $n = 3$, then l can equal 0, 1, or 2. Because the shell has four values of l, it has three subshells.

Exercise 1.2.2: n = 3 Shell Structure

How many orbitals are contained within the principal shell with $n = 3$?

Hint

For each allowed value of l, calculate the allowed values of m_l. The sum of the number of orbitals in each subshell is the number of orbitals in the principal shell.

Answer

If $n = 3$, then l can equal 0, 1, or 2.

When $l = 0$, then m_l can be only 0. Thus, the $l = 0$ subshell has only one orbital.

When $l = 1$, then m_l can be 0 or ±1. The $l = 1$ subshell has three orbitals.

When $l = 2$, then m_l can be 0, ±1, or ±2. The $l = 2$ subshell has five orbitals

The total number of orbitals in the $n = 3$ principal shell is the sum of the number of orbitals in each subshell (1 + 3 + 5 = 9).

The total number of orbitals is equal to n^2 ($3^2 = 9$).

Exercise 1.2.3: n = 4 Subshell Structure

How many orbitals are contained within the principal shell with $n = 4$?

Hint

For each allowed value of l, calculate the allowed values of m_l. The sum of the number of orbitals in each subshell is the number of orbitals in the principal shell.

Answer

If $n = 4$, then l can equal 0, 1, 2, or 3.

When $l = 0$, then m_l can be only 0. Thus, the $l = 0$ subshell has only one orbital.

When $l = 1$, then m_l can be 0 or ±1. The $l = 1$ subshell has three orbitals.

When $l = 2$, then m_l can be 0, ±1, or ±2. The $l = 2$ subshell has five orbitals

When $l = 3$, then m_l can be 0, ±1, ±2, or ±3. The $l = 3$ subshell has seven orbitals.

The total number of orbitals in the $n = 4$ principal shell is the sum of the number of orbitals in each subshell (1 + 3 + 5 + 7 = 16) and is also equal to n^2 ($4^2 = 16$)

? Exercise 1.2.4: l = 5 Shell Structure

How many orbitals are contained within the subshell with $l = 5$?

Hint

For the specified value of l, calculate the allowed values of m_l.

Answer

If $l = 5$, then m_l can equal 0, ±1, ±2, ±3, ±4, ±5. Thus, the $l = 5$ subshell has eleven orbitals.

The total number of orbitals is equal to $2l + 1$ ((2 x 5) + 1 = 11).

Describing an Orbital

Each orbital in an atom is described by a set of three values for n, l, and m_l. Typically when defining an orbital scientists will use an abbreviated system to refer to an orbital or subshell, rather than specifying the values of n, l , and m_l.

In this system, the principal quantum number n is named first and is followed by a lowercase letter to denote the value of the angular momentum quantum number l (Table **1.2.1**) (These orbital designations are derived from historical terms for corresponding spectroscopic characteristics: *s*harp, *p*rinciple, *d*iffuse, and *f*undamental.)

Table **1.2.1**: Values of angular momentum quantum number, l, and corresponding abbreviations.

l	0	1	2	3
abbreviation	s	p	d	f

A 2*p* subshell has $n = 2$ and $l = 1$. A 2*p* subshell has three orbitals, which correspond to $m_l = -1$, 0, and +1. In the abbreviatiod system, the three orbitals are denoted with a subscript lower case letter that represents an orientation in space (Table **1.2.2**). For a 2*p* subshell, the three orbitals are denoted as $2p_x$, $2p_y$, and $2p_z$. The correlation between m_l and a specific orientation in space is beyond the scope of this course.

Table **1.2.2**: Values of magnetic quantum number, m_l, and corresponding abbreviations.

l	m_l	abbreviation
2 (*p*)	0, ±1	*x*, *y*, z
3 (*d*)	0, ±1, ±2	*xz*, *yz*, *xy*, x^2-y^2, z^2

Summary

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*).

Every shell has an *ns* subshell. Any shell with $n \geq 2$ also has an *np* subshell, and any shell with $n \geq 3$ also has an *nd* subshell.

Each subshell has 2*l* + 1 orbitals

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.

✓ Example 1.2.5

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.

Hint

List the quantum numbers (n, l) that correspond to an $n = 2p$ orbital. Then list the allowed combinations of n, l, and m_l. Use the allowed values of m_s to determine the maximum number of electrons in each $2p$ subshell.

Answer

For a $2p$ orbital, we know that $n = 2$, $l = 1$, 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). 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). Hence the $2p$ subshell, which consists of three $2p$ orbitals ($2p_x$, $2p_y$, and $2p_z$), can contain a total of six electrons, two in each orbital.

? Exercise 1.2.6

List all the allowed combinations of the four quantum numbers (n, l, m_l, m_s) for a $6s$ orbital, and predict the total number of electrons it can contain.

Hint

List the quantum numbers (n, l) that correspond to an $n = 6s$ orbital. Then list the allowed combinations of n, l, and m_l. Use the allowed values of m_s to determine the maximum number of electrons in each $6s$ subshell.

Answer

For a $6s$ orbital, we know that $n = 6$, $l = 0$, and $m_l = -l, (-l + 1), \ldots, (l - 1), l$. There is only one possible combinations of (n, l, m_l): (6, 0, 0)Because m_s is independent of the other quantum numbers and can have values of only +½ and −½, there are two possible combinations of (n, l, m_l, m_s): (6, 0, 0, +½) and (6, 0, 0, −½). Hence the $6s$ subshell, which consists of one $6s$ orbital and can contain a total of two electrons.

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1.3: Probability Density and Nodes

Estimated Time to Read: 6 min

Atomic orbitals are mathematically derived regions of space with different probabilities of containing an electron. An orbital can be viewed as a probability map of finding an electron at a specific point in space.

Probability Density

One way of representing electron probability distributions was illustrated previously for the 1*s* orbital of hydrogen. Ψ^2 gives the probability of finding an electron in a given volume of space, and a plot of Ψ^2 versus distance from the nucleus (r) is a plot of the *probability density*. The 1*s* orbital is spherically symmetrical so the probability of finding a 1*s* electron at any given point depends only on its distance from the nucleus. The probability density is greatest at $r = 0$ (at the nucleus) and decreases steadily with increasing distance. At very large values of r, the electron probability density is very small but is not equal to zero.

Radial Probability Density

The *radial probability density* is the probability of finding an electron at a distance r from the nucleus. It is calculated by adding together the probabilities of an electron being at all points on a series of spherical shells of radius r_1, r_2, r_3,…, r_{x-1}, r_x. In effect, the atom is divided into very thin concentric shells, much like the layers of an onion (Figure **1.3.1*a***), and the radial probability density calculates the probability of finding an electron on each spherical Layer. Although the electron probability density is greatest at $r = 0$ (Figure **1.3.1*b***), is lowest at $r = 0$(Figure **1.3.1*c***). The surface area of the spherical shells increases more rapidly with r than the electron probability density decreases; therefore, the plot of radial probability has a maximum at a particular distance (Figure **1.3.1*d***).

> Overall, when r is very small, the surface area of a spherical shell is so small that the total probability of finding an electron close to the nucleus is very low; at the nucleus, the electron probability vanishes (Figure **1.3.1*d***).

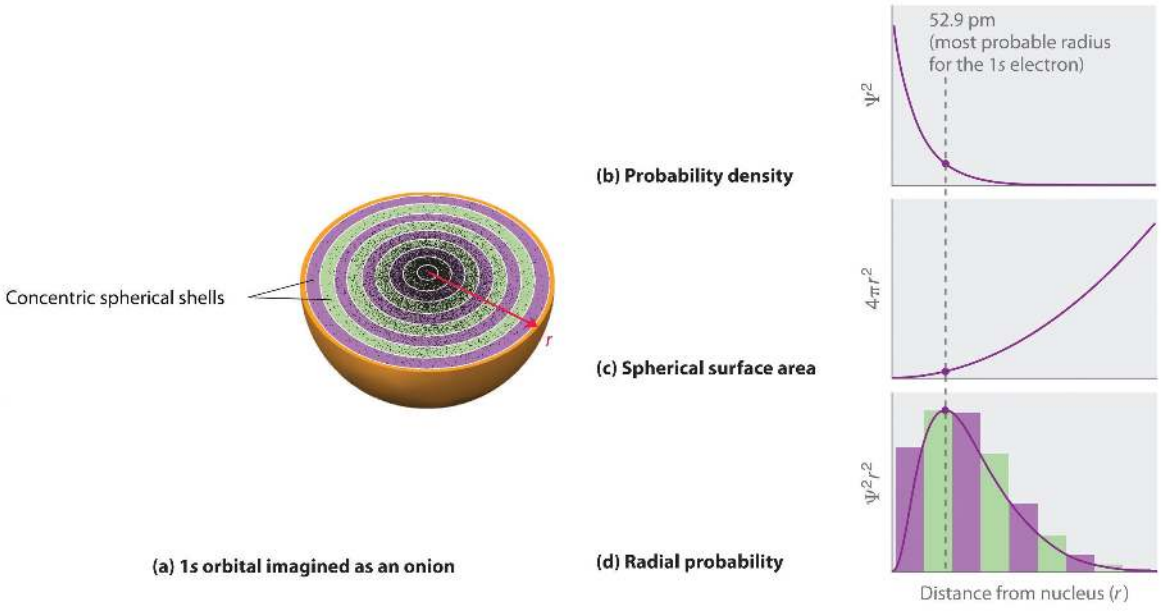


Figure 1.3.1: Most Probable Radius for the Electron in the Ground State of the Hydrogen Atom. (a) Imagine dividing the atom's total volume into very thin concentric shells as shown in the onion drawing. (b) A plot of electron probability density Ψ^2 versus r shows that the electron probability density is greatest at $r = 0$ and falls off smoothly with increasing r. The density of the dots is therefore greatest in the innermost shells of the onion. (c) The surface area of each shell, given by $4\pi r^2$, increases rapidly with increasing r. (d) If we count the number of dots in each spherical shell, we obtain the total probability of finding the electron at a given value of r. Because the surface area of each shell increases more rapidly with increasing r than the electron probability density decreases, a plot of electron probability versus r (the *radial probability density* plot) shows a peak. This peak corresponds to the most probable radius for the electron, 52.9 pm, which is exactly the radius predicted by Bohr's model of the hydrogen atom.

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.

Nodes

Radial Nodes

Figure **1.3.2** compares the electron probability densities for the hydrogen 1*s*, 2*s*, and 3*s* orbitals. Note that all three are spherically symmetrical. Figure **1.3.2***c* shows that the 2*s* and 3*s* orbitals, the radial probability density does not fall off smoothly with increasing *r*. Instead, a series of minima and maxima are observed in the radial probability plots. The minima correspond to spherical *nodes*, which are regions with zero electron probability that alternate with spherical regions of nonzero electron probability. The existence of these nodes is a consequence of changes of wave *phase* in the wavefunction Ψ. These spherical nodes, which separate electron shells, are known as *radial nodes*. The number of *radial nodes* depends on the energy level of the orbital (n) and on the shape of the orbital (l). The number of radial nodes is equal to $n - l - 1$.

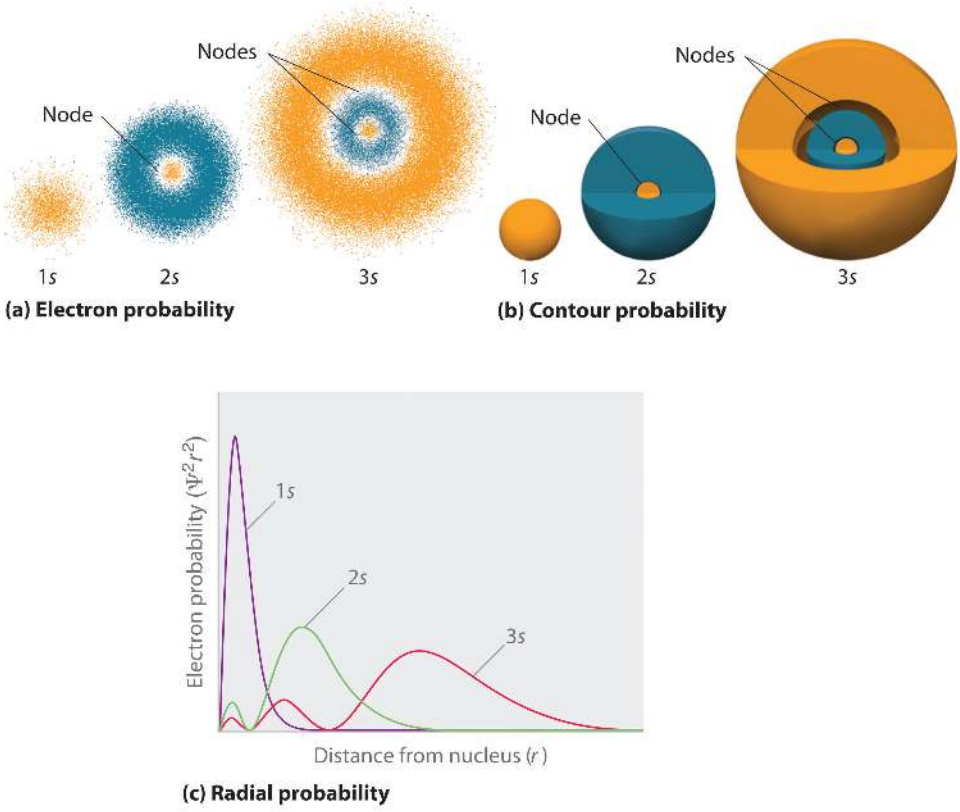


Figure 1.3.2: Probability Densities for the 1**s**, 2**s**, and 3**s** Orbitals of the Hydrogen Atom. (a) The electron probability density in any plane that contains the nucleus is shown. Note the presence of circular regions, or nodes, where the probability density is zero. (b) Contour surfaces enclose 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.

Angular Nodes

Angular nodes are planar nodes that are a result of the shape of an orbital. The number of angular nodes in any orbital is equal to l. For s-orbitals ($l = 0$) so they have zero angular nodes. For p-orbitals ($l = 1$) so they have one angular node, and for d-orbitals ($l = 2$)

so they have two angular nodes. Planar nodes can be flat planes (like the nodes in all p orbitals) or they can have a conical shape, like the two angular nodes in the d_{z^2} orbital. Angular nodes in some p and d orbitals are shown in Figure **1.3.3**.

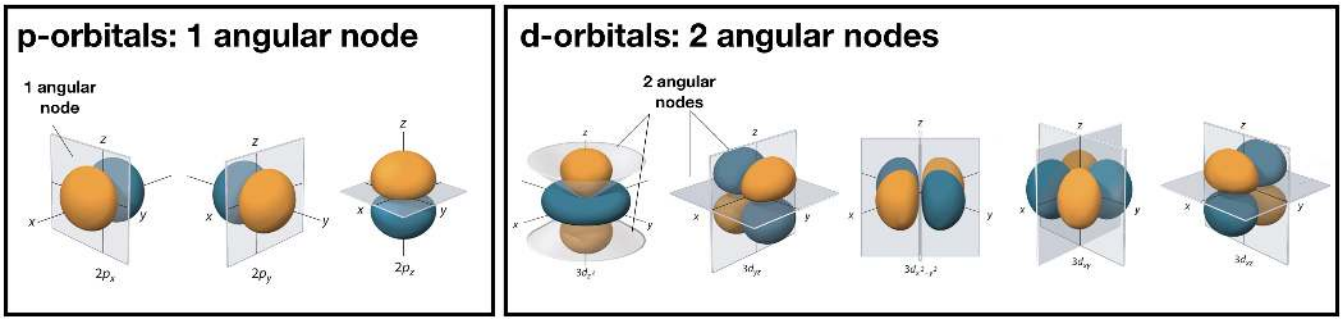


Figure 1.3.3: The angular nodes in p-orbitals and d-orbitals. Every p orbital has one angular node, and every d orbital has two angular nodes. The number of angular nodes in any orbital is equal to the value of the quantum number, l. (CC BY-NC-SA; anonymous by request)

? Exercise 1.3.1

How many radial nodes are in the s, p, d, and f orbitals in the first four shells? $n = 1, 2, 3, 4$? Do you notice any patterns in your answers?

Hint

You can use the mathematical relationship between the number of radial nodes and the values of n and l: number of radial nodes is $n - 1 - l$.

Answer: s orbitals

1s: $n - 1 - l = 1 - 1 - 0 = 0$, zero radial nodes

2s: $n - 1 - l = 2 - 1 - 0 = 1$, one radial node

3s: $n - 1 - l = 3 - 1 - 0 = 2$, two radial nodes

4s: $n - 1 - l = 4 - 1 - 0 = 3$, three radial nodes

Answer: p orbitals

2p: $n - 1 - l = 2 - 1 - 1 = 0$, zero radial nodes

3p: $n - 1 - l = 3 - 1 - 1 = 1$, one radial node

4p: $n - 1 - l = 4 - 1 - 1 = 2$, two radial nodes

Answer: d orbitals

3d: $n - 1 - l = 3 - 1 - 2 = 0$, zero radial nodes

4d: $n - 1 - l = 4 - 1 - 2 = 1$, one radial nodes

Answer: f orbitals

4f: $n - 1 - l = 4 - 1 - 3 = 0$, zero radial nodes

Answer: patterns

You may notice the pattern that the first orbital of any type (1s, 2p, 3d...) has zero radial nodes, the second orbital of a type (2s, 3p, 4d...) has one radial node, the third orbital of a type has two radial nodes (3s, 4p, 5d...)...etc.

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1.4: Representations of Atomic Orbitals

Estimated Time to Read: 5 min

Atomic Orbitals

Three things happen to atomic orbitals as *n* increases:

1. They become larger, extending farther from the nucleus.
2. They become higher in energy because of their increased distance from the nucleus.
3. They contain more radial nodes.

s Orbitals (l=0)

s orbitals are spherically symmetrical. They have no angular nodes but may have radial nodes.

Orbitals are generally drawn as three-dimensional surfaces that enclose 90% of the electron density, as was shown for the hydrogen 1*s*, 2*s*, and 3*s* orbitals in Figure 1.3.2b. 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.

p Orbitals (l=1)

As the value of *l* increases, the number of orbitals in a given subshell increases, and the shapes of the orbitals become more complex. p orbitals have a two-lobed shape split by an angular nodal plane. p orbitals may have radial nodes, depending on the value of *n*.

For the 2*p* subshell $l = 1$, so there are three values of m_l (−1, 0, and +1), and there are three 2*p* orbitals. Figure **1.4.1** depicts a 2*p* orbital.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 $\mathbf{2p_z}$ orbital.

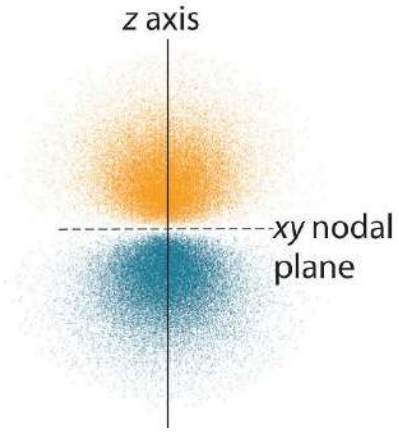


Figure 1.4.1: Electron probability distribution for a 2*p* Orbital. The nodal plane of zero electron density separates the two lobes of the 2*p* orbital. The colors correspond to regions of space where the phase of the wave function is positive (orange) and negative (blue).

Figure **1.4.2** shows the contour surfaces, which enclose 90% of the total electron probability, for all three 2*p* orbitals. All orbitals have identical shapes 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. Each orbital is oriented along the axis indicated by the subscript, and the nodal plane that is perpendicular to that axis bisects each 2*p* orbital. The shapes of the 90% probability surfaces of the 3*p*, 4*p*, and higher-energy *p* orbitals are essentially the same as those shown in Figure **1.4.2**.

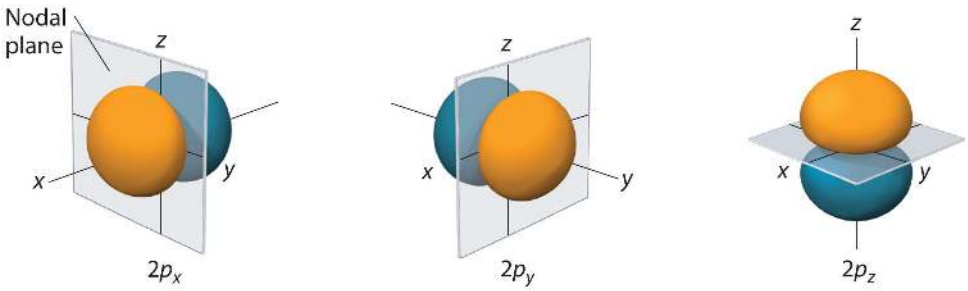


Figure 1.4.2: Three equivalent 2*p* orbitals of the hydrogen atom. The surfaces shown enclose 90% of the total electron probability for the three hydrogen 2p orbitals. These three orbitals have the same shape but different orientations. Each orbital consist of two lobes arranged along an axis that is bisected by a perpendicular nodal plane. The colors correspond to regions of space where the phase of the wave function is positive (orange) and negative (blue).

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.

The hydrogen 3d orbitals, shown in Figure **1.4.3**, 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. For three of the d orbitals, the lobes of electron density are oriented between the xy, xz, and yz 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 $3d_{x^2-y^2}$ 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. For the (dz^2\) orbital, the phase of the wave function is positive for the two lobes that lie along the z axis, and 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 **1.4.3**.

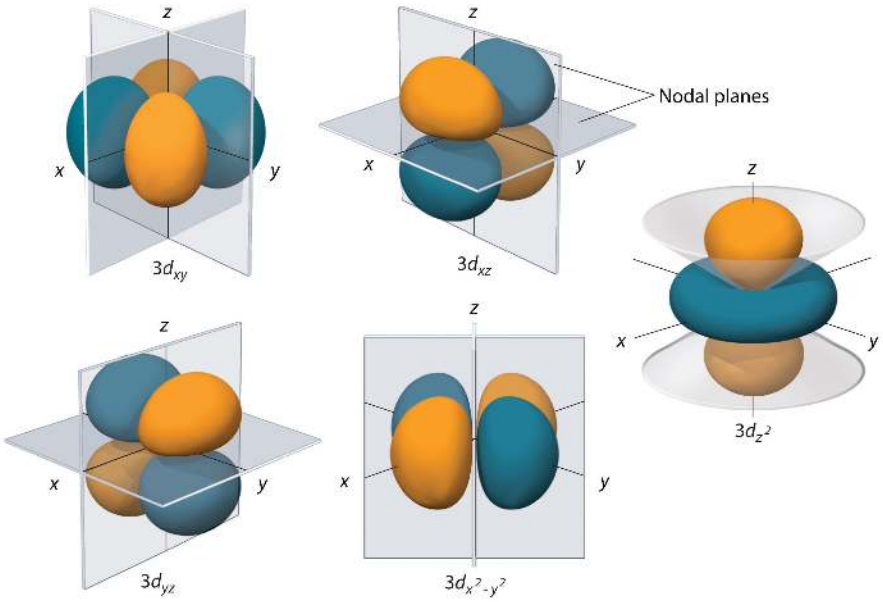


Figure 1.4.3: Five equivalent 3d orbitals of the hydrogen atom. The surfaces shown enclose 90% of the total electron probability for the five hydrogen 3d orbitals. Four of the five 3d orbitals consist of four lobes arranged in a plane that is intersected by two perpendicular nodal planes. These four 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 colors correspond to regions of space where the phase of the wave function is positive (orange) and negative (blue).

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. Because f orbitals are not particularly important for our purposes, we do not discuss them further, and orbitals with higher values of l are not discussed at all.

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1.5: Energies of Atomic Orbitals

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Single-Electron Atoms

Although we have discussed the shapes of orbitals, we have said little about their comparative energies. We begin our discussion of orbital energies by considering atoms or ions with only a single electron (such as H or He^+).

The relative energies of the atomic orbitals with $n \le 4$ for a hydrogen atom are shown in Figure **1.5.1**. 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. Quantum mechanics predicts that in the hydrogen atom, all orbitals with the same value of *n* (ex. the three 2*p* orbitals) are *degenerate*, meaning that they have the same energy.

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 for the $n = 2$ shell there are 4 orbitals with different electron density distributions (one 2*s* and three 2*p* orbitals). Likewise, for the $n = 3$ principal shell there are 9 orbitals (one 3*s*, three 3*p*, and five 3*d* orbitals), and for the $n = 4$ shell there are 16 orbitals (one 4*s*, three 4*p*, five 4*d*, and seven 4*f* orbitals). Figure **1.5.1** shows 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.

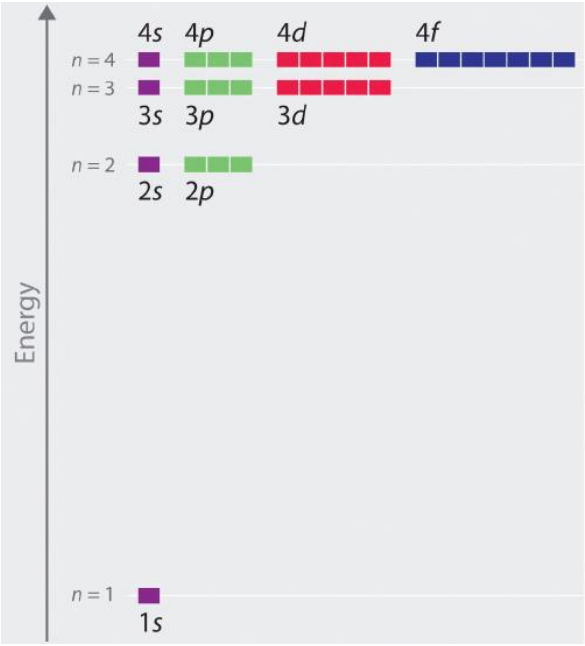


Figure 1.5.1: Orbital energy level diagram for the hydrogen atom with a single electron. Each box corresponds to one orbital. Note that the difference in energy between orbitals decreases rapidly with increasing values of *n*.

The energies of the orbitals in any species with only one electron can be calculated by a minor variation of Bohr's equation, which can be extended to other single-electron species by incorporating the nuclear charge Z (the number of protons in the nucleus):

$$E = -\frac{Z^2}{n^2} Rhc \tag{1.5.1}$$

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 p_x, p_y, and p_z orbitals, are degenerate.

Multi-Electron Atoms

Unlike in hydrogen-like atoms with only one electron, in multielectron atoms the values of quantum numbers *n and l* determine the energies of an orbital. The energies of the different orbitals for a typical multielectron atom are shown in Figure **1.5.21**. Within a given principal shell of a multielectron atom, the orbital energies increase with increasing *l*. An *ns* orbital always lies below the corresponding *np* orbital, which in turn lies below the *nd* orbital.

These energy differences are caused by the effects of *shielding* and *penetration*, the extent to which a given orbital lies inside other filled orbitals. For example, an electron in the 2*s* orbital penetrates inside a filled 1*s* orbital more than an electron in a 2*p* orbital does. Since electrons, all being negatively charged, repel each other, an electron closer to the nucleus partially *shields* an electron farther from the nucleus from the attractive effect of the positively charged nucleus. Hence in an atom with a filled 1*s* orbital, the effective nuclear charge (Z_{eff}) experienced by a 2*s* electron is greater than the Z_{eff} experienced by a 2*p* electron. Consequently, the 2*s* electron is more tightly bound to the nucleus and has a lower energy, consistent with the order of energies shown in Figure **1.5.2**. We will discuss *shielding* and *penetration* in more detail in a later section. For now, you should note that the energies of different orbitals in the same shell varies depending on the shapes of the orbitals. As the shapes become more complex, they allow less electron density near the nucleus, which destabilizes the electrons, and increases the energy of the orbital.

Notice in Figure **1.5.2** that the difference in energies between subshells can be so large that the energies of orbitals from different principal shells can become approximately equal. For example, the energy of the 3*d* orbitals in most atoms is actually *between* the energies of the 4*s* and the 4*p* orbitals.



Figure **1.5.2**: Orbital energy level diagram for a typical multielectron atom. Each box corresponds to one orbital.

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1.6: Rules Governing Ground State Electron Configurations

Estimated Time to Read: 4 min

Introduction

In addition to having different energy levels, orbitals also have different shapes and orientations, and each can be occupied by two electrons. For each principal quantum number, *n*, there is up to one *s* orbital, three *p* orbitals, five *d* orbitals and seven *f* orbitals. Each orbital can hold up to two electrons of different spin (m_s = +1/2, -1/2); therefore, the *s* subshell can hold two electrons, the *p* subshell can hold six electrons, the *d* subshell can hold ten electrons, and the *f* subshell can hold 14 electrons.

The ground state electron configuration specifies the lowest-energy arrangement of electrons into subshells for a given element. Ground state electron configurations are the foundation for understanding molecular bonding, properties, and structures. The following rules explain how to determine the lowest energy arrangement of electrons into the orbitals. The ground state electron configurations contribute to a fundamental understanding of the periodic table and will later be used to understand different atomic properties.

The Aufbau Principle

The *Aufbau Principle* (also called the *building-up principle* or the *Aufbau rule*) states that, in the ground state of an atom or ion, electrons fill atomic orbitals of the lowest available energy level before occupying higher-energy levels Figure **1.6.1**. In general, an electron will occupy an atomic orbital with the lowest value of n, l, m_l, in that order of priority.

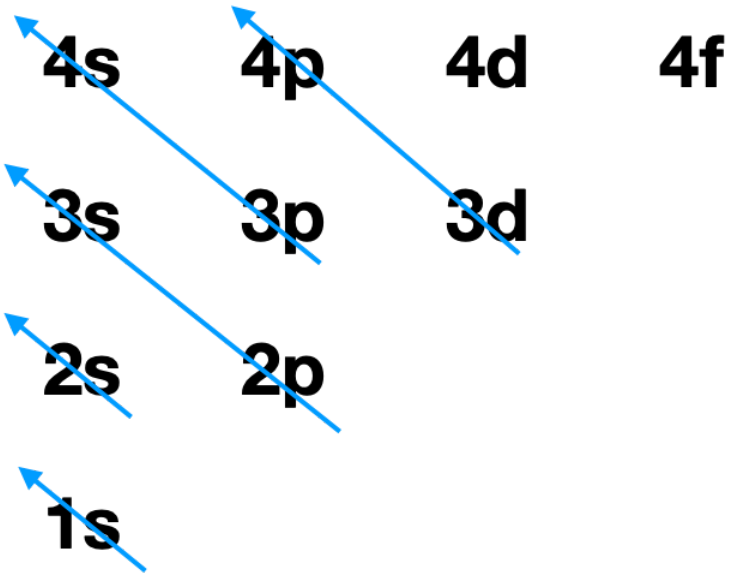


Figure 1.6.1: The order of filling of ground state electron orbitals is 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, etc... (CC-BY-NC-SA; Kathryn Haas)

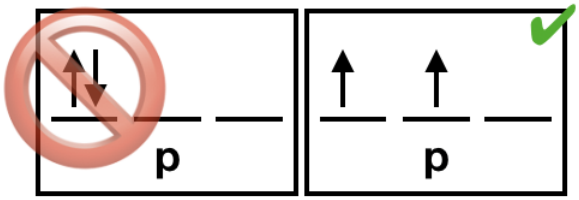
> Electrons will occupy the lowest energy orbitals in order to minimize the total energy. The two quantum numbers that are related to energy in multi-electron atoms are n, and l. Thus, orbitals with the lowest values of n and l will fill first.

Hund's Rule of Maximum Multiplicity

When electron fill into orbitals, the *multiplicity* refers to the number of unpaired electrons. *Multiplicity* is calculated as *n* + 1, where *n* is the number of unpaired electrons. *Hund's Rule of Maximum Multiplicity* states that for a given electron configuration, the lowest energy arrangement of electrons in degenerate orbitals is the arrangement with the greatest multiplicity (or the greatest number of unpaired electrons). This rule is used to predict the ground state of an atom or molecule with one or more open electronic shells.

Hund's rule is based on empirical observation of atomic spectra, and it is a consequence of the energy required to pair two electrons in the same orbital. This energy of repulsion between two electrons in the same orbitals is a Coulombic energy of repulsion, Π_c, caused by two electrons with like charge sharing the same area of space (an orbital). When more than one electron occupies a set of degenerate orbitals, the most favorable arrangement is one where the number of paired electrons is minimized.

A simplified definition of Hund's rule is that the lowest energy arrangement is the one with the greatest number of unpaired electrons. This implies that if two or more orbitals of equal energy are available, electrons will occupy them singly before filling them in pairs. Examples of ground state arrangements of electrons in three degenerate p-orbitals is given in Figure **1.6.2**.



# of electrons in a p-subshell	Arrangement (unpaired electrons, n)	Spin Multiplicity (n + 1)
1	↑ _ _ (n = 1)	2
2	↑ ↑ _ (n = 2)	3
3	↑ ↑ ↑ (n = 3)	4
4	↑↓ ↑ ↑ (n = 2)	3
5	↑↓ ↑↓ ↑ (n = 1)	2
6	↑↓ ↑↓ ↑↓ (n = 0)	1

Figure 1.6.2: Hund's rule is that the number of unpaired electrons (*multiplicity*) must be maximized in the ground state. (CC-BY-NC-SA; Libretexts)

The Pauli Exclusion Principle

The Pauli exclusion principle states that it is impossible for two electrons of a multi-electron atom to have the same set of values for all four quantum numbers. Two electrons in different orbitals will have a different set of n, l, and m_l values. When two electrons reside in the same orbital, they posses the same n, l, and m_l values, therefore their m_s must be different. Thus, two electrons in the same orbital must have opposite spin values of $+\frac{1}{2}$ and $-\frac{1}{2}$. The value of m_s for an unpaired electron is conventionally assigned a value of $+\frac{1}{2}$.

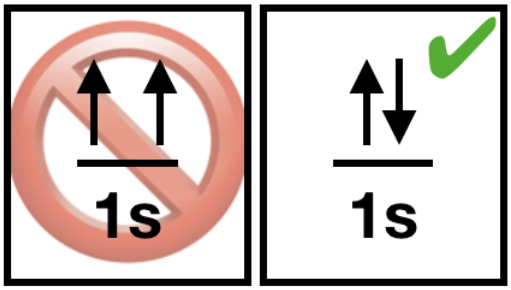


Figure 1.6.3: Pauli's principle tells us that paired electrons must have opposite spin. CC-BY-NC-SA; Libretexts)

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1.7: How to Write a Ground State Electron Configuration

Estimated Time to Read: 5 min

Basic Steps

Electron configurations list every subshell for an atom or ion and how many electrons are in each subshell. Subshells are described by writing the principal quantum number *n* followed by the symbol for the angular momentum quantum number *l* (s, p, d, or f). The the total number of electrons in each subshell is written as a superscript. The lowest energy subshell is written first, and additional subshells are written in order of increasing energy.

Example 1.7.1

Write the ground state electron configuration for sodium, Na.

Solution: Method 1

1. Find the number of electrons in the atom: Sodium has 11 electrons.
2. List the subshells following the model shown in Figure 1.6.3: 1s 2s 2p 3s
3. Fill the subshells until all electrons have been accounted for. Remember: each *s* subshell can hold 2 electrons, each *p* subshell can hold six electrons, each *d* subshell can hold 10 electrons, and each *f* subshell can hold 14 electrons: $1s^2\ 2s^2\ 2p^6\ 3s^1$

Solution: Method 2

1. Locate the atom on the periodic table.

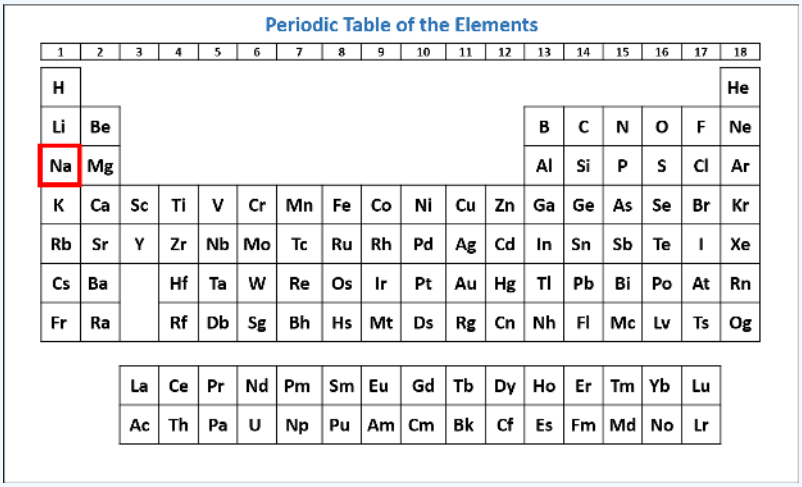


Figure 1.7.1: Periodic table of the elements with the location of sodium (Na) highlighted. (CC-BY-NC-SA; Kathryn A. Newton)

2. Starting at hydrogen and the 1s subshell, read across each row of the periodic table until you get to your chosen element. As you read across each row, list each subshell and the number of electrons in the subshell.

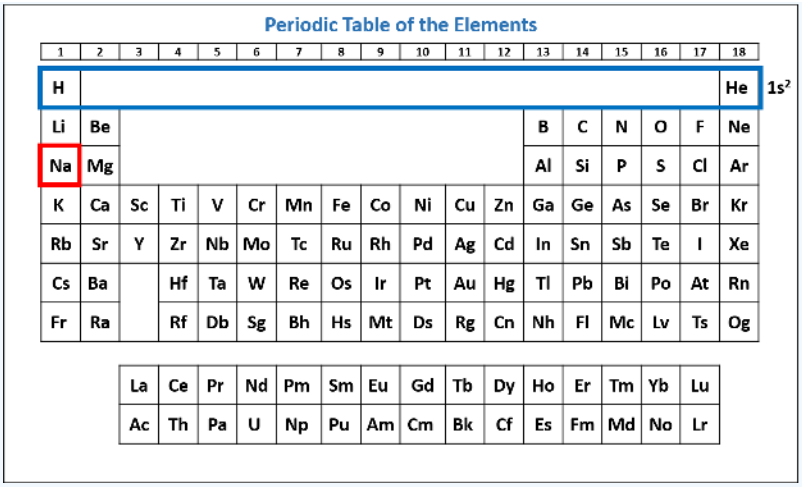


Figure 1.7.2: Periodic table of the elements with the $1s^2$ subshell highlighted. Na has two electrons in the 1s subshell. (CC-BY-NC-SA; Kathryn A. Newton)

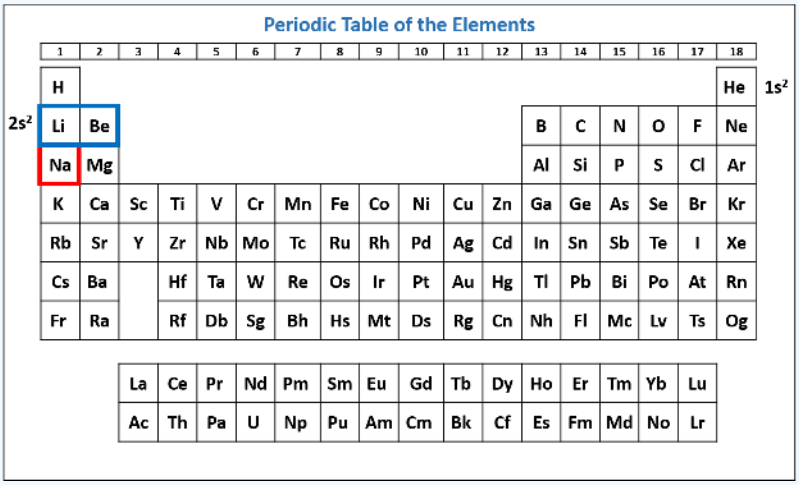


Figure 1.7.3: Periodic table of the elements with the $2s^2$ subshell highlighted. Na has two electrons in the 2s subshell. (CC-BY-NC-SA; Kathryn A. Newton)

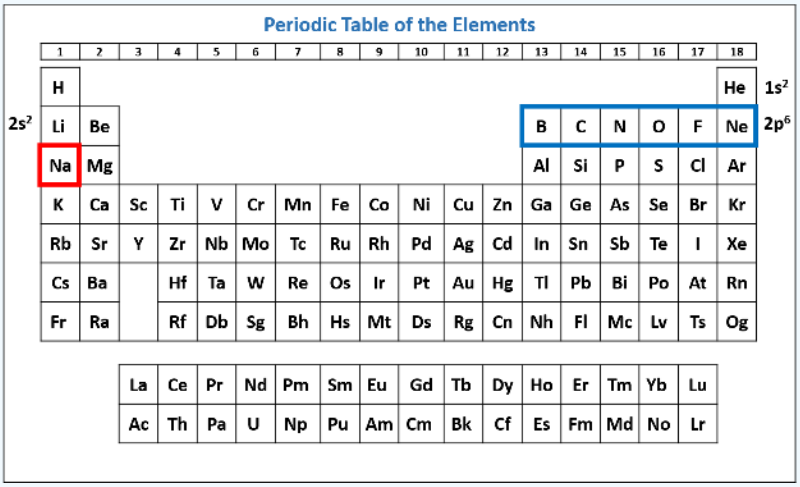


Figure 1.7.4: Periodic table of the elements with the $2p^6$ subshell highlighted. Na has six electrons in the 2p subshell. (CC-BY-NC-SA; Kathryn A. Newton)

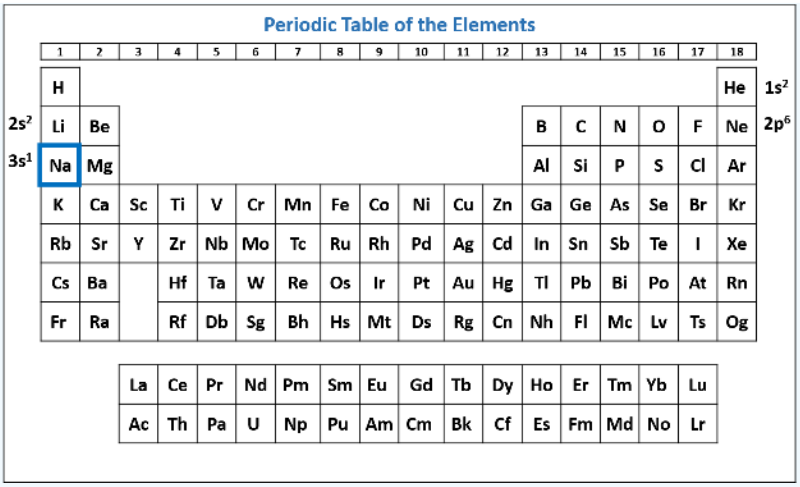


Figure 1.7.5: Periodic table of the elements with the $3s^1$ subshell highlighted. Na has one electron in the 3s subshell. (CC-BY-NC-SA; Kathryn A. Newton)

3. Combine the list into a single electron configuration. Na's electron configuration is $1s^2\ 2s^2\ 2p^6\ 3s^1$.

Noble Gas Configurations

Because writing the entire electron configuration can become cumbersome, there is a shorthand option. It is done by using the symbol of the noble gas in the period above the element to represent the electron configuration before it.

Example 1.7.2

Write the noble gas electron configuration for sodium (Na).

Solution

1. Locate the atom on the periodic table.

2. Locate the noble gas element in the period above the element of interest.

3. Continue the electron configuration from the noble gas until you reach the element of interest.

4. Put the noble gas in brackets and write the remainder of the electron configuration.

Na has the same electron configuration as Ne with the addition of $3s^1$.

Na's noble gas configuration is $[Ne]3s^1$.

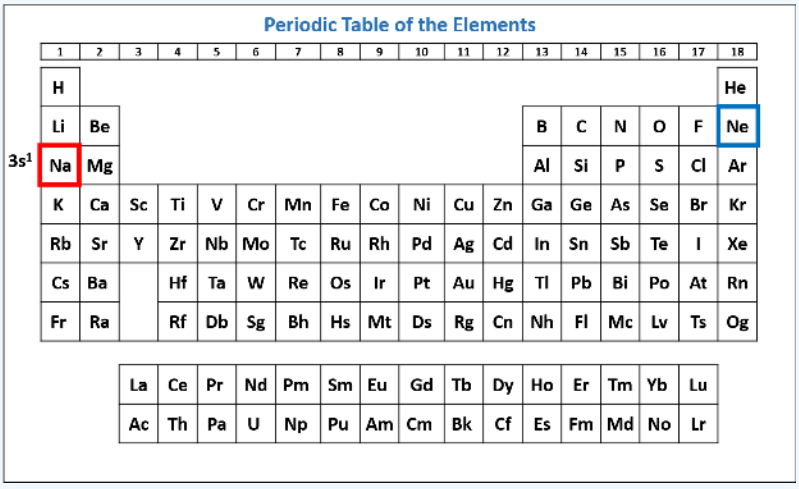


Figure 1.7.6: Periodic table of the elements with the locations of sodium (Na) and neon (Ne) highlighted. (CC-BY-NC-SA; Kathryn A. Newton)

Ion Configurations

Cations

Cations are formed when a neutral atom loses electrons. To write an electron configuration for a cation, start by writing the electron configuration for the neutral atom. Then determine the number of electrons that were lost to form the cation. (The loss of a single electron results in a +1 charge, the loss of two electrons results in a +2 charge, and so on.) Subtract the number of lost electrons from the highest energy shell in the neutral configuration. When there is more than one orbital with the same principal quantum number, the electrons will be removed from the *d* subshell before any are removed from the *p* subshell and will be removed from the *p* subshell before any are removed from *s* subshell.

Example 1.7.3

Write the electron configuration for Si^{4+}.

Solution

1. Write the configuration of the neutral atom. Si: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^2$
2. Determine how many electrons were lost. Si^{4+} was formed by the loss of four electrons.
3. Remove electrons from the highest shell, starting with the highest energy subshell.

   Si^{+}: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^{\mathbf{1}}$

   Si^{2+}: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^{\mathbf{0}}$

   Si^{3+}: $1s^2\ 2s^2\ 2p^6\ 3s^{\mathbf{1}}$

   Si^{4+}: $1s^2\ 2s^2\ 2p^6\ 3s^{\mathbf{0}}$, which is typically written as $1s^2\ 2s^2\ 2p^6$ or as [Ne]

Anions

Anions are formed when a neutral atom gains electrons. To write the electron configuraiton for a cation, start by writing the electron configuration for the neutral atom. Then determine the number of electrons that were added to form the anion. (The addition of a single electron results in a -1 charge, the addition of two electrons results in a -2 charge, and so on.) Add the additional electrons to the highest energy shell in the neutral configuration. When there is more than one orbital with the same principal quantum number, the electrons will be added to any partially filled subshells first, and any remaining electrons will be added to the *s* subshell before the *p* subshell before the *d* subshell.

Example 1.7.4

Write the electron configuration for As^{3-}.

Solution

1. Write the configuration of the neutral atom. As: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^3$
2. Determine how many electrons were gained. As^{3-} was formed by the addition of three electrons.
3. Add electrons from the highest shell, starting with any partially filled subshells.

   As^{-}: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^4$

   As^{2-}: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^5$

   As^{3-}: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6$ or [Kr]

Problems

? Exercise 1.7.1

Write the expanded and shortened ground state electron configuration for Cl.

Answer

Expanded: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$

Noble Gas: [Ne] $3s^2\ 3p^5$

? Exercise 1.7.2

Write the ground state electron configuration for P^{3-}.

Answer

Expanded: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$

Noble Gas: [Ar]

References

1. Housecroft, Catherine E. and Alan G. Sharpe, “Inorganic Chemistry,” 3rd ed. England: Pearson Education Limited: 2008.
2. Tro, Nivaldo J. “Chemistry: A Molecular Approach,” 8th ed. Upper Saddle River, New Jersey: Prentice Hall: 2007.
3. Silberberg, Martin S. "Chemistry: The Molecular Nature of Matter and Change," 4th ed. Boston: McGraw Hill: 2006.

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1.8: Magnetic Properties

Estimated Time to Read: 5 min

The magnetic moment of a system measures the strength and the direction of its magnetism. The term itself usually refers to the magnetic dipole moment. Anything that is magnetic, like a bar magnet or a loop of electric current, has a magnetic moment. A magnetic moment is a vector quantity, with a magnitude and a direction. An electron has an electron magnetic dipole moment, generated by the electron's intrinsic spin property, making it an electric charge in motion. There are many different magnetic forms: including paramagnetism, diamagnetism, ferromagnetism, and anti-ferromagnetism. Only paramagnetism and diamagnetism are discussed here.

Paramagnetism

Paramagnetism refers to the magnetic state of an atom with *one or more unpaired electrons*. The unpaired electrons are attracted by a magnetic field due to the electrons' magnetic dipole moments. Hund's Rule states that electrons must occupy every orbital singly before any orbital is doubly occupied. This may leave the atom with many unpaired electrons. Because unpaired electrons can orient in either direction, they exhibit magnetic moments that can align with a magnet. This capability allows paramagnetic atoms to be attracted to magnetic fields. Diatomic oxygen, O_2, is paramagnetic; it is attracted to the magnet. In contrast, molecular nitrogen, N_2, has no unpaired electrons and is diamagnetic (discussed below); it is therefore unaffected by the magnet.The following video shows liquid oxygen attracted into a magnetic field created by a strong magnet.



Liquid Oxygen is attracted to a magnetic field: Paramagnetism of Liquid Oxygen, YouTube(opens in new window) [youtu.be]

> Paramagnetism is a form of magnetism whereby materials are attracted to an externally applied magnetic field. Paramagnetic species have one or more unpaired electrons.

Diamagnetism

Diamagnetic species are characterized by paired electrons; they have *no unpaired electrons*. According to the Pauli Exclusion Principle which states that no two identical electrons may take up the same quantum state at the same time, the electron spins are oriented in opposite directions. This causes the magnetic fields of the electrons to cancel out. Thus, there is no net magnetic moment, and the atom cannot be attracted into a magnetic field. In fact, diamagnetic substances are weakly *repelled* by a magnetic field as demonstrated with the pyrolytic carbon sheet in Figure 1.8.1. Diamagnetism, to some degree, is a property of all materials and always makes a weak contribution to the material's response to a magnetic field. For materials that show other form of magnetism (such paramagnetism), the diamagnetic contribution becomes negligible.

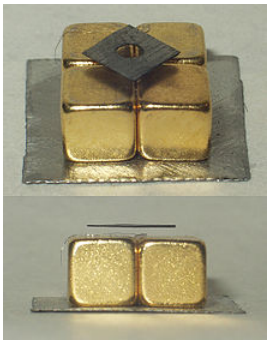


Figure 1.8.1: Levitating pyrolytic carbon: A small (~6 mm) piece of pyrolytic graphite levitating over a permanent neodymium magnet array (5 mm cubes on a piece of steel). Note that the poles of the magnets are aligned vertically and alternate (two with north facing up, and two with south facing up, diagonally). [Wikipedia]

Diamagnetic materials are repelled by an applied magnetic field. Diamagnetic species have no unpaired electrons.

How to determine if a substance is paramagnetic or diamagnetic

The magnetic form of a substance can be determined by examining its electron configuration. If it includes unpaired electrons, then the substance is paramagnetic. If all electrons are paired, then the substance is diamagnetic. This process can be broken into four steps:

1. Write the electron configuration
2. Draw the energy diagram for the valence orbitals by applying Hund's Rule
3. Look for unpaired electrons
4. Decide if the substance is paramagnetic (one or more electrons unpaired) or diamagnetic (all electrons paired)

Example 1.8.1: Chlorine

Are chlorine atoms paramagnetic or diamagnetic?

Solution

1. Write the electron configuration. Cl: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$
2. Draw the energy diagram for the valence orbitals.

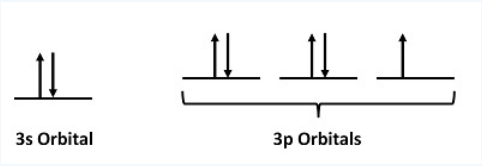


Figure 1.8.2: Energy diagram showing the valence orbitals of a Cl atom.

3. Look for unpaired electrons.
4. Determine whether the substance is paramagnetic or diamagnetic. Since there is an unpaired electron, the Cl atom is paramagnetic.

Example 1.8.2: Zinc

Are zinc atoms paramagnetic or diamagnetic?

Solution

1. Write the electron configuration. Zn: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}$
2. Draw the energy diagram for the valence orbitals.

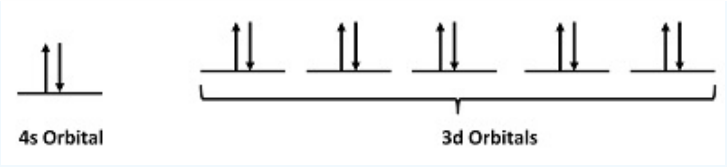
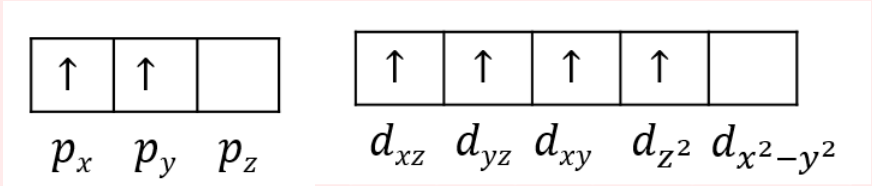


Figure 1.8.3: Energy diagram showing the valence orbitals of a Zn atom.

3. Look for unpaired electrons.
4. Determine whether the substance is paramagnetic or diamagnetic. Since there is are no unpaired electrons, the Zn atom is diamagnetic.

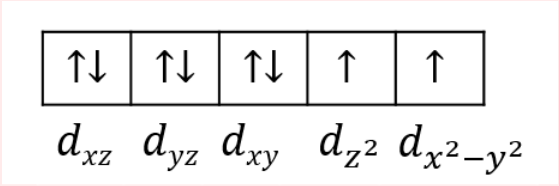
Caution

Having an even number of electrons in a subshell does not mean that all electrons in the subshell are paired! According to Hund's rule, no electrons will be paired until all orbitals in a subshell have at least one unpaired electron.



p^2 configuration

d^4 configuration



d^8 configuration

Figure 1.8.4: Energy diagrams showing diamagnetic electron configurations with even numbers of electrons in the subshell: p^2, d^4, d^8. (CC-BY-NC-SA; Kathryn A. Newton)



Determining Magnetic Properties from Orbital Diagrams, YouTube(opens in new window) [youtu.be]

Problems

Exercise 1.8.1

Decide if a boron atom is paramagnetic or diamagnetic.

Answer

B: $1s^2\ 2s^2\ 2p^1$

This configuration has one unpaired electron in the 2p subshell.Because it has one unpaired electron, it is paramagnetic

Exercise 1.8.2

Decide if a fluoride ion is paramagnetic or diamagnetic.

Answer

F: $1s^2\ 2s^2\ 2p^5$

F^-: $1s^2\ 2s^2\ 2p^6$

This configuration has no unpaired electrons. Because it has no unpaired electrons, it is diamagnetic.

Exercise 1.8.3

Decide if a bromine atom is paramagnetic or diamagnetic.

Answer

Br: [Ar] $4s^2\ 3d^{10}\ 4p^5$

This configuration has one unpaired electron in the 2p subshell (and four paired electrons). Because it has one unpaired electron, it is paramagnetic.

Exercise 1.8.1

Decide if Fe^{2+} is paramagnetic or diamagnetic.

Answer

Fe: [Ar] $4s^2\ 3d^6$

Fe^{2+}: [Ar] $3d^6$

This configuration has two paired electrons and four unpaired electrons in the 3d subshell. Because it has at least one unpaired electron, it is paramagnetic.

References

1. Pettrucci, Ralph H. General Chemistry: Principles and Modern Applications. 9th. Upper Saddle River: Pearson Prentice Hall, 2007
2. Sherman, Alan, Sharon J. Sherman, and Leonard Russikoff. Basic Concepts of Chemistry Fifth Edition. Boston, MA: Houghton Mifflin Company, 1992. Print.

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1.9: Electron Configurations for Transition Metal Elements

Estimated Time to Read: 6 min

Basic Steps

Writing an electron configuration for a transition metal element follows the same basic steps as for writing an electron configuration for an element in the s-block or p-block. List each subshell, and then fill each subshell with an appropriate number of electrons until all electrons in the element are accounted for. Transition elements have electrons in the d orbital, which introduces some additional nuance in the electron configurations. First, recall that the $n = 3$ shell is the first shell to have a *d* subshell. Second, recall that the 4s subshell is lower in energy than the 3d subshell. Thus, when filling electrons into orbitals the correct order of filling is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ \mathbf{4s^2\ 3d^{10}\ 4p^6}$. Similarly, the 5s will be filled before the 4d, and the 6s will be filled before the 5d.

Some elements in the d block will also have electrons in the *f* subshell. The $n = 4$ shell is the first shell to have a *f* subshell. Thus, the 6s subshell is lower in energy than the 4f subshell, and the correct order of filling is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^{10}\ 5p^6\ \mathbf{6s^2\ 4f^{14}\ 5d^{10}\ 6p^6}$. Similarly, the 7s will be filled before the 5f, which will be filled before the 6d subshell.

Example 1.9.1

Write the ground state electron configuration for vanadium (V).

Solution: Method 1

1. Find the number of electrons in the atom: Vanadium has 23 electrons.
2. List the subshells following the model shown in Figure 1.6.3: 1s 2s 2p 3s 3p 4s 3d
3. Fill the subshells until all electrons have been accounted for. Remember: each *s* subshell can hold 2 electrons, each *p* subshell can hold six electrons, each *d* subshell can hold 10 electrons, and each *f* subshell can hold 14 electrons: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^3$

Solution: Method 2

1. Locate the atom on the periodic table.

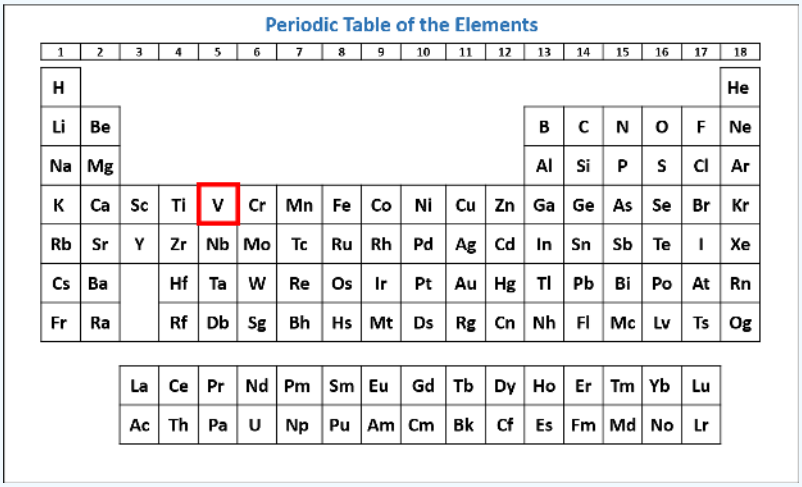


Figure 1.9.1: Periodic table of the elements with the location of vanadium (V) highlighted. (CC-BY-NC-SA; Kathryn A. Newton)

2. Starting at hydrogen and the 1s subshell, read across each row of the periodic table until you get to your chosen element. As you read across each row, list each subshell and the number of electrons in the subshell.

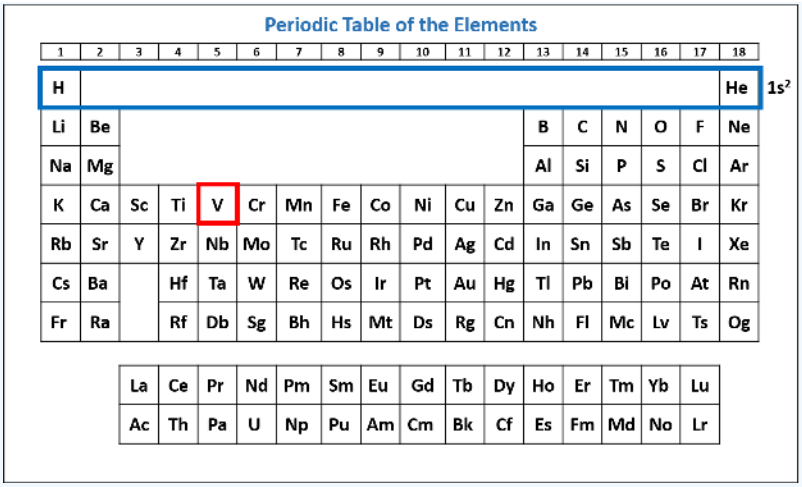


Figure 1.9.2: Periodic table of the elements with the $1s^2$ subshell highlighted. V has two electrons in the 1s subshell. (CC-BY-NC-SA; Kathryn A. Newton)

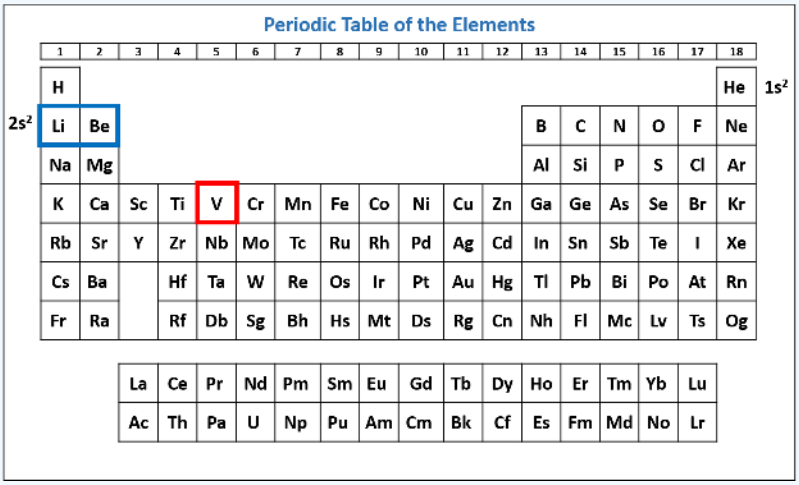


Figure 1.9.3: Periodic table of the elements with the $2s^2$ subshell highlighted. V has two electrons in the 2s subshell. (CC-BY-NC-SA; Kathryn A. Newton)

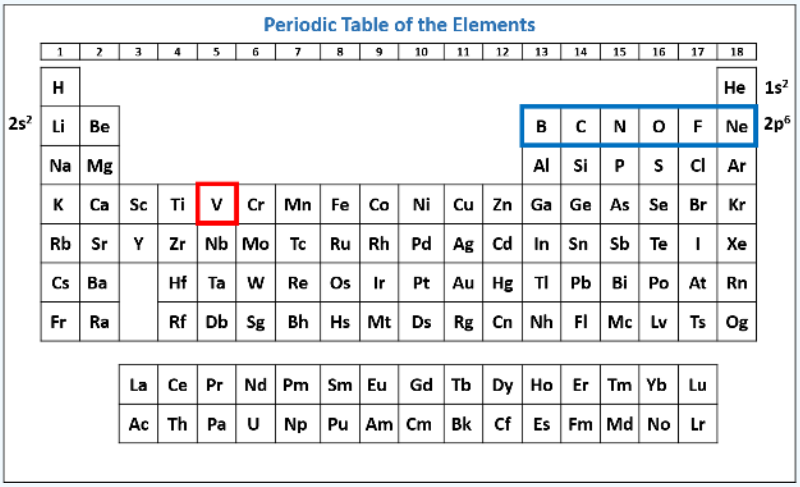


Figure 1.9.4: Periodic table of the elements with the $2p^6$ subshell highlighted. V has six electrons in the 2p subshell. (CC-BY-NC-SA; Kathryn A. Newton)

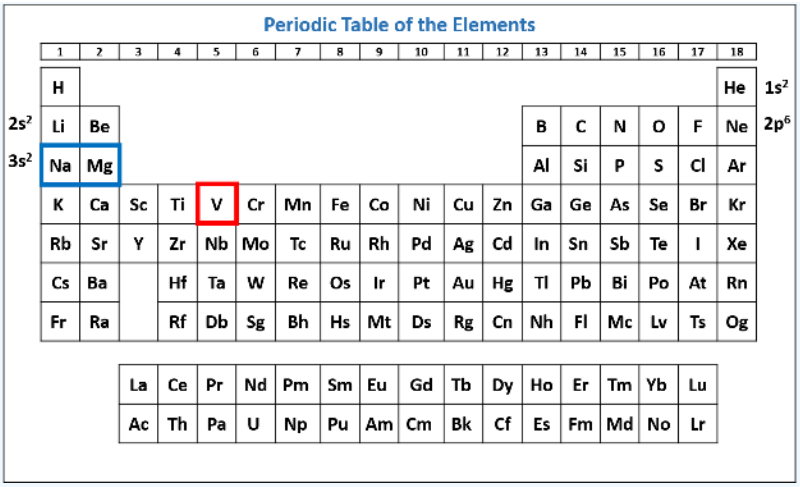


Figure 1.9.5: Periodic table of the elements with the $3s^2$ subshell highlighted. V has two electrons in the 3s subshell. (CC-BY-NC-SA; Kathryn A. Newton)

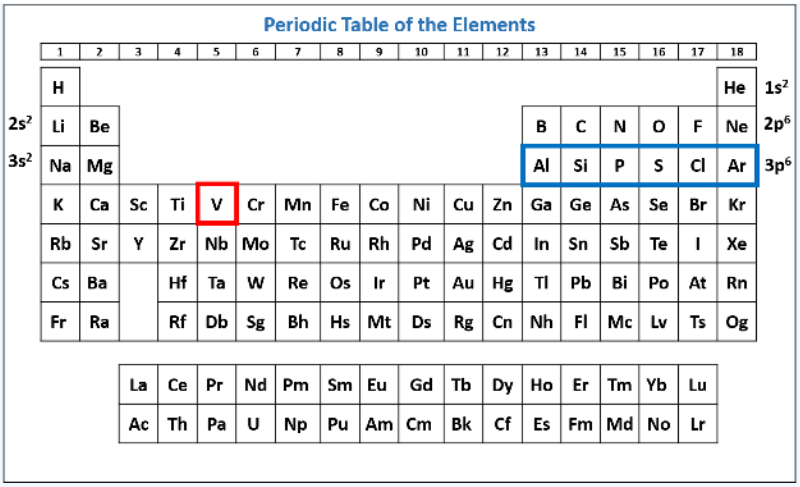


Figure 1.9.6: Periodic table of the elements with the $3p^6$ subshell highlighted. V has six electrons in the 3p subshell. (CC-BY-NC-SA; Kathryn A. Newton)

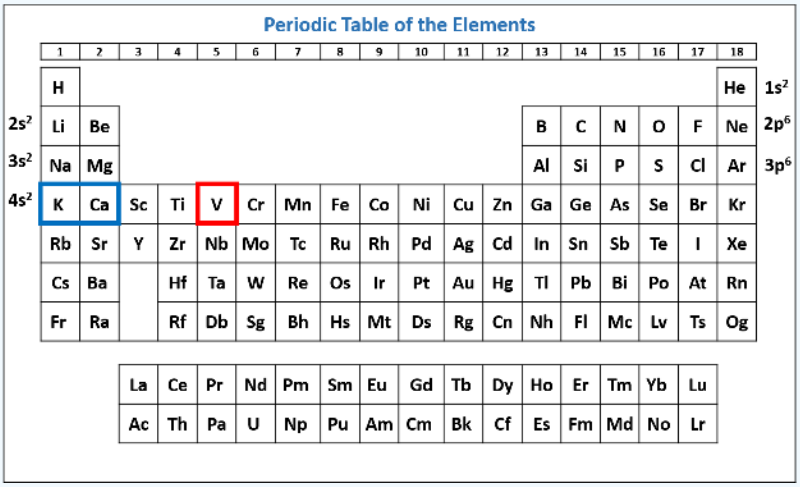


Figure 1.9.7: Periodic table of the elements with the $4s^2$ subshell highlighted. V has two electrons in the 4s subshell. (CC-BY-NC-SA; Kathryn A. Newton)

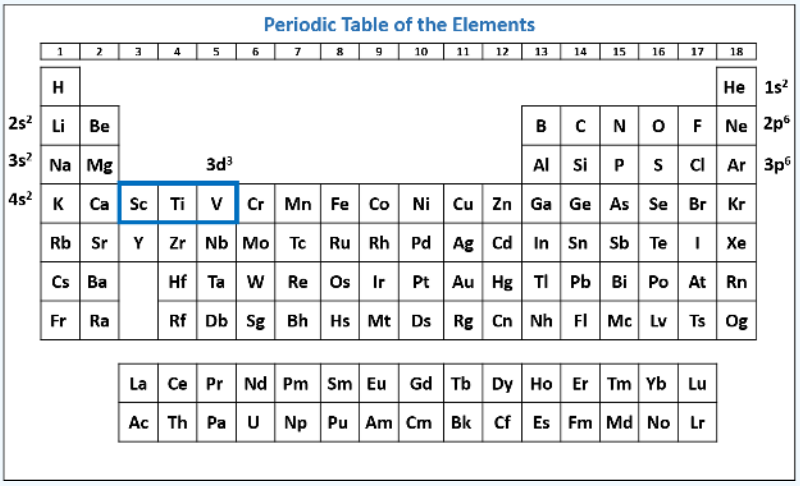


Figure 1.9.8: Periodic table of the elements with the $3d^3$ subshell highlighted. V has three electrons in the 3d subshell. (CC-BY-NC-SA; Kathryn A. Newton)

3. Combine the list into a single electron configuration. V's electron configuration is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^3$ or [Ar] $4s^2\ 3d^3$

Example 1.9.2

Write the ground state electron configuration for osmium (Os).

Solution

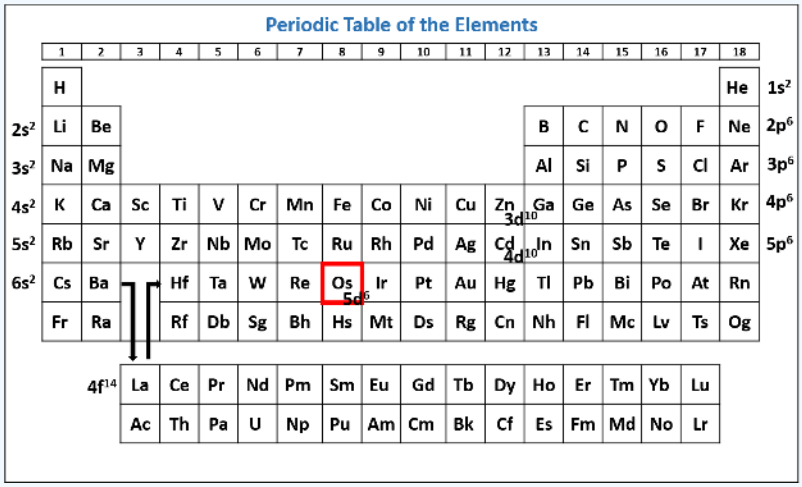


Figure 1.9.9: Periodic table of the elements showing the construction of the electron configuration of osmium (Os). (CC-BY-NC-SA; Kathryn A. Newton)

Exceptions to Expected Electron Configurations

There are some exceptions to the order of filling of orbitals that is shown in Figure 1.6.1. For example, the electron configurations of the transition metals chromium (Cr) and copper (Cu), are not those we would expect. Rather, Cr and Cu take on half-filled and fully-filled 3d configurations.

The electron configuration of chromium (Cr) includes a half-filled 3d subshell.

Cr: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^{\mathbf{1}}\ 3d^{\mathbf{5}}$

The electron configuration of copper (Cu) includes a fully-filled 3d subshell.

Cu: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^{\mathbf{1}}\ 3d^{\mathbf{10}}$

The actual electron configuration of these elements may be rationalized in terms of an added stability associated with a half-filled (ns^1, np^3, nd^5, nf^7) or filled (ns^2, np^6, nd^{10}, nf^{14}) subshell. In fact, this "special stability" is really another consequence of the *instability* caused by pairing an electron with another in the same orbital. (There are repulsive forces between two electrons in the same orbital.) Recall the small differences in energy between higher energy subshells. In the case of Cr, the repulsive forces between two electrons in the 4s would be greater than the energy gained by shifting an electron into the 3d. Thus, the added stability is enough to shift an electron from one orbital to another. In the case of Cu, the repulsive forces between two electrons in the 4s orbital is greater than between two electrons paired in a 3d orbital so one electron is shifted from the 4s to the 3d. In heavier elements, other more complex effects can also be important and lead to many additional anomalies. For example, cerium has an electron configuration of $[Xe]6s^24f^15d^1$, which is impossible to rationalize in simple terms. In most cases, however, these apparent anomalies do not have important chemical consequences. Figure **1.9.10** indicates which elements have a non-standard configuration.

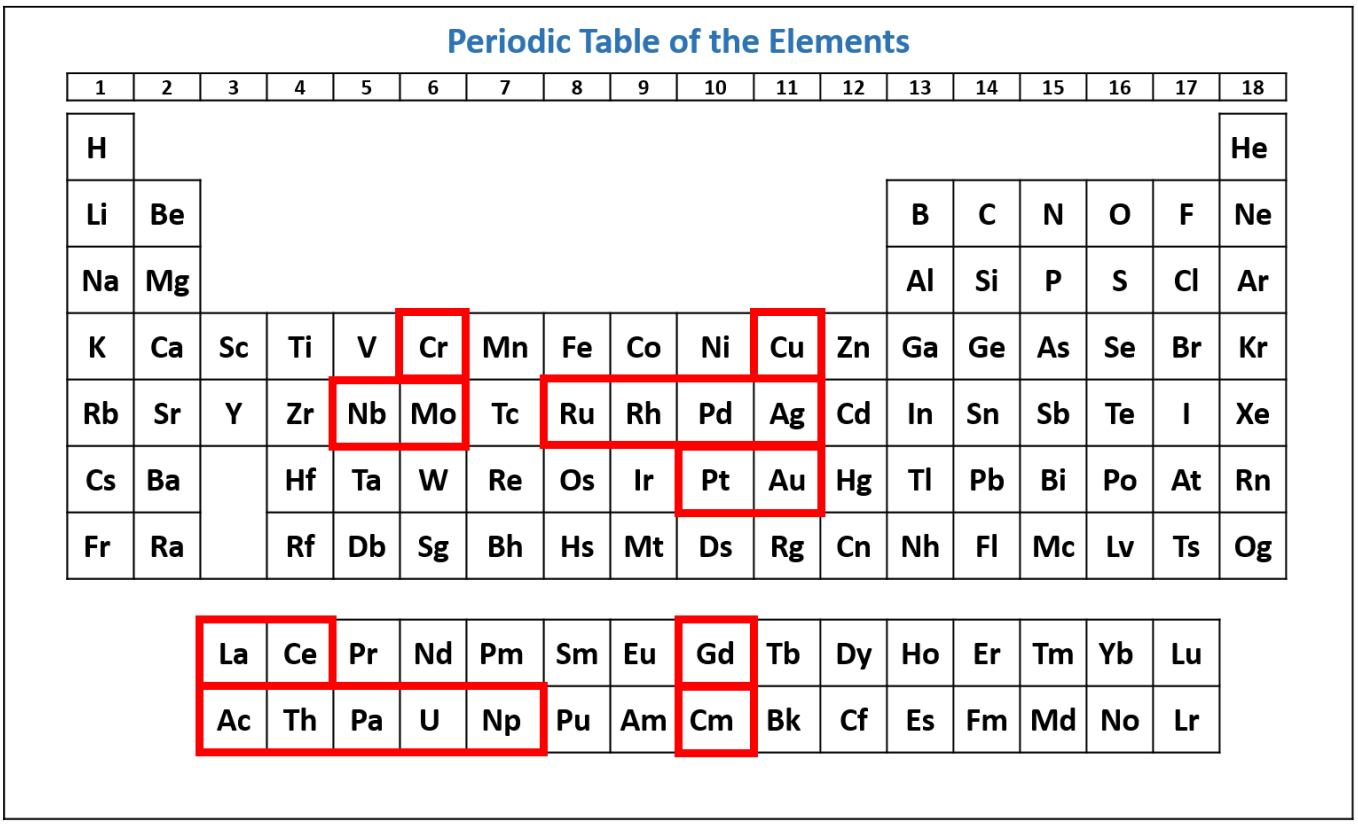


Figure 1.9.10: Periodic table of the elements. The highlighted elements have a non-standard electron configuration. (CC-BY-NC-SA; Kathryn A. Newton)



Electron Configuration of Transition Metals: Electron Configuration of Transition Metals, YouTube(opens in new window) [youtu.be]

Electron Configurations of Transition Metal Ions

Transition metal elements are unique in the sense that they can have multiple oxidation states. While negative oxidation states are possible for some transition metal elements, we will focus on the positive oxidation states, which are more common.

Writing an electron configuration for a transition metal ion starts with the same steps as writing the configuration of an s- or p-block cation: Write the electron configuration for the neutral atom and then determine the number of electrons that are lost to form the cation. The electrons will be removed from the highest energy shell in the neutral configuration. This means that electrons will be removed from the 4s subshell before any electrons are removed from the 3d subshell, and similarly electrons will be removed

from the 5s subshell before they are removed from the 4d subshell. If the highest energy s subshell is empty, then additional electrons will be removed from the highest energy d subshell.

Example 1.9.3

Write an electron configuration for V^{4+}.

Solution

1. Write the configuration of the neutral atom. V: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^3$
2. Determine how many electrons were lost. V^{4+} was formed by the loss of four electrons.
3. Remove electrons from the highest shell, starting with the highest energy subshell.

   V^{+}: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^{\mathbf{1}}\ 3d^3$

   V^{2+}: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^{\mathbf{0}}\ 3d^3$

   V^{3+}: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^{\mathbf{0}}\ 3d^{\mathbf{2}}$

   V^{4+}: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^{\mathbf{0}}\ 3d^{\mathbf{1}}$, which is typically written as $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{\mathbf{1}}$ or [Ar] $3d^1$

Problems

Exercise 1.9.1

Write the expanded and shortened ground state electron configuration for nickel (Ni).

Answer

Expanded: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^8$

Noble Gas: [Ar] $4s^2\ 3d^8$

Exercise 1.9.2

Write the expanded and shortened ground state electron configuration for rhodium (Rh).

Answer

Expanded: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^7$

Noble Gas: [Kr] $5s^2\ 4d^7$

Exercise 1.9.3

Write the ground state electron configuration for Ni^{2+}.

Answer

Neutral Ni: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^8$

Ni^{2+}: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^8$ or [Ar] $3d^8$

Exercise 1.9.4

Write the ground state electron configuration for Rh^{3+}.

Answer

Neutral Rh: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^7$

Rh^{3+}: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 4d^6$ or [Kr] $4d^6$

? Exercise 1.9.1

Osmium is stable with oxidation states of +2, +3, +4, and +8. Write the electron configuration for Os^{2+} and Os^{3+}.

Answer

Neutral Os: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^{10}\ 5p^6\ 6s^2\ 4f^{14}\ 5d^6$

Os^{2+}: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^{10}\ 5p^6\ \mathbf{6s^0}\ 4f^{14}\ 5d^6$ or [Xe] $4f^{14}\ 5d^6$

Answer

Os^{3+}: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^{10}\ 5p^6\ \mathbf{6s^0}\ 4f^{14}\ 5d^5$ or [Xe] $4f^{14}\ 5d^5$

References

1. Petrucci, Ralph. Harwood, William. Herring, Geoffrey. Madura, Jeffery. *General Chemistry: Principles and Modern Applications, 9th Edition.* Pearson Education, Inc. New Jersey, 2007.
2. Hein, et al. Introduction to General, Organic, and Biochemistry. 9th ed. Hoboken, NJ 2009.

Contributors

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1.10: The Periodic Table and Periodic Properties

Estimated Time to Read: 5 min

The Periodic Table

The Periodic Table of Elements categorizes like elements together. Dmitri Mendeleev, a Russian scientist, was the first to create a widely accepted arrangement of the elements in 1869. Mendeleev believed that when the elements are arranged in order of increasing atomic mass, certain sets of properties recur periodically. Although most modern periodic tables are arranged in eighteen groups (columns) of elements, Mendeleev's original periodic table had the elements organized into eight groups and twelve periods (rows).

On the periodic table, elements that have similar properties are in the same groups (vertical). From left to right, the atomic number (z) of the elements increases from one period to the next (horizontal). The groups are numbered at the top of each column and the periods on the left next to each row. The main group elements are groups 1,2 and 13 through 18. These groups contain the most naturally abundant elements, and are the most important for life. The elements shaded in light pink in the table above are known as transition metals. The two rows of elements starting at z=58, are sometimes called inner transition metals and have that have been extracted and placed at the bottom of the table, because they would make the table too wide if kept continuous. The 14 elements following lanthanum (z=57) are called lanthanides, and the 14 following actinium (z=89) are called actinides.

Elements in the periodic table can be placed into two broad categories, metals and nonmetals. Most metals are good conductors of heat and electricity, are malleable and ductile, and are moderate to high melting points. In general, nonmetals are nonconductors of heat and electricity, are nonmalleable solids, and many are gases at room temperature. Just as shown in the table above, metals and nonmetals on the periodic table are often separated by a stairstep diagonal line, and several elements near this line are often called metalloids (Si, Ge, As, Sb, Te, and At). Metalloids are elements that look like metals and in some ways behave like metals but also have some nonmetallic properties. The group to the farthest right of the table, shaded orange, is known as the noble gases. Noble gases are treated as a special group of nonmetals.

Alkali Metals/Alkali Earth Metals

The Alkali metals are comprised of group 1 of the periodic table and consist of Lithium, Sodium, Rubidium, Cesium, and Francium. These metals are highly reactive and form ionic compounds (when a nonmetal and a metal come together) as well as many other compounds. Alkali metals all have a charge of +1 and have the largest atom sizes than any of the other elements on each of their respective periods.

Alkali Earth Metals are located in group 2 and consist of Beryllium, Magnesium, Calcium, Strontium, Barium, and Radium. Unlike the Alkali metals, the earth metals have a smaller atom size and are not as reactive. These metals may also form ionic and other compounds and have a charge of +2.

Transition Metals

The transition metals range from groups IIIB to XIIB on the periodic table. These metals form positively charged ions, are very hard, and have very high melting and boiling points. Transition metals are also good conductors of electricity and are malleable.

Lanthanides and Actinides

Lanthanides (shown in row ** in chart above) and Actinides (shown in row * in chart above), form the block of two rows that are placed at the bottom of the periodic table for space issues. These are also considered to be transition metals. Lanthanides are form the top row of this block and are very soft metals with high boiling and melting points. Actinides form the bottom row and are radioactive. They also form compounds with most nonmetals. To find out why these elements have their own section, check out the electron configurations page.

Metalloids

Metalloids are located along the staircase separating the metals from the nonmetals on the periodic table. Boron, silicon, germanium, arsenic, antimony, and tellurium all have metal and nonmetal properties. For example, Silicon has a metallic luster but

is brittle and is an inefficient conductor of electricity like a nonmetal. As the metalloids have a combination of both metallic and nonmetal characteristics, they are intermediate conductors of electricity or "semiconductors".

Halogens

Halogens are comprised of the five nonmetal elements Flourine, Chlorine, Bromine, Iodine, and Astatine. They are located on group 17 of the periodic table and have a charge of -1. The term "halogen" means "salt-former" and compounds that contain one of the halogens are salts. The physical properties of halogens vary significantly as they can exist as solids, liquids, and gases at room temperature. However in general, halogens are very reactive, especially with the alkali metals and earth metals of groups 1 and 2 with which they form ionic compounds.

Noble Gases

The noble gases consist of group 18 (sometimes reffered to as group O) of the periodic table of elements. The noble gases have very low boiling and melting points and are all gases at room temperature. They are also very nonreactive as they already have a full valence shell with 8 electrons. Therefore, the noble gases have little tendency to lose or gain electrons.

A Summary of Periodic Properties

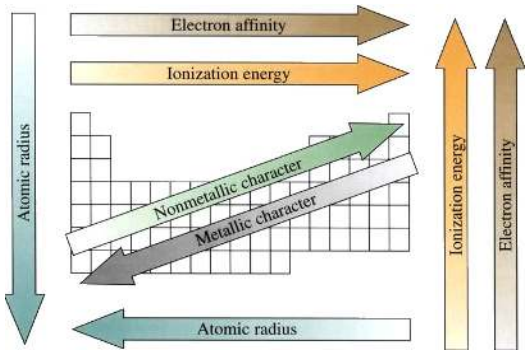


Figure 1.10.1: Courtesy of Wikipedia for releasing this image into the public domain

Problems

? Exercise 1.10.1

Which element is an example of a metalloid

a. S
b. Zn
c. Ge
d. Re
e. none of these

Answer

c. Ge

? Exercise 1.10.2

In the periodic table, the vertical (up and down) columns are called

a. periods
b. transitions
c. families/groups
d. metalloids
e. none of these

Answer

c. families/groups

? Exercise 1.10.3

Why are noble gases inert (nonreactive)?

Answer

Noble gases are inert because they already have a full valence electron shell and have little tendency to gain or lose electrons.

? Exercise 1.10.4

Lanthanides and Actinides are

a. alkali earth metals
b. transition metals
c. metalloids
d. alkali metals
e. none of these

Answer

b. transtion metals

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1.11: Atomic Radius

Estimated Time to Read: 6 min

Determining Atomic Radius

The atomic radius is one-half the distance between the nuclei of two atoms (just like a radius is half the diameter of a circle). However, this idea is complicated by the fact that not all atoms are normally bound together in the same way. Some are bound by covalent bonds in molecules, some are attracted to each other in ionic crystals, and others are held in metallic crystals. The SI units for measuring atomic radii are the nanometer (nm) and the picometer (pm). $1\,nm = 1 \times 10^{-9}\,m$ and $1\,pm = 1 \times 10^{-12}\,m$.

Atomic radii can be obtained from quantum mechanical calculations or can be determined experimentally. When calculated, the atomic radius is defined as the radius of the spherical volume in which the electron can be observed with 90% probability. Calculate atomic radii are shown in Figure **1.11.1**.

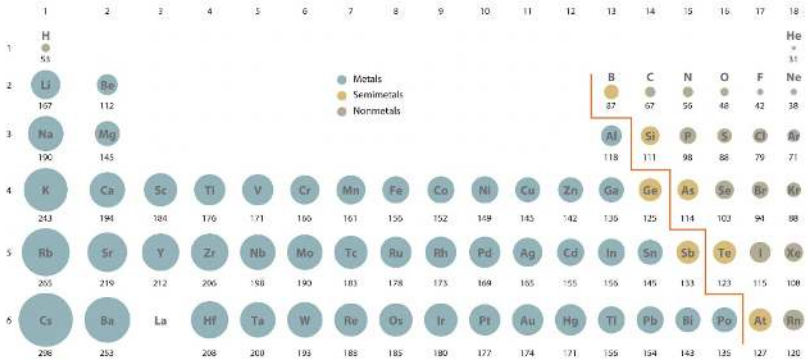


Figure 1.11.1: Calculated atomic radii of the elements in the periodic table (CC-BY-NC-SA; Kai Ladskron)

The measurement of atomic or ionic size will depend on a number of factors, including the covalent character of bonding in any particular molecule, coordination number, physical state (liquid, solid, gas), the identity of nearby atoms/ions, variation in crystal structure, and distortions within regular crystal structures. You should keep in mind that the size of an atom or ion is a "fuzzy" measure, and the radius under a different set of conditions will probably change slightly. Depending on how the atomic radius is measured, it will be classified as a (Figure **1.11.2**):

- **Covalent radius:** The radius of an atom is derived from the bond length within a nonpolar molecule; one-half the distance between the nuclei of two atoms within a covalent bond.
- **Metallic or Crystal radius**: The radius of an atom is determined using electron density maps from X-ray data; one-half the distance between the nuclei of two neighboring atoms in a crystal structure.
- **van der Waals radius:** The radius of an atom is determined by collision with other atoms; one-half the distance between two atoms that are not bonded but are brought together by intermolecular forces.

The relative atomic sizes shown in Figure **1.11.3** were derived from crystallographic data.

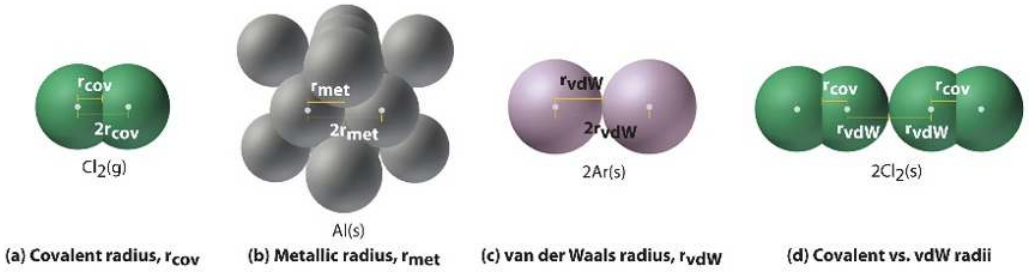


Figure 1.11.2: Definitions of Measured Atomic Radii: a) covalent radius, b) metallic radius, c) van der Waals radius, and d) a comparison of covalent and van der Waals radii (CC-BY-NC-SA; Kai Ladskron)

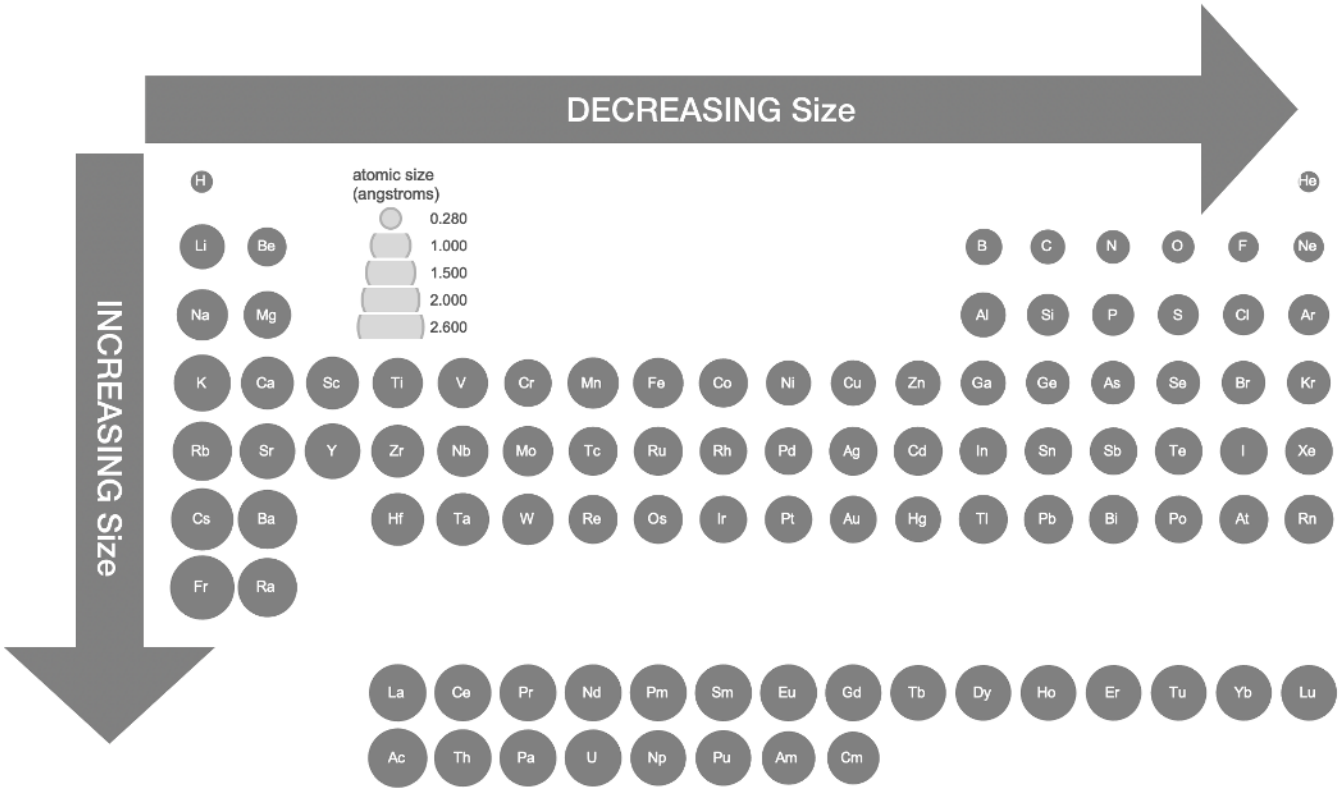


Figure 1.11.3. *Atomic Radii Calculated from Crystalographic Data. Data from Cordero, Beatriz, Veronica Gomez, Ana E. Platero-Prats, Marc Reves, Jorge Echeverria, Eduard Cremades, Flavia Barragan, and Santiago Alvarez. "Covalent Radii Revisited." Dalton Transactions, no. 21 (2008): 2832–38. doi:10.1039/b801115j.*[1] (CC-BY-NC-SA; LibreText)

Trends in Atomic Radius

Moving from left to right across a period, a proton is added to the nucleus for each element, making the nucleus more positively charged. At the same time, an electron is added the the electron energy shell, adding negative charge. The effect of increasing the number of protons is greater than that of increasing the number of electrons; therefore, there nuclear attraction for the electrons increases with the addition of each proton and electron. This means that the nucleus attracts the electrons more strongly, pulling the atom's shell closer to the nucleus. As a result, the atomic radius decreases as you move left to right across a period (Figure 1.11.4).

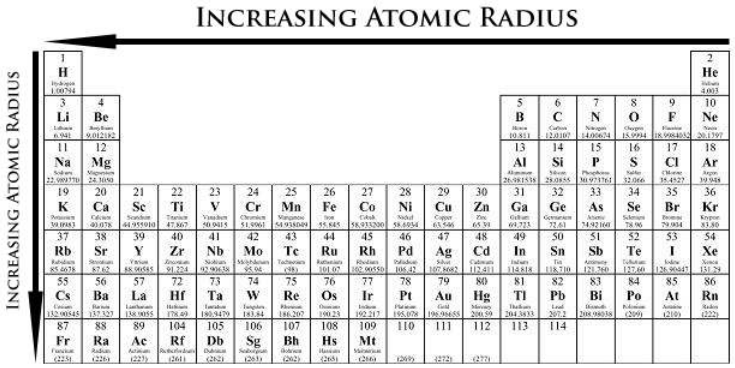


Figure 1.11.4: Periodic Table showing Atomic Radius Trend (LibreText)

Down a group, atomic radius increases. The valence electrons occupy higher energy shells due to the increasing quantum number (*n*). As a result, the valence electrons are further away from the nucleus as *n* increases.

- Atomic radius **decreases** from left to right within a period. This is caused by the increase in the number of protons and electrons across a period. One proton has a greater effect than one electron; thus, electrons are pulled towards the nucleus, resulting in a smaller radius.
- Atomic radius **increases from top to bottom** within a group. This is caused by electrons being add to higher energy levels that are futher from the nucleus.

Trends in Ionic Radius

An ionic radius is one-half the distance between the nuclei of two ions in an ionic bond. The distance must be apportioned for the smaller cation and larger anion. Trends in ionic radius follow the general trends in atomic radius for ions of the same charge. Ionic radius varies with the charge of the ion (and number of electrons) and the electron configuration.

Cations

Compared to their atoms, cations have the same number of protons but fewer electrons. Removal of electrons from an atom to form a cation results in a significant increase in effective nuclear charge, resulting in all other electrons being more strongly attracted to the nucleus. The result is a contraction in size from the atom to cation. Figure **1.11.5** visually illustrates the relative size of atoms and some cations of the first four periods; the data is available in tabular format in Figure **1.11.6**.

Anions

Compared to their atoms, anions have the same number of protons but more electrons. Addition of electrons to an atom to form an anion results in a decrease in effective nuclear charge, which corresponds to a decrease in attractive force between the nucleus and electrons. Lower attractive force leads to expansion, where the size of the atom becomes larger in the formation of an anion. Figure **1.11.5** visually illustrates the relative size of atoms and some anions of the first four periods, while the data is available in tabular format in Figure **1.11.6**.

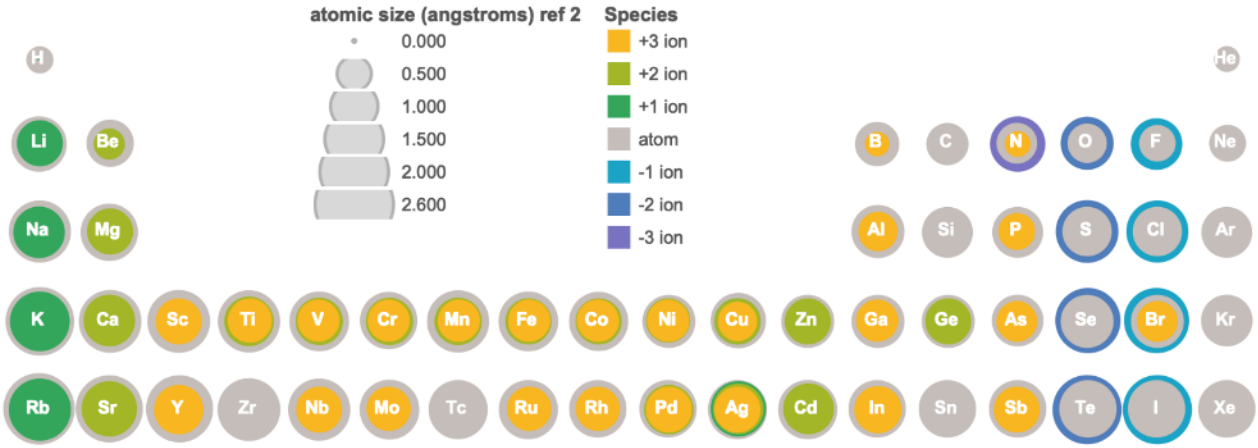


Figure 1.11.5. The relative size of atoms and ions of the first four periods of the periodic table. Atomic radii are indicated by grey circles. Cationic radii are shown in green (+1), yellow-green(+2), and yellow (+3) circles. Anionic radii are shown as aqua (-1), blue (-2), and purple (-3) circles.[1-3] (ChemLibre)

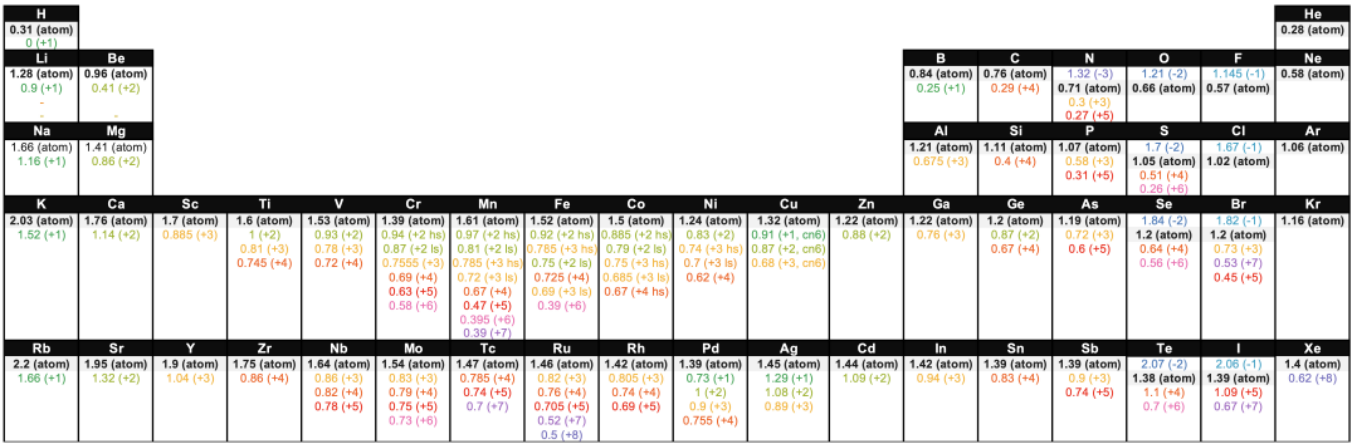


Figure 1.11.6. Atomic and ionic radii in Angstroms of elements in the first four periods of the periodic table. Radii from each element are listed from largest to smallest. Ionic charge is indicated in parentheses. (hs = high spin, ls = low spin, cn6 = coordination number is 6).[1-3] (ChemLibre)

Problems

? Exercise 1.11.1

True or False? Nitrogen has a larger atomic radius than oxygen.

Answer

True

Atomic radius increases from right to left on the periodic table. Therefore, nitrogen is larger than oxygen.

? Exercise 1.11.2

Which atom has a smaller atomic radius smaller than that of sulfur (S)?

a. Oxygen (O)
b. Chlorine (Cl)
c. Calcium (Ca)
d. Lithium (Li)
e. None of the above

Answer

a. Oxygen (O)

Periodic trends indicate that atomic radius increases up a group and from left to right across a period. Therefore, oxygen has a smaller atomic radius sulfur

? Exercise 1.11.3

True or False? A nonmetal has a smaller ionic radius compared with a metal of the same period.

Answer

False

The reasoning behind this lies in the fact that a metal usually loses an electron in becoming an ion while a non-metal gains an electron. This results in a smaller ionic radius for the metal ion and a larger ionic radius for the non-metal ion.

? Exercise 1.11.4

Arrange these elements according to decreasing atomic size: Na, C, Sr, Cu, Fr

Answer

Fr, Sr, Cu, Na, C

? Exercise 1.11.5

Which has a larger atomic radius: nitrogen or oxygen?

Answer

Atomic radius increases from right to left on the periodic table. Therefore, nitrogen is larger than oxygen

? Exercise 1.11.6

Which of these elements has a smaller atomic radius than sulfur (S): O, Cl, Ca, Li

Answer

Oxygen (O) is the only element in the list with a smaller atomic radius than S. Periodic trends indicate that atomic radius increases down a group (from top to bottom) and from left to right across a period.

References

1. Cordero, Beatriz, Veronica Gomez, Ana E. Platero-Prats, Marc Reves, Jorge Echeverria, Eduard Cremades, Flavia Barragan, and Santiago Alvarez. *"Covalent Radii Revisited." Dalton Transactions, no. 21 (2008): 2832–38. doi:10.1039/b801115j.*
2. R. D. Shannon (1976). "Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides". *Acta Crystallogr A.* **32** (5): 751–767. Bibcode:1976AcCrA..32..751S. doi:10.1107/S0567739476001551.
3. Wikipedia articles on Atomic Radius and Ionic Radius.

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1.12: Ionization Energy

Estimated Time to Read: 4 min

Definition of Ionization Energy

Ionization energy is the energy required to remove an electron from a neutral atom in its gaseous phase. Ionization energy is always positive. Some elements can lose more than one electron and thus have several ionization energies. The first ionization energy is the energy required to remove the outermost, or highest energy, valence electron. The second ionization energy is the energy required to remove the next highest energy valence electron from a gaseous cation, etc. Below are the chemical equations describing the first and second ionization energies:

Equation 1.12.1: First Ionization Energy

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

Equation 1.12.2: Second Ionization Energy

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

Table **1.12.1** gives the ionization energies for the period three elements. Notice how the second ionization energy for sodium, third ionization energy for magnesium, fourth ionization energy for aluminum, etc. are all much greater than the preceding ionization energy. This occurs because the preceding configuration was in a stable octet formation; therefore a much larger amount of energy is required to ionize the valence electron and break the octet formation.

Table 1.12.1: Ionization Energies of certain elements (1st IE, 2nd IE, etc.)

Element	1st	2nd	3rd	4th	5th	6th	7th
Na	496	4562					
Mg	738	1451	7733				
Al	577	1817	2745	11580			
Si	786	1577	3232	4356	16090		
P	1060	1903	2912	4957	6274	21270	
S	999.6	2251	3361	4564	7013	8496	27110
Cl	1256	2297	3822	5158	6542	9362	11020
Ar	1520	2666	3931	5771	7238	8781	12000

Trends in Ionization Energy

The lower the ionization energy is, the more readily the atom becomes a cation. Therefore, the higher the ionization energy is, the less readily the atom becomes a cation (Figure **1.12.1**). Generally, elements on the right side of the periodic table have a higher ionization energy because their valence shell is nearly filled. The highest ionization energies are the noble gases because they all have high effective charge due to their octet formation. Elements on the left side of the periodic table have low ionization energies because losing an electron allows them to have the noble gas configuration. Therefore, it requires less energy to remove one of their valence electrons, and ionization energy increases from left to right on the periodic table.

This trend can also be explained by the fact that the effective nuclear charge increases from the left to the right within a period as the number of protons increases. With each addition of a proton, the pull of the nucleus on the outmost electron increases, and it becomes more difficult to overcome the attractive forces of the nucleus and remove this electron from the atom.

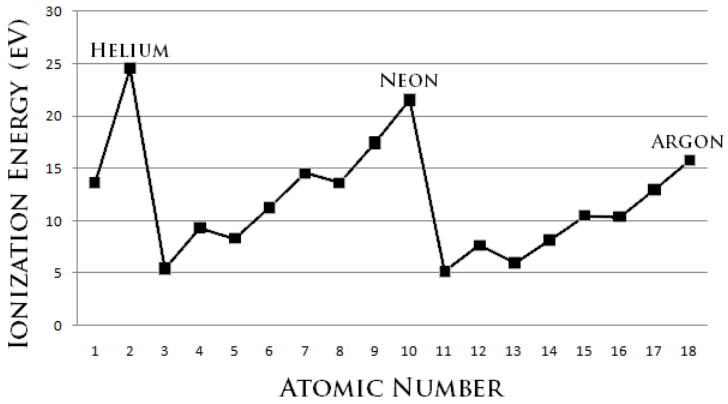


Figure 1.12.1: Graph showing the Ionization Energy of the Elements from Hydrogen to Argon (LibreText)

Within the main group elements, the trend is broken two times (Figure **1.12.2**). First, the group 13 elements have a lower ionization energy than the group 2 elements. Second, the group 16 elements have a lower ionization energy than the group 15 elements. This is explained by the fact that the filled and half-filled subshells in group 2 and group 15, respectively, are particularly stable electron configurations; thus, the electrons within these subshells have unusually low energy and require greater energy to be removed from the atom.

The increase in ionization energy across the period is less pronounced within the d-block, and even less pronounced within the f-block. This is because the effective nuclear charge on the outmost electrons does not increase as much because inner d and f orbitals are getting filled. Following the d-block, group 13 elements have a lower ionization energy than the group 12 elements. This is because in group 13 electrons are added to a new p subshell.

Ionization energy becomes smaller down a group as electrons are added to higher energy shells and the distance from the nucleus increases (*n* increases). The attractive forces of the nucleus are diminished as the electrons are further from the nucleus.

Generally, any subsequent ionization energies (2nd, 3rd, etc.) follow the same periodic trend as the first ionization energy.

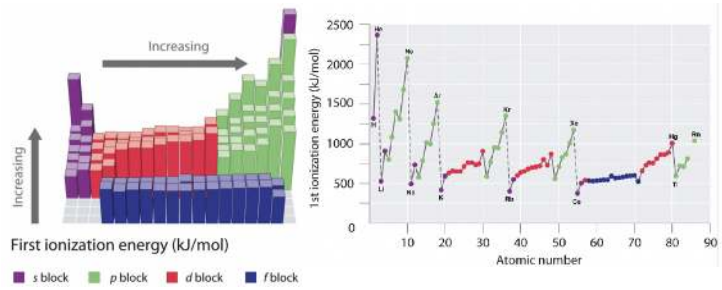


Figure 1.12.2: First ionization energies as a third dimension in the periodic table (left) and as function of atomic number (right) (CC-BY-NC-SA, LibreText)

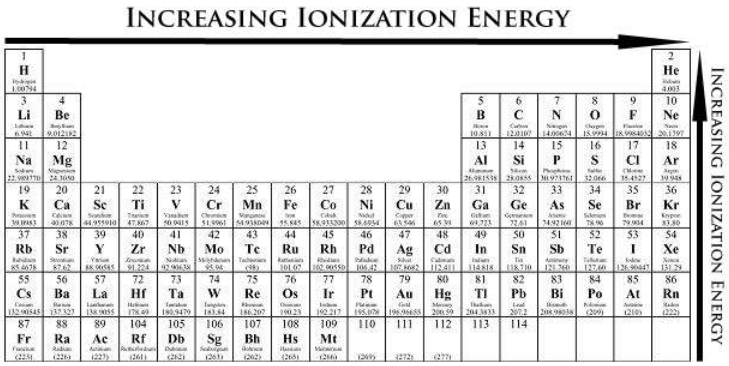


Figure 1.12.3: Periodic Table Showing Ionization Energy Trend (LibreText)

- 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 increasing electron energy shell.
- The noble gases possess very high ionization energies because of their full valence shells.

Problems

Exercise 1.12.1

Based on the periodic trends for ionization energy, which element has the highest ionization energy?

a. Fluorine (F)
b. Nitrogen (N)
c. Helium (He)

Answer

c. Helium (He)

Exercise 1.12.2

Which reaction do you expect to occur?

a. $\mathrm{I_2(g) + 2\,Br(aq) \longrightarrow Br_2(s) + 2\,I(aq)}$
b. $\mathrm{Cl_2(g) + 2\,I(aq) \longrightarrow I_2(s) + 2\,Cl(aq)}$

Answer

a.

Exercise 1.12.3

Based on the periodic trends for ionization energy, which element has the highest ionization energy?

Answer

Helium,He

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1.13: Electron Affinity

Estimated Time to Read: 4 min

Definition of Electron Affinity

Electron affinity is a quantitative measurement of the energy change that occurs when an electron is added to a neutral gaseous atom. The more negative the electron affinity value, the higher the electron affinity and the more easily an electron is added to an atom. Electron affinity can be either positive or negative. The greater the negative value, the more stable the anion is.

Equation 1.13.1: Exothermic, positive electron affinity

$$\mathbf{X(g) + e^- \longrightarrow X^- + Energy}$$

Equation 1.13.2: Endothermic, negative electron affinity

$$\mathbf{X(g) + e^- + Energy \longrightarrow X^-}$$

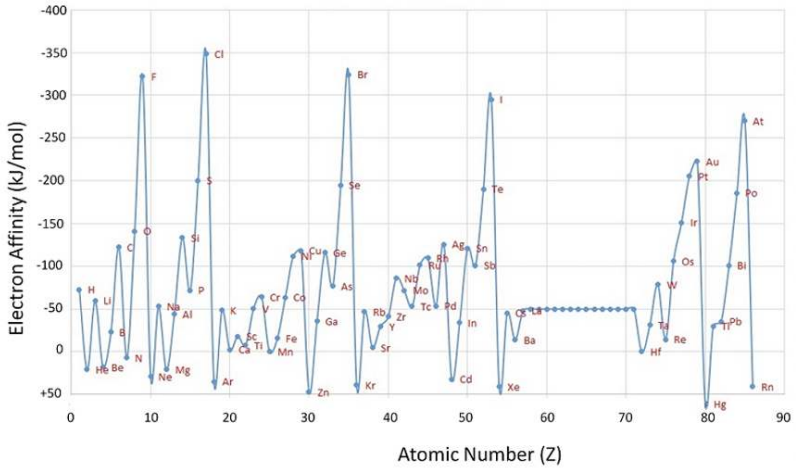


Figure 1.13.1: Electron affinity values (CC-BY-NC-SA, LibreText)

Figure **1.13.1** shows that most elements have negative electron affinities, meaning that the addition of a free electron to a neutral atom is exothermic. However, this is not always the case. Some elements (the noble gases, Be, N, Mg, Zn, Cd, and Hg) have positive electron affinities. Zn, Cd, and Hg are group 12 elements with a full d subshell, which is particularly stable, and an additional electron would need to be added to a p orbital of a higher shell which is energetically unfavorable. Similarly, Be and Mg have filled s subshells, which are also stable, and adding an additional electron would require a new subshell, which is energetically unfavorable. Ca and Sr have electron affinities of about 0, and that of Ba is only slightly negative. This shows that higher periods make the addition of an electron to a new p subshell slightly more favorable. Nitrogen has a half-filled p subshell, which is also a quite stable electron configuration, and therefore, adding an electron is not favorable. The addition of an electron is slightly more favorable for the other group 15 elements, however.

Trends in Electron Affinity

Moving from left to right across a period, atoms become smaller as the nuclear charge and the attractive forces of the nucleus become stronger. Electrons added to the valence shell are stabilized by the attractive force of the nucleus, thus the electron affinity increases (becomes more negative) more from left to right across a period. Electron affinity generally decreases (becomes less negative) down a group of elements as the distance from the nucleus of valence electrons increases as electrons are added to higher energy shells (*n* increases). The attractive forces of the nucleus decrease with a larger distance between the negatively-charged electron and the positively-charged nucleus, and therefore, electron affinity decreases.

Generally, the elements on the right side of the periodic table will have large negative electron affinity. However, Nitrogen, Oxygen, and Fluorine do not follow this trend. The noble gas electron configuration will be close to zero because they will not easily gain electrons. The general trend is also broken for group 2 and group 15 elements because these elements have full and half-

filled subshells, respectively. In addition, group 1 elements have higher electron affinities than group 3 elements. This is because adding an electron to a group 1 element produces a full s subshell, which is fairly stable. For the d-block elements, the electron affinity tends to increase from group 3 to group 11, but the trend is broken multiple times and each element would need to be investigated individually. There is a large drop in electron affinity from group 17 to group 18 which is explained by the fact that the addition of an electron to a group 17 element produces a filled shell, while a group 18 element already has a full shell and the addition of an electron would require a new shell. Similarly, there is a sharp drop in electron affinity from group 11 to group 12, as an addition of an electron to a group 11 atom produces a full subshell, while the addition of an electron to a group 12 element would require the start of new subshell.

In general, electron affinity decreases down a group. For the s-block there is a steady decrease down a group.For the p block elements the electron affinity tends to first increase from period 2 to 3, and then decreases. For d block elements there is no clear trend for the electron affinity.

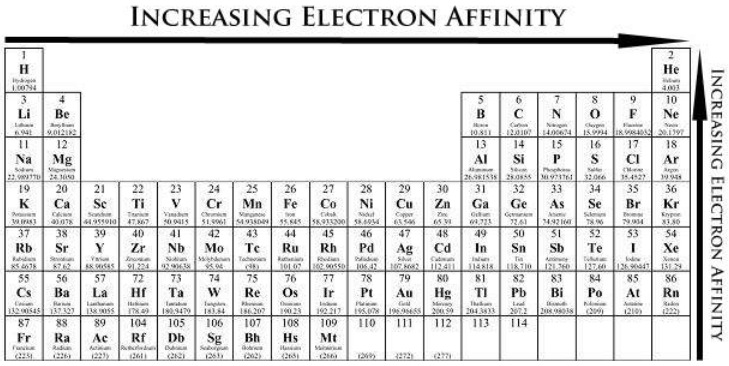


Figure 1.13.2: Periodic Table showing Electron Affinity Trend

- Electron affinity increases (becomes more negative) from left to right within a period. This is caused by the decrease in atomic radius.
- Electron affinity decreases (becomes less negative) from top to bottom within a group. This is caused by the increase in atomic radius.

Problems

? Exercise 1.13.1

Arrange the following elements in order of decreasing electron affinity: fluorine (F), phosphorous (P), sulfur (S), boron (B).

Answer

F > S > P > B

? Exercise 1.13.2

Arrange these elements according to increasingly negative electron affinity: Ba, F, Si, Ca, O .

Answer

Ba, Ca, Si, O, F

The following series of problems reviews general understanding of the aforementioned material.

Exercise 1.13.3

Rewrite the following list in order of decreasing electron affinity: fluorine (F), phosphorous (P), sulfur (S), boron (B).

Answer

Fluorine (F)>Sulfur (S)>Phosphorous (P)>Boron (B). Explanation: Electron affinity generally increases from left to right and from bottom to top.

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1.14: Other Periodic Properties of Atoms

Estimated Time to Read: 3 min

Melting Point Trends

The melting points is the amount of energy required to break a bond(s) to change the solid phase of a substance to a liquid. Generally, the stronger the bond between the atoms of an element, the more energy required to break that bond. Because temperature is directly proportional to energy, a high bond dissociation energy correlates to a high temperature. Melting points are varied and do not generally form a distinguishable trend across the periodic table. However, certain conclusions can be drawn from Figure 1.14.7.

- Metals generally possess a *high melting point*.
- Most non-metals possess *low melting points*.
- The non-metal carbon possesses *the highest melting point of all the elements*. The semi-metal boron also possesses a high melting point.

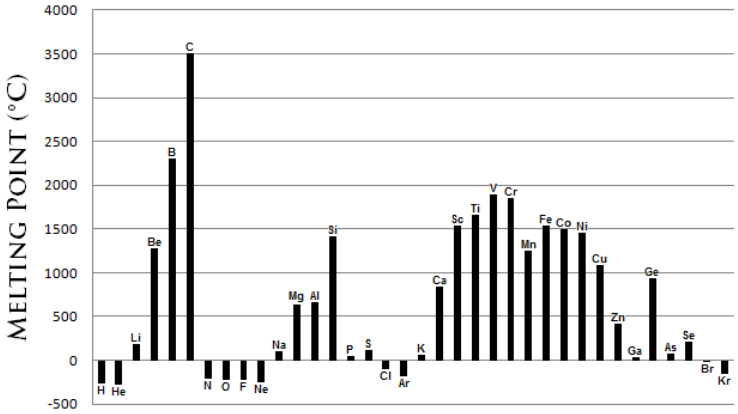


Figure 1.14.1: Chart of Melting Points of Various Elements

Metallic Character Trends

The metallic character of an element can be defined as how readily an atom can lose an electron. From right to left across a period, metallic character increases because the attraction between valence electron and the nucleus is weaker, enabling an easier loss of electrons. Metallic character increases as you move down a group because the atomic size is increasing. When the atomic size increases, the outer shells are farther away. The principal quantum number increases and average electron density moves farther from nucleus. The electrons of the valence shell have less attraction to the nucleus and, as a result, can lose electrons more readily. This causes an increase in metallic character.

- Metallic characteristics decrease from left to right across a period. This is caused by the decrease in radius (caused by Z_{eff}, as stated above) of the atom that allows the outer electrons to ionize more readily.
- Metallic characteristics increase down a group. Electron shielding causes the atomic radius to increase thus the outer electrons ionizes more readily than electrons in smaller atoms.
- Metallic character relates to the ability to lose electrons, and nonmetallic character relates to the ability to gain electrons.

Another easier way to remember the trend of metallic character is that moving left and down toward the bottom-left corner of the periodic table, metallic character increases toward Groups 1 and 2, or the alkali and alkaline earth **metal groups**. Likewise, moving up and to the right to the upper-right corner of the periodic table, metallic character decreases because you are passing by to the right side of the staircase, which indicate the **nonmetals**. These include the Group 8, the **noble gases**, and other common gases such as oxygen and nitrogen.

In other words:

- Move left across period and down the group: increase metallic character (heading towards alkali and alkaline metals)
- Move right across period and up the group: decrease metallic character (heading towards nonmetals like noble gases)

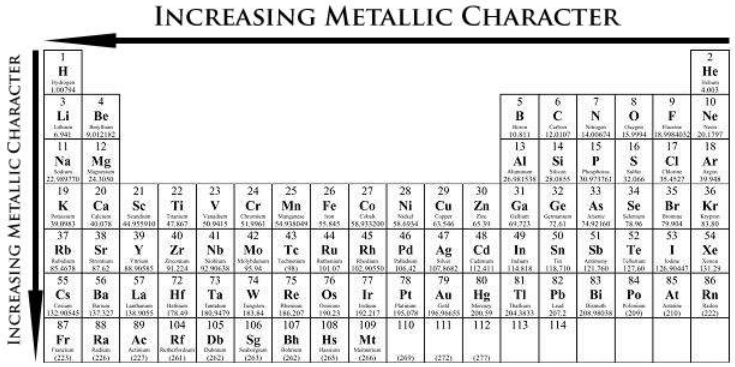


Figure 1.14.2: Periodic Table of Metallic Character Trend

Problems

? Exercise 1.14.1

Which has more metallic character, Lead (Pb) or Tin (Sn)?

Answer

Lead

Lead and tin share the same column. Metallic character increases down a column. Lead is under tin, so lead has more metallic character.

? Exercise 1.14.2

Which element has a higher melting point: chlorine (Cl) or bromine (Br)?

Answer

Bromine

In non-metals, melting point increases down a column. Because chlorine and bromine share the same column, bromine possesses the higher melting point.

? Exercise 1.14.3

Arrange these elements according to increasing metallic character: Li, S, Ag, Cs, Ge

Answer

Li, S, Ge, Ag, Cs

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1.15: Effective Nuclear Charge and Shielding

Estimate Time to Read: 8 min

Coulomb's Law

Coulomb's Law is from classical physics (Equation 1); it tells us that particles with opposite electrostatic charges (q_1, q_2) are attracted to each other, and the larger the charge on either particle or the closer the distance (r) between them, the stronger the force of attraction (F). Coulombs' law works well for predicting the energy of an electron in a hydrogen atom because H has only one electron. It also works for hydrogen-like atoms: any nucleus with exactly one electron (a He^+ ion, for example, has one electron). However, Coulomb's law is insufficient for predicting the energies of electrons in multi-electron atoms and ions.Coulomb's law explains why atomic size decreases as the charge on the nucleus increases, but it can't explain the nuances and variations in size as we go across the periodic table. Coulomb's Law also explains why electrons in different shells (n), at different distances from the nucleus, have different energies. But on its own, Coulomb's law doesn't quite explain why electron subshells within a shell (like 2s vs. 2p) would have different energies. To explain these things, we need to consider how both electron *shielding* and *penetration* result in variations in effective nuclear charge (Z*) that depend on shell and subshell.

Equation 1.15.1. Coulomb's Law

$$F = k\frac{q_1 q_2}{r^2}$$

Effective Nuclear Charge (Z*)

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. However, electrons within a multi-electron atom interact with the nucleus and with all other electrons. Each electron in a multi-electron atom experiences both attraction to the nucleus and repulsion from the other electrons. The presence of multiple electrons decreases the nuclear attraction to some extent. Each electron in a multi-electron atom experiences a different magnitude of (and attraction to) the nuclear charge depending on what specific shell and subshell the electron occupies. The amount of positive nuclear charge experienced by any individual electron is the **effective nuclear charge (Z*)**.

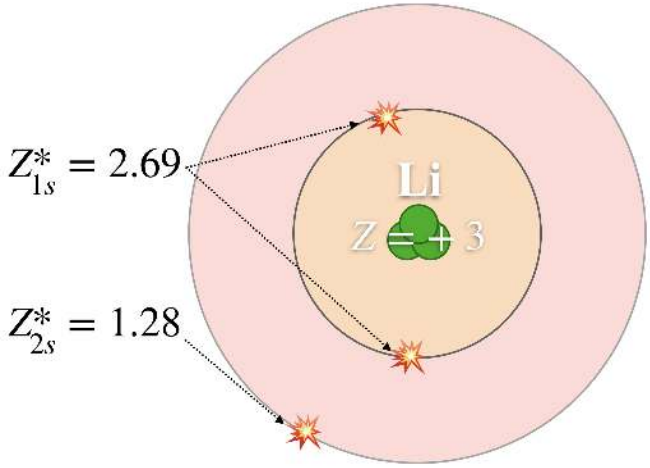


Figure 1.15.1: In a lithium atom, the nuclear charge (Z) is +3. 1s electrons experience an effective nuclear charge (Z*) of +2.69, and 2s electrons experience an Z* of +1.28. (CC-BY-NC-SA; Kathryn Haas)

For example, in lithium (Li), none of the three electrons "feel" the full +3 charge from the nucleus (Figure 1.15.1). Rather, each electron "feels" a Z* that is less than the actual Z and that depends on the electron's orbital. The actual nuclear charge in Li is $Z = +3$; the 1s electrons experience a $Z^* = +2.69$, and the 2s electron experiences a $Z^* = +1.28$. In general, core electrons (or the electrons closest to the nucleus), "feel" a Z* that is close to, but less than, Z. On the other hand, outer valence electrons experience a Z* that is much less than Z.

- Core electrons: $Z^* \lesssim Z$

- Valence electrons: $Z^* \ll Z$

If an electron is far from the nucleus, 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. The farther an electron is from the nucleus, the more electrons between that electron and the nucleus, and the greater the actual nuclear charge Z is than the effective nuclear charge Z*. This effect is called *electron shielding*.

Shielding

Shielding *is the reduction of true nuclear charge (Z) to the effective nuclear charge (Z*) by other electrons in a multi-electron atom or ion*. Shielding occurs in all atoms and ions that have more than one electron. H is the only atom in which shielding does not occur.

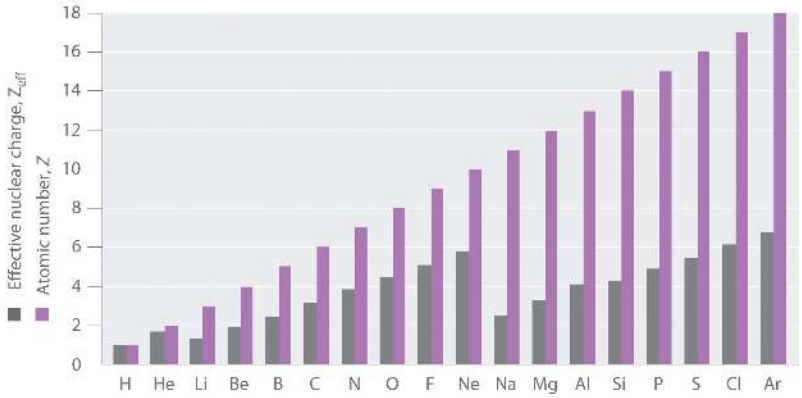


Figure 1.15.2: Relationship between the Effective Nuclear Charge Z_{eff} and the Atomic Number Z for the Outer Electrons of the Elements of the First Three Rows of the Periodic Table. Except for hydrogen, Z_{eff} is *always* less than Z, and Z_{eff} increases from left to right as you go across a row. (CC-BY-NC-SA, LibreText)

Electrons in a multi-electron atom interact with the nucleus and all other electrons in the atom. To describe shielding, we choose an electron-of-interest in a multi-electron atom and treat all the "other" electrons as a group. While the positive charge of the nucleus attracts our electron, the negative charges of the "other" electrons repel our electron-of-interest. The attractive and repulsive forces partially cancel each other; however, there are fewer "other" electrons than there are protons in our atom so the nuclear charge is never completely canceled. The "other" electrons partially block, or *shield*, part of the nuclear charge so that our electron-of-interest experiences a partially-reduced nuclear charge, the Z*.

In reality, there is not a one-for-one "canceling" of the nuclear charge by each electron. Partly due to *penetration*, no single electron can completely shield a full unit of positive charge. Core electrons shield valence electrons, but valence electrons have little effect on the Z* of core electrons. The ability to shield, and be shielded by, other electrons strongly depends the electron orbital's average distance from the nucleus and its penetration; thus shielding depends on both shell (n) and subshell (l).

Electron Penetration

Coulomb's law shows us that distance of an electron from its nucleus is important in determining the electron's energy (its attraction to the nucleus). The shell number (n) determines approximately how far an electron is from the nucleus *on average*. Thus, all orbitals in the same shell (s,p,d) have similar sizes and similar average distance of their electrons from the nucleus. But there is another distance-related factor that plays a critical role in determining orbital energy levels: penetration. **Penetration** *describes the ability of an electron in a given subshell to penetrate into other shells and subshells to get close to the nucleus*. **Penetration *is the extent to which an electron can approach the nucleus***. Penetration depends on both the shell (n) and subshell (l).

The penetration of individual orbitals can be visualized using the radial probability functions, which show the probability of locating an electron in an orbital as a function of distance from the nucleus. Figure **1.15.3** shows the radial probability function of the 1s, 2s, and 2p orbitals. From these plots, we can see that the probability peak of the 1s orbital closest to the nucleus; thus it is

the most penetrating. While the 2s and 2p have most of their probability at a farther distance from the nucleus (compared to 1s), the 2s orbital and the 2p orbital have different extents of penetration. Notice that the 2s orbital is able to penetrate the 1s orbital because of the central 2s lobe. The 2p orbital penetrates somewhat into the 1s, but it cannot approach the nucleus as closely as the 2s orbital can. While the 2s orbital penetrates more than 2p, the average probability of the 2p is slightly *closer* than that of the 2s. The order of Z* in 2s and 2p subshells depends on which factor (average distance or penetration) is more important. In the first two rows of the periodic table, penetration is the dominant factor that results in 2s having a lower energy than 2p.

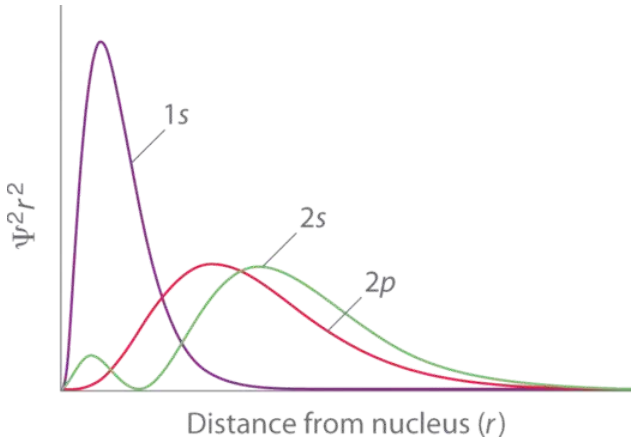


Figure 1.15.3: Orbital Penetration. A comparison of the radial probability distribution of the 2s and 2p orbitals for various states of the hydrogen atom shows that the 2s orbital penetrates inside the 1s orbital more than the 2p orbital does. Consequently, when an electron is in the small inner lobe of the 2s orbital, it experiences a relatively large value of Z*, which causes the energy of the 2s orbital to be lower than the energy of the 2p orbital. (CC-BY-NC-SA, LibreText)

An electron orbital's penetration affects its ability to shield other electrons and affects the extent to which it is shielded by other electrons. In general, electron orbitals that have greater penetration experience stronger attraction to the nucleus and less shielding by other electrons; these electrons thus experience a larger Z*. Electrons in orbitals that have greater penetration also shield other electrons to a greater extent.

Within the same shell value (n), the penetrating power of an electron follows this trend in subshells (m_l):

$$s > p > d > f$$

Problems

? Exercise 1.15.1

Compare the 2s and 2p orbitals:

1. Which is closer to the nucleus on average?
2. Which is more penetrating?
3. Which orbital experiences a stronger Z* and is thus lower in energy. Explain.

Answer

1. The 2s orbital is closer to the nucleus on average.
2. The 2s orbital is more penetrating than 2p.
3. You might "know" that the 2s orbital is lower in energy than 2p because 2s fills first. But a close inspection of Figures 1.1.2.3 and 1.1.2.4 indicates that while the 2s and 2p elements are degenerate in Ne (element 10), for elements with atomic number 11 and greater 2p has a higher Z* than 2s! This example illustrates that both average distance and penetration are factors in determining Z*, and the factor that is more important may change as we increase in atomic number.

? Exercise 1.15.2

Peruse the Hyperphysics page that shows radial probability functions of several orbitals (click around on various orbitals). Compare the 2p and 3s orbitals:

1. Which is farther from the nucleus on average?
2. Which is more penetrating?
3. Which orbital is lower in energy?

Answer

1. The 3s orbital reaches farther away from the nucleus and is on average farther from the nucleus than 2p.
2. The 3s orbital is more penetrating than 2p, even though 3s is farther on average!
3. The 2p orbital is lower in energy than 3s; this is because 2p is still significantly closer to the nucleus on average and experiences a stronger Z*. (Penetration is not the only consideration!)

? Exercise 1.15.3

Which atom, Li, or N, has a stronger valence Z*? Explain why.

Answer

A nitrogen atom has a stronger effective nuclear charge (Z*) than lithium due to its greater number of protons; even though N also has more electrons that would shield the nuclear charge, each electron only partially shields each proton. This means that atoms with greater atomic number always have greater Z* for any given electron.

? Exercise 1.15.4

Explain why 2s and 2p subshells are completely degenerate in a hydrogen atom.

Answer

The hydrogen atom has only one electron; thus there is no shielding to consider. When there are not other electrons to shield the nucleus, penetration and shielding are irrelevant, and subshells within a shell are degenerate.

? Exercise 1.15.5

Which electrons shield others more effectively: 3p or 3d?

Answer

3p shields better than 3d because p orbitals penetrate more than d orbitals within the same shell.

? Exercise 1.15.6

Explain why the ground state (most energetically favorable) electron configuration of Be is $1s^2 2s^2$ rather than alternative configurations like $1s^2 2s^1 2p^1$ or $1s^2 2p^2$.

Answer

This question is asking why the 2s orbital fills in Be before 2p is occupied. This is a multi-electron atom, therefore core electrons shield the 2s and 2p orbitals to different extents. In Be we expect the 2s orbital to fill before 2p because 2s penetrates more and experiences a higher Z*.

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1.16: Slater's Rules

Estimated Time to Read: 7 min

We have previously described the concepts of electron shielding, orbital penetration and effective nuclear charge, but we did so in a qualitative manner. In this section, we explore one model for quantitatively estimating electron shielding and calculating the effective nuclear charge experienced by an electron in an atom. The model we will use is known as Slater's Rules (J.C. Slater, *Phys Rev* **1930**, *36*, 57).

Effective Nuclear Charge

The effective nuclear charge Z_{eff} is less than the actual nuclear charge (Z) because of the repulsive interaction between core and valence electrons. We can quantitatively represent this difference between Z and Z_{eff} as follows:

Equation **1.16.1**

$$S = Z - Z_{eff} \tag{1.16.1}$$

Rearranging this formula to solve for Z_{eff} we obtain Equation **1.16.1**

$$Z_{eff} = Z - S \tag{1.16.2}$$

The shielding constant S is estimated using Slater's Rules. Then the shielding constant is substituted into Equation **1.16.2** to calculate an estimate of Z_{eff} for the corresponding atomic electron.

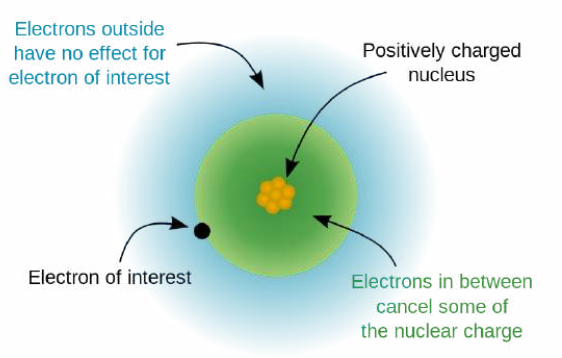


Figure 1.16.1: Shielding by electrons closer to the nucleus results in a lower effective nuclear charge. (Copyright; author via source)

Slater's Rules

Shielding is calculated for an electron-of-interest. Shielding occurs when "other" electrons in lower energy shells (or the same energy shell) provide a repulsive force to an electron-of-interest in a higher energy shell. The repulsive force negates some of the attractive force from the positive nucleus on the electron-of-interest. The "other" electrons in the same shell as the electron-of-interest shield least effectively, while those closest to the nucleus shield the most effectively. Slater's rules specify the degree of shielding for each inner shell electron and are used to calculate the overall shielding experienced by an electron in an s-, p-, d-, or f-orbital.

The shielding numbers in Table **1.16.1** were derived semi-empirically (i.e., derived from experiments) as opposed to theoretical calculations. This is because quantum mechanics makes calculating shielding effects quite difficult and outside the scope of this text.

Slater's Rules estimate effective nuclear charge for an electron-of-interest based on how many other electrons exist in the atom and on the location of the electron-of-interest. In the calculation of the shielding constant S, it is assumed that electrons closer to the nucleus than the electron-of-interest cancel some of the nuclear charge; those farther from the nucleus have no effect. For an electron-of-interest in an s or p orbital, electrons in the same shell (with the same principle quantum number *n*)will shield the electron-of-interest 0.35 units. *Conceptually, this means electrons in the same shell shield each other 35%.* Electrons in the lower energy shell *n-1* contribute 0.85 to S. All the electrons in even lower shells contribute 1.00 to S. *Conceptually, this means that s and p electrons are shielded 85% by the electrons one shell lower, and 100% by all electrons in shells n - 2 or lower.* For an electron-of-

interest in a d or f orbital, all electrons in the same shell (with the same principle quantum number *n*) and subshell (with the same angular momentum quantum number *l*) will shield the electron-of-interest 0.35 units. All other electrons contribute 1.00 to S. *Conceptually, this means that electrons in the same subshell shield each other 35%, and all other electrons shield 100%.* Note: The shielding constant S of a 1s electron is just S=0.3, no matter the element.

Table 1.16.1: Shielding values for electrons in inner orbitals based on their principle and angular moment quantum numbers relative to the orbital-of-interest.

Orbital of Electron-of-Interest	*n* and *l*	*n* and *l-1*	*n* and *l-2*	*n-1*	*n-2, n-3, etc.*
1s	0.30	-	-	-	-
ns, np	0.35	0.35	-	0.85	1.0
nd, nf	0.35	1.0	1.0	1.0	1.0

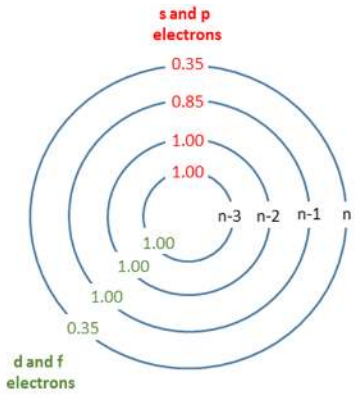


Figure 1.16.2: Graphical depiction of Slater's rules with shielding constants indicated. (CC-BY-NC-SA, Brett McCollum)

Calculating Shielding and Effective Nuclear Charge

Steps to Calculate Shielding and Effective Nuclear Charge

1. Write the electron configuration of the atom with orbitals arranged by increasing principle quantum number *n*, as shown here:

   (1s) (2s, 2p) (3s, 3p) (3d) (4s, 4p) (4d) (4f) (5s, 5p) . . .

2. Identify the electron of interest, and ignore all electrons that are higher in energy (to the right in the list). Higher energy electrons do not shield lower energy electrons.
3. Identify the principle quantum number *n* and angular momentum quantum number *l* of the electron-of-interest.
4. Assign shielding values to all other electrons that are lower in energy (to the right in the list).
   a. When the electron-of-interest is in a 1s orbital, the other electrons shield **0.30**.
   b. When the electron of interest is in a *ns* or *np* orbital
      - electrons in the same orbital shield **0.35**
      - electrons with *n* and *l-1* shield **0.35**
      - electrons with *n-1* shield **0.85**
      - all other electrons shield **1.00**
   c. When the electron-of-interest is in a *nd* or *nf* orbital
      - electrons in the same orbital shield **0.35**
      - all other electrons shield **1.00**
5. Sum the contributions of all electrons (except the electron-of-interest) to obtain the shielding constant S from the shielding values assigned to each electron, S_i.

Equation **1.16.3**

$$S = \sum n_i S_i \tag{1.16.3}$$

6. Subtract the shielding constant S from the nuclear charge Z to obtain the effective nuclear charge, as shown in Equation **1.16.2**



Example 1.16.1: Shielding of a 2*p* Electron on Nitrogen

What is the shielding constant experienced by a 2*p* electron in the nitrogen atom? What is the effective nuclear charge experienced by this electron?

Strategy:

1. Determine the electron configuration of nitrogen, then write it in the appropriate form.
2. Use the appropriate Slater Rules to calculate the shielding constant for the electron.
3. Subtract the shielding contant from the nuclear charge to find the effective nuclear charge.

Solution:

N: $1s^2\ 2s^2\ 2p^3$

N: $(1s^2)(2s^2,2p^3)$

From Table **1.16.1**:

- There are four 2s and 2p electrons that shield the 2p electron-of-interest equally at 0.35 units. The electron of interest does not shield itself!
- There are two 1s electrons that shield the 2p electron-of-interest at 0.85 units.

$$S[2p] = \underbrace{0.35(4)}_{\text{the 2s and 2p electrons}} + \underbrace{0.85(2)}_{\text{the 1s electrons}} = 3.10$$

For N, Z = 7

$$Z_{eff} = 7 - 3.1 = 3.9 \tag{1.16.4}$$

Example 1.16.2: Shielding of a 3d Electron on Bromine

What is the shielding constant experienced by a 3*d* electron in the bromine atom? What is the effective nuclear charge experienced by this electron?

Strategy:

1. Determine the electron configuration of nitrogen, then write it in the appropriate form.
2. Use the appropriate Slater Rules to calculate the shielding constant for the electron.
3. Subtract the shielding contant from the nuclear charge to find the effective nuclear charge.

Solution:

Br: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^5$

Br: $(1s^2)(2s^2,2p^6)(3s^2,3p^6)(3d^{10})(4s^2,4p^5)$

Ignore the group to the right of the 3d electrons. These are in higher energy orbtials and do not contribute to the shielding constant.

From Table **1.16.1**:

- There are nine 3d electrons that shield the 3d electron-of-interest equally at 0.35 units.
- There are eight 3s and 3p electrons that shield the 4d electron-of-interest equally at 1.00 units.
- There are eight 2s and 2p electrons that shield the 4d electron-of-interest at 1.00 units.
- There are two 1s electrons that shield the 4p electron-of-interest at 1.00 units.

$$S[3d] = \underbrace{0.35(9)}_{\text{the 3d electrons}} + \underbrace{1.00(8)}_{\text{the 3s and 3p electrons}} + \underbrace{1.00(8)}_{\text{the 2s and 2p electrons}} + \underbrace{1.00(2)}_{\text{the 1s electrons}} = 21.15$$

For Br, Z = 35

$$Z_{eff} = 35 - 21.15 = 13.85 \tag{1.16.5}$$

Problems

Exercise 1.16.1: Shielding of a Valence Electron on Boron

What is the shielding constant experienced by a valence *p*-electron in the boron atom? What is the effective nuclear charge experienced by this electron?

Answer

B: $1s^2\ 2s^2\ 2p^1$

B: $(1s^2)(2s^1)$

From Table **1.16.1**:

- There are two 2s electrons that shield the 2p electron-of-interest equally at 0.35 units. The electron of interest does not shield itself!
- There are two 1s electrons that shield the 2p electron-of-interest at 0.85 units.

$$S[2p] = \underbrace{0.35(2)}_{\text{the 2s electrons}} + \underbrace{0.85(2)}_{\text{the 1s electrons}} = 2.40$$

For B, Z = 5

$$Z_{eff} = 5 - 2.4 = 2.6 \tag{1.16.6}$$

Exercise 1.16.2: Shielding of a Valence Electron on Bromine

What is the shielding constant experienced by a valence *p*-electron in the bromine atom? What is the effective nuclear charge experienced by this electron?

Answer

Br: $(1s^2)(2s^2,2p^6)(3s^2,3p^6,3d^{10})(4s^2,4p^5)$

From Table **1.16.1**:

- There are six 4s and 4p electrons that shield the 4p electron-of-interest equally at 0.35 units.
- There are 18 3s, 3p, and 3d electrons that shield the 4p electron-of-interest equally at 0.85 units.
- There are eight 2s and 2p electrons that shield the 4p electron-of-interest at 1.00 units.
- There are two 1s electrons that shield the 4p electron-of-interest at 1.00 units.

$$S[4p] = \underbrace{0.35(6)}_{\text{the 4s and 4p electrons}} + \underbrace{0.85(18)}_{\text{the 3s, 3p, and 3d electrons}} + \underbrace{1.00(8)}_{\text{the 2s and 2p electrons}} + \underbrace{1.00(2)}_{\text{the 1s electrons}} = 27.4$$

For Br, Z = 35

$$Z_{eff} = 35 - 27.4 = 7.6 \tag{1.16.7}$$

Exercise 1.16.3: Shielding of a Valence Electron on Isoelectronic Species

What is the shielding constant experienced by the valence *p*-electrons in the three isoelectronic species: fluoride (F^-), neon (Ne), and sodium cation (Na^+)? What is the effective nuclear charge experienced by these electrons?

Answer

F^-, Ne, Na^+: $1s^2\ 2s^2\ 2p^6$

F^-, Ne, Na^+:: $(1s^2)(2s^2,2p^6)$

From Table **1.16.1**:

- There are five 2s and 2p electrons that shield the 2p electron-of-interest equally at 0.35 units.
- The electron of interest does not shield itself! There are two 1s electrons that shield the 2p electron-of-interest at 0.85 units.

$$S[2p] = \underbrace{0.35(6)}_{\text{the 2s and 2p electrons}} + \underbrace{0.85(2)}_{\text{the 1s electrons}} = 3.80$$

For F, Z = 9

$$Z_{eff} = 9 - 3.8 = 5.2 \tag{1.16.8}$$

For Ne, Z = 10

$$Z_{eff} = 10 - 3.8 = 6.2 \tag{1.16.9}$$

For Na, Z = 11

$$Z_{eff} = 11 - 3.8 = 7.2 \tag{1.16.10}$$

Exercise 1.16.4: Shielding of a 3d Electron on Copper

What is the shielding constant experienced by a valence *d*-electron in the copper atom?What is the effective nuclear charge experienced by this electron?

Answer

Cu: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1\ 3d^{10}$

Cu: $(1s^2)(2s^2,2p^6)(3s^2,3p^6)(3d^{10})(4s^1)$

Ignore the group to the right of the 3d electrons. These are in higher energy orbtials and do not contribute to the shielding constant.

From Table **1.16.1**

- There are nine 3d electrons that shield the 3d electron-of-interest equally at 0.35 units.
- There are eight 3s and 3p electrons that shield the 4d electron-of-interest equally at 1.00 units.
- There are eight 2s and 2p electrons that shield the 4d electron-of-interest at 1.00 units.
- There are two 1s electrons that shield the 4p electron-of-interest at 1.00 units.

$$S[3d] = \underbrace{0.35(9)}_{\text{the 3d electrons}} + \underbrace{1.00(8)}_{\text{the 3s and 3p electrons}} + \underbrace{1.00(8)}_{\text{the 2s and 2p electrons}} + \underbrace{1.00(2)}_{\text{the 1s electrons}} = 21.15$$

For Cu, Z = 29

$$Z_{eff} = 29 - 21.15 = 7.85 \tag{1.16.11}$$

Exercise 1.16.5: Shielding of a 3*d* Electron on Zinc

What is the shielding constant experienced by a valence *d*-electron in the zinc atom? What is the effective nuclear charge experienced by this electron?

Answer

Zn: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}$

Zn: $(1s^2)(2s^2,2p^6)(3s^2,3p^6)(3d^{10})(4s^2)$

Ignore the group to the right of the 3d electrons. These are in higher energy orbtials and do not contribute to the shielding constant.

From Table **1.16.1**

- There are nine 3d electrons that shield the 3d electron-of-interest equally at 0.35 units.
- There are eight 3s and 3p electrons that shield the 4d electron-of-interest equally at 1.00 units.
- There are eight 2s and 2p electrons that shield the 4d electron-of-interest at 1.00 units.
- There are two 1s electrons that shield the 4p electron-of-interest at 1.00 units.

$$S[3d] = \underbrace{0.35(9)}_{\text{the 3d electrons}} + \underbrace{1.00(8)}_{\text{the 3s and 3p electrons}} + \underbrace{1.00(8)}_{\text{the 2s and 2p electrons}} + \underbrace{1.00(2)}_{\text{the 1s electrons}} = 21.15$$

For Cu, Z = 30

$$Z_{eff} = 30 - 21.15 = 8.85 \tag{1.16.12}$$

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- Kimberley A. Waldron, Erin M. Fehringer, Amy E. Streeb, Jennifer E. Trosky and Joshua J. Pearson, "Screening Percentages Based on Slater Effective Nuclear Charge as a Versatile Tool for Teaching Periodic Trends", J. Chem. Educ., 2001, 78 (5), p 635

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1.17: Periodic Trends and Effective Nuclear Charge

Estimated Time to Read: 3 min

Idealized Values for Z_{eff}

Slater's rules are a set of simple rules for predicting S and Z_{eff} based on empirical evidence from quantum mechanical calculations. In other words, the Z_{eff} calculated from Slater's rules are approximate values. The values considered to be the most accurate are derived from quantum mechanical calculations directly. You can find these values in Figure **1.17.1** for convenience:

Z or Z_{eff}	H																	He
Z	1.00																	2.00
1s	1.00																	1.69
	Li	Be											B	C	N	O	F	Ne
Z	3.00	4.00											5.00	6.00	7.00	8.00	9.00	10.00
1s	2.69	3.69											4.68	5.67	6.67	7.66	8.65	9.64
2s	1.28	1.91											2.58	3.22	3.85	4.49	5.13	5.76
2p													2.42	3.14	3.83	4.45	5.10	5.76
	Na	Mg											Al	Si	P	S	Cl	Ar
Z	11.00	12.00											13.00	14.00	15.00	16.00	17.00	18.00
1s	10.63	11.61											12.59	13.58	14.56	15.54	16.52	17.51
2s	6.57	7.39											8.21	9.02	9.83	10.63	11.43	12.23
2p	6.80	7.83											8.96	9.95	10.96	11.98	12.99	14.01
3s	2.51	3.31											4.12	4.90	5.64	6.37	7.07	7.76
3p													4.07	4.29	4.89	5.48	6.12	6.76
	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Z	19.00	20.00	21.00	22.00	23.00	24.00	25.00	26.00	27.00	28.00	29.00	30.00	31.00	32.00	33.00	34.00	35.00	36.00
1s	18.49	19.47	20.46	21.44	22.43	23.41	24.40	25.38	26.37	27.35	28.34	29.33	30.31	31.29	32.28	33.26	34.25	35.23
2s	13.01	13.78	14.57	15.38	16.18	16.98	17.79	18.60	19.41	20.21	21.02	21.83	22.60	23.37	24.13	24.89	25.64	26.40
2p	15.03	16.04	17.06	18.07	19.07	20.08	21.08	22.09	23.09	24.10	25.10	26.10	27.09	28.08	29.07	30.07	31.06	32.05
3s	8.68	9.60	10.34	11.03	11.71	12.37	13.02	13.68	14.32	14.96	15.59	16.22	17.00	17.79	18.60	19.40	20.22	21.03
3p	7.73	8.66	9.41	10.10	10.79	11.47	12.11	12.78	13.44	14.09	14.73	15.37	16.20	17.01	17.85	18.71	19.57	20.43
4s	3.50	4.40	4.63	4.82	4.98	5.13	5.28	5.43	5.58	5.71	5.84	5.97	7.07	8.04	8.94	9.76	10.55	11.32
3d			7.12	8.14	8.98	9.76	10.53	11.18	11.86	12.53	13.20	13.88	15.09	16.25	17.38	18.48	19.56	20.63
4p													6.22	6.78	7.45	8.29	9.03	9.34
	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Z	37.00	38.00	39.00	40.00	41.00	42.00	43.00	44.00	45.00	46.00	47.00	48.00	49.00	50.00	51.00	52.00	53.00	54.00
1s	36.21	37.19	38.18	39.16	40.14	41.13	42.11	43.09	44.08	45.06	46.04	47.03	48.01	48.99	49.97	50.96	51.94	52.92
2s	27.16	27.90	28.62	29.37	30.13	30.88	31.63	32.38	33.16	33.88	34.63	35.39	36.12	36.86	37.60	38.33	39.07	39.80
2p	33.04	34.03	35.00	35.99	36.98	37.97	38.94	39.95	40.94	41.93	42.92	43.91	44.90	45.89	46.87	47.86	48.85	49.84
3s	21.84	22.66	23.55	24.36	25.17	25.98	26.79	27.60	28.44	29.22	30.03	30.84	31.63	32.42	33.21	34.00	34.79	35.58
3p	21.30	22.17	23.09	23.85	24.62	25.47	26.38	27.22	28.15	29.02	29.81	30.69	31.52	32.35	33.18	34.01	34.84	35.67
4s	12.39	13.44	14.26	14.90	15.28	16.10	17.20	17.66	18.58	18.99	19.87	20.87	21.76	22.66	23.54	24.41	25.30	26.17
3d	21.68	22.73	25.40	25.57	26.25	27.23	28.35	29.36	30.41	31.45	32.54	33.61	34.68	35.74	36.80	37.84	38.90	39.95
4p	10.88	11.93	12.75	13.46	14.08	14.98	15.81	16.44	17.14	17.72	18.56	19.41	20.37	21.27	22.18	23.12	24.03	24.96
5s	4.99	6.07	6.26	6.45	5.92	6.11	7.23	6.49	6.64	(empty)	6.76	8.19	9.51	10.63	11.62	12.54	13.40	14.22
4d			15.96	13.07	11.24	11.39	12.88	12.81	13.44	13.62	14.76	15.88	16.94	17.97	18.97	19.96	20.93	21.89
5p													8.47	9.10	10.00	10.81	11.61	12.43

Figure 1.17.1: Z_{eff} values calculated by Clementi et al. in 1963 and 1967 that are consistent with SCF Calculations. [Wikipedia: Effective Nuclear Charge]

General Periodic Trends in Ze_{ff}

The data from Figure **1.17.1** is plotted below in Figure **1.17.2**. Close inspection of Figure **1.17.2** shows that there are some predictable trends in Z_{eff}. The Z_{eff} for electrons in a given shell and subshell generally increase as atomic number increases; this trend holds true going across the periodic table and down the periodic table. You can see this trend as the positive slope in each series in Figure **1.17.2**. There is one obvious exception in Period 5 in elements 39 (Y) to 41. For Nb, the Z_{eff} of the 4s electrons actually decreases as atomic number increases. There is also an exception between Y and Zr in the 3d subshell, and between Tc and Ru in the 5s subshell.

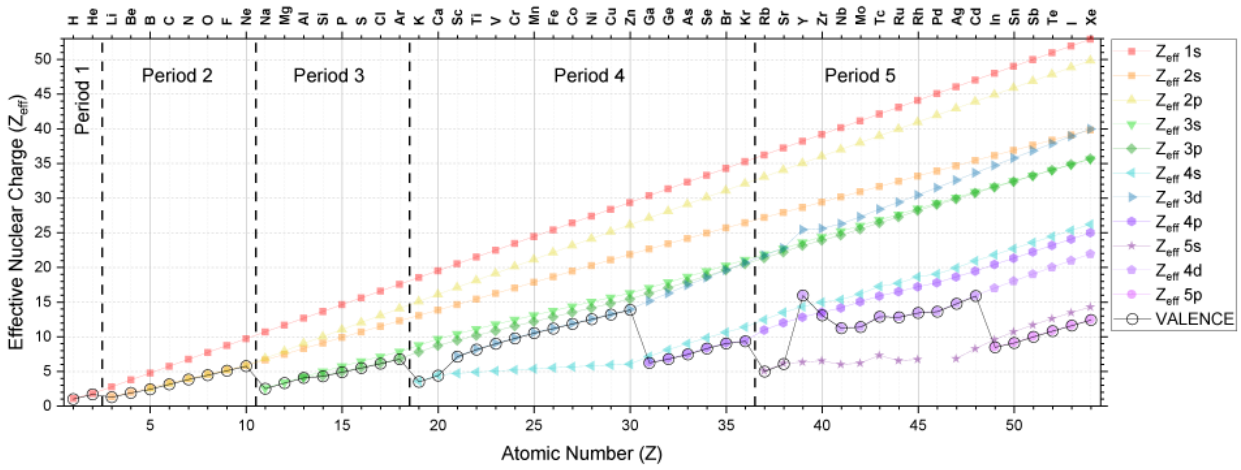


Figure 1.17.2: The Z_{eff} values for electrons in each subshell of the first 54 elements (H to Xe). Each subshell is plotted as a different series (see legend) and the valence shell is highlighted by a solid black line with open circles. (CC-BY-NC-SA, LibreText)

Trends in Z_{eff} of Valence Electrons

It is useful to understand trends Z_{eff} for the valence electrons specifically because the valence electrons determine atomic/ionic properties and chemical reactivity. The trends in the Z_{eff} of the valence electrons are not simple because as atomic number increases, the valence shell and/or subshell also change. The valence Z_{eff} is indicated in Figure **1.17.2** as a black line with open circles.

Down a column of the periodic table, the Z_{eff} of the valence electrons increases. This is a simple trend because type of subshell is consistent and there is an increase only in shell and in atomic number, Z. This trend is best illustrated by inspection of Figure **1.17.1**.

Across a row of the periodic table, generally Z_{eff} of the valence electrons increases across a period, but the trend does depend on shell and subshell.

- **Periods 1-3 (s and p subshells only):** The valence electron shell is constant as Z increases and the subshell changes from s to p. There is a gradual increase in valence Z_{eff}.
- **Periods 4 and 5 (s, p, and d subshells):** The valence shell and subshell change as atomic number increases. The Z_{eff} of the valence electrons generally increases going across a period as long as the subshell does not change. (There is an exception within the 4d subshell for elements 39-44, Y-Ru.) In general, going from an $(n)s$ subshell to an $(n-1)d$ subshell, there is a relatively large increase in valence Z_{eff}. Going from an $(n-1$d\) subshell to an $(n)p$ subshell, there is a relatively large decrease in Z_{eff}.
- **Crossing from one period to the next:** From Figure **1.17.2**, we can see that when Z increases by one proton and the period increases (for example, going from Ne to Na), there is a relatively large decrease in Z_{eff}. As Z increases by a small interval, the shell number increases, and so the electrons in the valence shell are much farther from the nucleus and are more shielded by the electrons in the lower energy shells.

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Contributors and Attributions

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1.18: The Effects of Shielding on Periodic Properties

Estimated Time to Read: 8 min

Z_{eff} modulates attraction

A modified form of Coulomb's Law is given in Equation 1.18.1, where e is the charge of an electron, Z_{eff} is the effective nuclear charge experienced by that electron, and r is the radius (distance of the electron from the nucleus).

Equation 1.18.1:

$$F_{eff} = k\frac{Z_{eff}e^2}{r^2}$$

This formula suggests that if we can estimate Z_{eff}, then we can predict the attractive force experienced by and the energy of an electron in a multi-electron atom. The attraction of the nucleus to the valence electrons determines the atomic radius, ionization energy, and electron affinity. The stronger the attraction, and the stronger Z_{eff}, the closer the electrons are pulled toward the nucleus. This in turn results in a smaller size, higher ionization energy, and higher electron affinity.

The Lanthanide Contraction describes the atomic radius trend that the Lanthanide series exhibits. Another important feature of the The Lanthanide Contraction is the 5s and 5p orbitals penetrate the 4f sub-shell so the 4f orbital is not shielded from the increasing nuclear change, which causes the atomic radius of the atom to decrease. This decrease in size continues throughout the series.

Atomic Radius

Atomic radius generally decreases from left to right across a period of elements. As the nuclear charge (Z) increases, the effective nuclear charge (Z*) of the valence electrons also increases. However, with each addition of a proton there is an addition of an electron. The electrons are added into the valence shell and weakly shielded by the other electrons in the valence shell. Therefore, as Z increases, Z_{eff} increases more gradually due to shielding. The observed change in atomic radius is a balance of a compression caused by increasing Z and an expansion in the number of electrons. As a result, the atomic radius decreases *gradually* across a period.

Atomic size generally increases going down a group. As valence electrons occupy higher level shells due to the increasing quantum number (n), size increases despite the fact that Z and Z* are increasing going down the group.

Scandide Contraction

The Scandide Contraction is an atomic radius trend experienced by the d-block elements. Normally atomic radius decreases significantly as nuclear charge increases across a period of the periodic table. In the transition metal elements, the atomic radii only decreases slightly as compared to decreases across the s or p block. D-block elements have the same number of s orbital electrons and only differing in the number of d orbital electrons. The d orbital electrons are inner shell electrons and each additional electron is added to the same shell and subshell. The d orbital electrons are poorly shielding compared to the s and p orbital electrons so effective nuclear charge increases more rapidly across the d-block, resulting in a smaller change in the atomic radius across the period.

Lanthanide Contraction

The Lanthanide series is in the f-block of the periodic table and includes elements 57-70 (La-Yb). As expected based on the periodic trend, the atomic radius of these elements decreases as the atomic number increases (Figure 1.18.1).

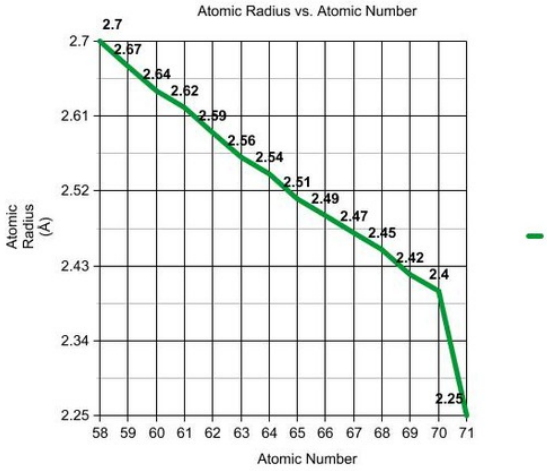
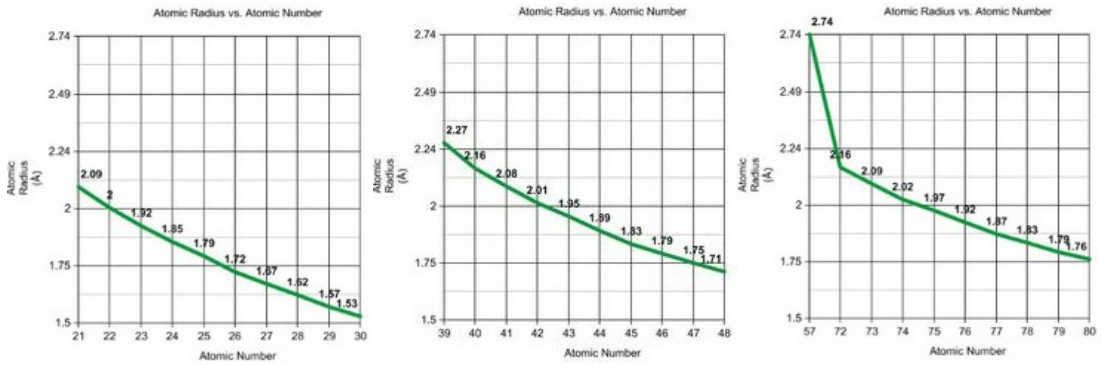


Figure 1.18.1: Atomic radius decreases as the atomic number increases across the Lanthanide Series. [LibreText]

Figure **1.18.2** shows the atomic radii of the first three rows of transition metal elements. Consider the elements with atomic numbers 23, 41, and 73, which are in the same column of the periodic table. The elements 23 and 41 they have a large difference in atomic radii, but the elements 41 and 73 have only a small difference in atomic radii. In general for d-block elements, the atomic radii differ greatly between the Row 1 and Row 2 elements, but the atomic radii differ little between Row 2 and Row 3 elements. This is deviation in the trend is caused by the introduction of 4f electrons in Row 3 and is known as *Lanthanide Contraction*. As a reminder, s orbitals are the most effective at shielding, followed by the p and d orbitals with the f orbitals being the least effective. The Lanthanide Contraction is the result of the poor shielding effect of the 4f electrons. Because the 4f electrons are poorly shielding, the 5d valence electrons experience a greater effective nuclear charge than would otherwise be expected. When shielding is poor, the positively charged nucleus has a greater attraction to the electrons, and atomic radius decreases more rapidly as the atomic number increases.



Row 1 3d Elements | Row 2, 4d Elements | Row 3, 5d Elements

Figure 1.18.2: Atomic radii of transition metals elements in Period 4 (left), Period 5 (center), and Period 6 (right) [LibreText]

The Lanthanide Contraction can be seen by further comparing the elements with f electrons and those without f electrons in the d block. Pd and Pt are such elements. Pd has 4d electrons while Pt has 5d and 4f electrons. These 2 elements have roughly the same atomic radius. This is due to Lanthanide Contraction and shielding. While we would expect Pt to have a significantly larger radius because more electrons and protons are added, it does not because the 4f electrons are poor at shielding. When the shielding is not good there will be a greater nuclear charge, thus pulling the electrons in closer, resulting in a smaller than expected radius.

Ionization Energy

Ionization energy is the energy required to remove an electron from a neutral gaseous atom. Across a period, the number of protons and the effective nuclear charge increase. As a result, the atomic radius decreases. If we consider Equation 1, increasing effective charge and decreasing radii results in greater attractive forces by the nucleus for electrons. Thus, greater energy is required for an electron to overcome the attractive force of the nucleus and the ionization energy increases.

In general, ionization energies increase from left to right and decrease down a group; however, there are variations in these trends that would be expected from the effects of penetration and shielding.

- **Across a period:** As Z_{eff} increases across a period, the ionization energy of the elements generally increases from left to right. However there are breaks or variation in the trends in the following cases:
  - IE is especially low when removal of an electron creates a newly empty p subshell (examples include B, Al, Sc)
  - IE energy is especially low where removal of an electron results in a half-filled p or d subshell (examples include O, S)
  - IE increases more gradually across the d- and f-subshells compared to s- and p- subshells. This is because d- and f-electrons are weakly penetrating and experience especially low Z_{eff}.
- **From one period to the next:** There is an especially large decrease in IE with the start of every new period (from He to Li or from Ne to Na for example). This is consistent with the idea that IE is especially low when removal of an electron creates a newly empty s-subshell.
- **Noble gases:** The noble gases posses very high ionization energies. Note that helium has the highest ionization energy of all the elements.
- **Down a group:** Although Z_{eff} increases going down a group, there is no reliable trend in IE going down any group; in some cases IE increases going down a group, while in other cases IE decreases going down a group.

Trends in Electron Affinity

Electron affinity is the change in energy when an electron is added to a neutral gaseous atom. The trends in electron affinity mimic the trends in ionization energy.

- **Across a period**: Similar to ionization energy, EA generally increases (more negative, more exothermic)across a row of the periodic table; this observation is consistent with the increase in effective nuclear charge (Z_{eff}) from left to right across a period. However, there are variations across a period that are similar to variations in ionization energy and that can be explained by shielding, penetration, and electron configuration.
- **Down a group**: Like the case of ionization energy trends, EA does not consistently decrease going down a column of the periodic table despite the fact that Z_{eff} increases down a group.

The trend in EA follows a zig-zag pattern similar to the one seen with ionization energies, except that it is displaced by one unit from the trend in IE_1, two units from IE_2, and so on. For example, EA peaks at F, while IE_1 peaks at Ne, IE_2 peaks at Na, and IE_3 peaks at Mg. A plot of EA for the first 13 elements is shown overlaid on plots of IE_1, IE_2, and IE_3 in Figure **1.18.3**, where the shifts in the peaks and valleys within each zig-zag trend are indicated.

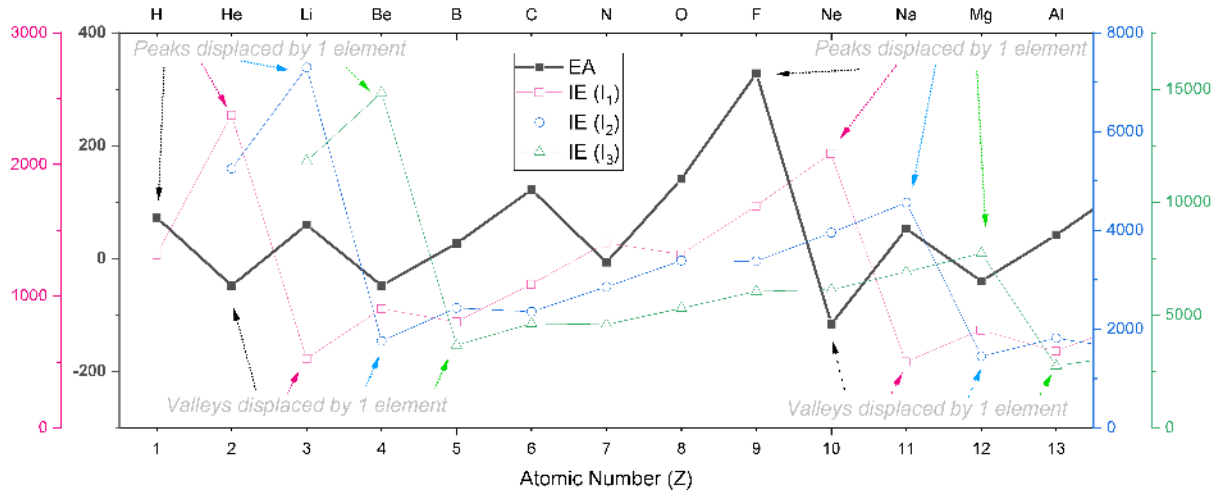


Figure 1.18.3: A plot of electron affinity (the zeroth ionization energy) is overlaid on plots of the first (IE_1), second (IE_2), and third (IE_3) ionization energies. Each plot is shown using separate y-axes. Trends in EA are similar to those in ionization energies, except that the peaks and valleys of the trends are shifted by one unit, as indicated. These plots are shown in units of kJ/mole. (CC-BY-NC-SA; Kathryn Haas)

Problems

Exercise 1.18.1

Compare trends in Z* and atomic size. Explain how and why atomic size depends on Z_{eff}.

Answer

On the periodic table, atomic radius generally decreases across the periods (left to right) and increases down the groups. As atomic number increases across the periodic table, nuclear charge (Z) increases and Z* increases. In turn, the atomic radius decreases because the higher nuclear charge (and thus higher Z*) pulls electrons closer to the nucleus. Atomic radius increases down the periodic table because the shell number increases. Despite an increase in Z* going down the periodic table, larger atomic radii result from electrons occupying higher shells.

Exercise 1.18.2

Compare trends in Z_{eff} and ionization energy. Explain how and why ionization energy depends on Z_{eff}.

Answer

Ionization energies (IE) are inversely related to atomic radius; IE increases across the periods and decreases down the groups. Since the nucleus holds valence electrons more strongly (due to higher Z*) across the periods, IE increases because valence electrons are harder to remove. Down the periodic table, larger atomic radii cause electrons in valence orbitals to be shielded by core electrons. Recall that shielding reduces the nuclear charge available to electrons in higher orbital levels, resulting in a lower Z*. With more shielding and lower Z*, the valence electrons are held less tightly by the nucleus such that ionization energy decreases (i.e., valence electrons are easier to remove).

Exercise 1.18.3

What is the cause of Lanthanide Contraction?

Answer

The Lanthanide Contraction is caused by a poor shielding effect of the 4f electrons

Exercise 1.18.4

Which element has a greater atomic radius Gd or Tb and why?

Answer

Gd because as atomic number increases, the atomic radius decreases..

Exercise 1.18.5

Which element has a smaller atomic radius Dy or Yb and why?

Answer

Yb because it has a larger atomic number.

Exercise 1.18.6

Why do elements in Rows 2 and 3 that are in the same column have similar atomic radii?

Answer

Because the elements in Row 3 have 4f electrons. These electrons are do not shield good, causing a greater nuclear charge. This greater nuclear charge has a greater pull on the electrons.

Exercise 1.18.7

Place the following elements in order of increasing atomic radius: Eu, Ce, Pr, Ho.

Answer

Ho, Eu, Pr, Ce

References

1. Petrucci, Harwood, Herring, and Madura. *General Chemistry Principles & Modern Applications*. 9th ed. Prentice Hall. Print.
2. Cotton, Simon. *Lanthanide and Actinide Chemistry*. Wiley. Print.
3. Electron Affinity (data page), Wikipedia. en.Wikipedia.org/wiki/Electron_affinity_(data_page) Accessed 12/3/19.

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CHAPTER OVERVIEW

Unit 2: Acid-Base and Donor-Acceptor Chemistry

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2.1: Definitions of Acid and Base

Acids

An acid (from the Greek *oxein* then Latin *acidus/acére* meaning sour) is a chemical substance whose aqueous solutions were characterized by a sour taste, the ability to turn blue litmus red, and the ability to react with bases and certain metals (like calcium) to form salts. Aqueous solutions of acids have a pH smaller than 7. The lower the pH, the higher the acidity and thus the higher the concentration of hydrogen ions in the solution (using the Arrhenius or Brønsted-Lowry definition).

Some notes on acids-bases, pH and the use of logarithms in calculations are available.

There are a number of common definitions for acids, for example, the **Arrhenius**, **Brønsted-Lowry**, and the **Lewis** definition. The Arrhenius definition defines acids as substances which increase the concentration of hydrogen ions (H^+), when dissolved in water. The Brønsted-Lowry definition is an expansion of this and defines an acid as a substance which can act as an H^+ donor. By this definition, any compound which can be easily deprotonated can be considered an acid. Examples include alcohols and amines which contain O-H or N-H fragments. A Lewis acid is a substance which can accept a pair of electrons to form a covalent bond. Examples of Lewis acids include all metal cations, and electron-deficient molecules such as boron trifluoride and aluminium trichloride.

Common examples of acids include hydrochloric acid (a solution of hydrogen chloride gas in water, this is the acid found in the stomach that activates digestive enzymes), acetic acid (vinegar is a dilute solution, generally under 5%), sulfuric acid (used in wet-cell car batteries), and tartaric acid (a solid used in baking). As these examples show, acids can be solutions or pure substances, and can be derived from solids, liquids, or gases.

$HCl(aq) + NaOH(aq) \rightleftarrows NaCl + H_2O$
$HOAc(aq) + NaOH(aq) \rightleftarrows NaOAc + H_2O$
$H_2SO_4(aq) + 2NaOH(aq) \rightleftarrows Na_2SO_4 + 2H_2O$
$HO_2CCH(OH)CH(OH)CO_2H(aq) + 2NaOH(aq) \rightleftarrows Na_2Tartrate + 2H_2O$

Bases

The "modern" concept of a base in chemistry, stems from Guillaume-François Rouelle who in 1754 suggested that a base was a substance which reacted with acids "by giving it a concrete base or solid form" (as a salt). In addition they gave aqueous solutions which were characterized as slippery to the touch, tasted bitter, changed the colour of indicators (e.g., turned red litmus paper blue), and promoted certain chemical reactions (base catalysis). Examples of bases are the hydroxides of the alkali and alkaline earth metals (NaOH, $Ca(OH)_2$, etc.).

For a substance to be classified as an Arrhenius base, it must produce hydroxide ions in solution. In order to do so, Arrhenius believed the base must contain hydroxide in the formula. This made the Arrhenius model limited, as it did not readily explain the basic properties of aqueous solutions of ammonia (NH_3.aq, often written as NH_4OH to better fit the Arrhenius model) or its organic derivatives (amines). In the more general Brønsted-Lowry acid-base theory, a base is a substance that can accept hydrogen ions (H^+). In the Lewis model, a base is an electron pair donor.

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2.2: Electronegativity

Electronegativity is the measurement of an atom to compete for electrons in a bond. The higher the electronegativity, the greater its ability to gain electrons in a bond. Electronegativity will be important when we later determine polar and nonpolar molecules. Electronegativity is related with ionization energy and electron affinity. Electrons with low ionization energies have low electronegativities because their nuclei do not exert a strong attractive force on electrons. Elements with high ionization energies have high electronegativities due to the strong pull exerted by the positive nucleus on the negative electrons. Therefore the electronegativity increases from bottom to top and from left to right.

Definitions of Electronegativity

Linus Pauling introduced the first electronegativity scale in 1932 in order to explain the extra stability of molecules with polar bonds.[1] The electronegativity of an atom, represented by the Greek letter χ (chi), can be defined as the tendency of an atom to draw electrons to itself *in a chemical bond*. On the Pauling scale, the electronegativity difference between two atoms A and B was defined in terms of the dissociation energies E_d of the A-A, B-B, and A-B bonds:

Equation **2.2.1**:

$$\chi_A - \chi_B = \sqrt{E_d(AB) - [E_d(AA) + E_d(BB)]/2}$$

where the energies are expressed in electron volts. Pauling's scale of electronegativity ranges from Fluorine (most electronegative = 4.0) to Francium (least electronegative = 0.7). [2,3] The polarity of bonds and assignment of formal charges is predicted by electronegativity differences.

V·T·E **Periodic table of electronegativity using the Pauling scale**

→ Atomic radius decreases → Ionization energy increases → Electronegativity increases →

Group →	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
↓ Period																		
1	H 2.20																	He
2	Li 0.98	Be 1.57											B 2.04	C 2.55	N 3.04	O 3.44	F 3.98	Ne
3	Na 0.93	Mg 1.31											Al 1.61	Si 1.90	P 2.19	S 2.58	Cl 3.16	Ar
4	K 0.82	Ca 1.00	Sc 1.36	Ti 1.54	V 1.63	Cr 1.66	Mn 1.55	Fe 1.83	Co 1.88	Ni 1.91	Cu 1.90	Zn 1.65	Ga 1.81	Ge 2.01	As 2.18	Se 2.55	Br 2.96	Kr 3.00
5	Rb 0.82	Sr 0.95	Y 1.22	Zr 1.33	Nb 1.6	Mo 2.16	Tc 1.9	Ru 2.2	Rh 2.28	Pd 2.20	Ag 1.93	Cd 1.69	In 1.78	Sn 1.96	Sb 2.05	Te 2.1	I 2.66	Xe 2.60
6	Cs 0.79	Ba 0.89	*	Hf 1.3	Ta 1.5	W 2.36	Re 1.9	Os 2.2	Ir 2.20	Pt 2.28	Au 2.54	Hg 2.00	Tl 1.62	Pb 1.87	Bi 2.02	Po 2.0	At 2.2	Rn 2.2
7	Fr 0.7	Ra 0.9	**	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Fl	Uup	Lv	Uus	Uuo
* Lanthanoids			La 1.1	Ce 1.12	Pr 1.13	Nd 1.14	Pm 1.13	Sm 1.17	Eu 1.2	Gd 1.2	Tb 1.1	Dy 1.22	Ho 1.23	Er 1.24	Tm 1.25	Yb 1.1	Lu 1.27	
** Actinoids			Ac 1.1	Th 1.3	Pa 1.5	U 1.38	Np 1.36	Pu 1.28	Am 1.13	Cm 1.28	Bk 1.3	Cf 1.3	Es 1.3	Fm 1.3	Md 1.3	No 1.3	Lr 1.3	

Figure **2.2.1**: Table of Pauling electronegativities from [Wikipedia]

While directly relevant to the strength of chemical bonds, the Pauling definition of electronegativity has a significant limitation: calculating each value requires data from several compounds in which specific atoms are bonded. This means that the scale cannot be successfully applied to all situations. To overcome this limitation, alternative electronegativity scales were developed based on different thermochemical measurements or calculations. These other scales are listed in Table \PageIndes1 below. More thorough descriptions of how values in each scale are calculated are described on Wikipedia's Electronegativity page and a concise history of electronegativity scales is summarized in ref 4.

Table **2.2.1**: Electronegativity Scales and Their Defining Characterisitics

Scale Developer	Year first described	Characteristics
Linus Pauling[1]	1932	Based on bond energies
Robert S. Mulliken[5,6]	1934	Based on valence electron properties of atoms (electron affinity and ionization energy)
Louis Allred & Eugene G. Rochow[7]	1958	Based on electrostatic force (effective nuclear charge)
Robert T. Sanderson[8]	1983	Based on atomic electron density
Ralph G. Pearson[9]	1985	Related to Hard-Soft Acid-Based theory
Leland C. Allen, Joseph Mann, Terry L. Meek[10,11,12]	1989, 2000	Average ionization energies of valence shell electrons, configuration energies (CE) $$\mathrm{CE} = \frac{n\varepsilon_s + m\varepsilon_p}{n+m}$$ n = number of s electrons m = number of p electrons $\varepsilon_s, \varepsilon_p$ = experimental 1-electron s and p energies

The primary advantage to the scale developed by Mann, Meek, and Allen[12] is that it is based on configuration energy (CE), the average ionization energies of valence electrons in ground state free atoms. A scale based on ionization energies can be calculated more directly for any element. However, a critique of all electronegativity scales, including this one, is that they are all based on assumptions that fail in some cases.

There is a relationship between electronegativity and atomic size because both are related to ionization energy. Like ionization energy, there is a general trend across the periodic table for both electronegativity and atomic size; in general, smaller atoms toward the top right-hand side of the periodic table have greater electronegativity values and smaller atomic size.

Electronegativity Trends

Electronegativity is a qualitative property, and although there is no standardized method for calculating electronegativity the most common scale for quantifying electronegativity is the Pauling scale (Table A2), named after the chemist Linus Pauling. The numbers assigned by the Pauling scale are dimensionless due to the qualitative nature of electronegativity. Electronegativity values for each element can be found on certain periodic tables (Figure **2.2.2**.

Periodic Table of Elements

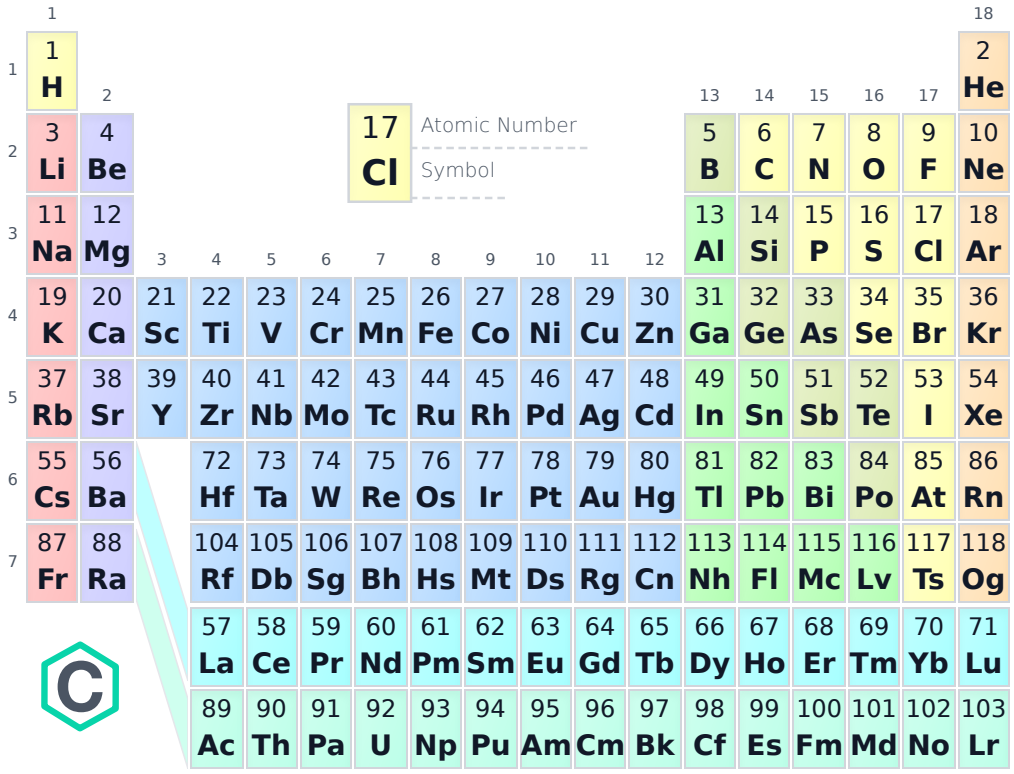


Figure 2.2.2: Periodic Table with Electronegativity Values

Electronegativity measures an atom's tendency to attract and form bonds with electrons. This property exists due to the electronic configuration of atoms. Most atoms follow the octet rule (having the valence, or outer, shell comprise of 8 electrons). Because elements on the left side of the periodic table have less than a half-full valence shell, the energy required to gain electrons is significantly higher compared with the energy required to lose electrons. As a result, the elements on the left side of the periodic table generally lose electrons when forming bonds. Conversely, elements on the right side of the periodic table are more energy-efficient in gaining electrons to create a complete valence shell of 8 electrons. The nature of electronegativity is effectively described thus: the more inclined an atom is to gain electrons, the more likely that atom will pull electrons toward itself.

- **From left to right across a period of elements, electronegativity increases.** If the valence shell of an atom is less than half full, it requires less energy to lose an electron than to gain one. Conversely, if the valence shell is more than half full, it is easier to pull an electron into the valence shell than to donate one.
- **From top to bottom down a group, electronegativity decreases.** This is because atomic number increases down a group, and thus there is an increased distance between the valence electrons and nucleus, or a greater atomic radius.
- **Important exceptions of the above rules include the noble gases, lanthanides, and actinides.** The noble gases possess a complete valence shell and do not usually attract electrons. The lanthanides and actinides possess more complicated chemistry that does not generally follow any trends. Therefore, noble gases, lanthanides, and actinides do not have electronegativity values.
- **As for the transition metals, although they have electronegativity values, there is little variance among them across the period and up and down a group.** This is because their metallic properties affect their ability to attract electrons as easily as the other elements.

According to these two general trends, the *most electronegative element is **fluorine***, with 3.98 Pauling units.

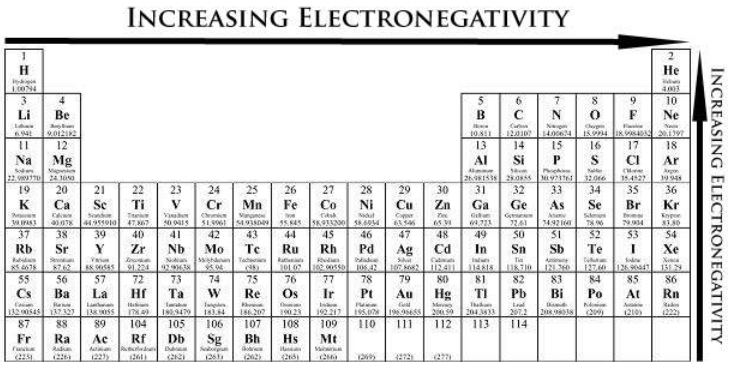


Figure **2.2.3**: Periodic Table showing Electronegativity Trend (LibreText)

Acknowledgment

- Matthew Salem (UC Davis) (Pauling Electronegativity)
- Introduction to Inorganic Chemistry Wikibook (https://chem.libretexts.org/Bookshel..._Bond_Strength)
- Kathryn Haas (Duke) (https://chem.libretexts.org/@go/page/219071)

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2.3: Acid-Base Theories and Concepts

> *In a very real sense, we can make an acid anything we wish. The differences between the various acid-base concepts are not concerned with which is 'right', but which is most convenient to use in a particular situation.*
>
> *James E. Huheey, Ellen A. Keiter, and Richard L. Keiter*

There are three primary theories of acid-base chemistry that are often taught together: Arrhenius theory, Brønsted-Lowry theory, and Lewis acid-base theory. Each theory is introduced below.

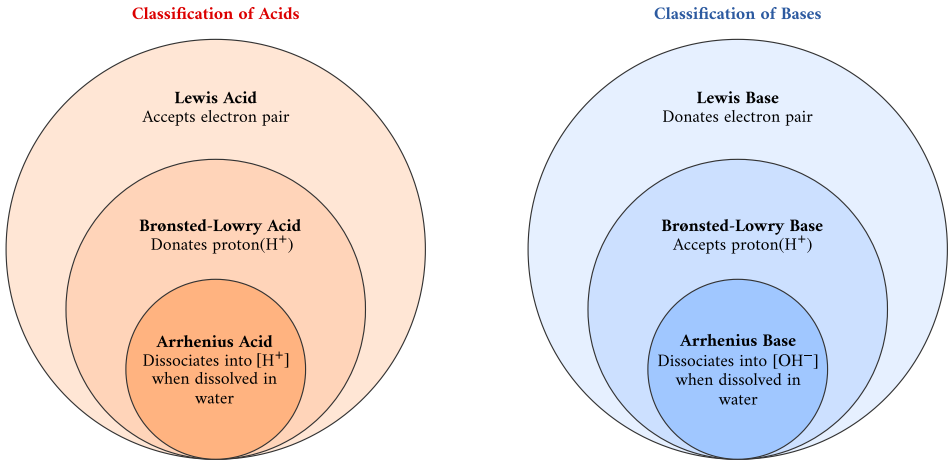


Figure **2.3.1**: Hierarchal definitions of acids and bases via the three primary theories. These theories are designed to be "superset" of the previous classification. (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

Arrhenius Acids and Bases

To qualify as an Arrhenius acid, upon the introduction to water, the chemical must either cause, directly or otherwise:

- an increase in the aqueous hydronium concentration, or
- a decrease in the aqueous hydroxide concentration.

The Swedish chemist Svante Arrhenius attributed the properties of acidity to hydrogen ions ($\mathbf{H^+}$) in 1884. An Arrhenius acid is a substance that, when added to water, increases the concentration of $\mathbf{H^+}$ ions in the water. Note that chemists often write $\mathbf{H^+(aq)}$ and refer to the hydrogen ion when describing acid-base reactions, but the free hydrogen nucleus does not exist alone in water. It exists in a hydrated form which for simplicity is often written as the hydronium (hydroxonium) ion, $\mathbf{H_3O^+}$. Thus, an Arrhenius acid can also be described as a substance that increases the concentration of hydronium ions when added to water. This definition stems from the equilibrium dissociation (self-ionization) of water into hydronium and hydroxide ($\mathbf{OH^-}$) ions:

$$\mathbf{H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)}$$

with K_w defined as $[\mathbf{H^+}][\mathbf{OH^-}]$.

The value of K_w varies with temperature, as shown in the table below where at 25 °C K_w is approximately $\mathbf{1.0 \times 10^{-14}}$, i.e. $\mathbf{pK_w = 14}$.

Water temperature	K_w / 10^{-14}	pK_w
0 °C	0.112	14.95
25 °C	1.023	13.99
50 °C	5.495	13.26
75 °C	19.95	12.70
100 °C	56.23	12.25

In pure water the majority of molecules are $\mathbf{H_2O}$, but the molecules are constantly dissociating and re-associating, and at any time a small number of the molecules (about 1 in 10^7) are hydronium and an equal number are hydroxide. Because the numbers are equal, pure water is neutral (not acidic or basic) and has an electrical conductivity of 5.5 microSiemen, μS/m. For comparison, sea water's conductivity is about one million times higher, 5 S/m (due to the dissolved salt).

Proton vs. Hydron

Although the term proton is often used for $\mathbf{H^+}$, this should really be reserved for $\mathbf{H}$ (protium) not $\mathbf{D}$ (deuterium) or $\mathbf{T}$ (tritium). The more general term, hydron covers all isotopes of hydrogen.

To qualify as an Arrhenius base, upon the introduction to water, the chemical must either cause, directly or otherwise:

- a decrease in the aqueous hydronium concentration, or
- an increase in the aqueous hydroxide concentration.

The definition is expressed in terms of an equilibrium expression:

$$\mathbf{acid + base \rightleftharpoons conjugate\ base + conjugate\ acid.}$$

With an acid, $\mathbf{HA}$, the equation can be written symbolically as:

$$\mathbf{HA + B \rightleftharpoons A^- + HB^+}$$

The double harpoons sign, $\rightleftharpoons$, is used because the reaction can occur in both forward and backward directions. The acid, $\mathbf{HA}$, can lose a hydron to become its conjugate base, $\mathbf{A^-}$. The base, $\mathbf{B}$, can accept a hydron to become its conjugate acid, $\mathbf{HB^+}$. Most acid-base reactions are fast so that the components of the reaction are usually in dynamic equilibrium with each other.

Brønsted-Lowry Acids and Bases

While the Arrhenius concept is useful for describing many reactions, it has limitations. In 1923, chemists Johannes Nicolaus Brønsted and Thomas Martin Lowry independently recognized that acid-base reactions involve the transfer of a hydron. A Brønsted-Lowry acid (or simply Brønsted acid) is a species that donates a hydron to a Brønsted-Lowry base. The Brønsted-Lowry acid-base theory has several advantages over the Arrhenius theory. Consider the following reactions of acetic acid ($\mathbf{CH_3COOH}$):

$$\mathbf{CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+}$$

$$\mathbf{CH_3COOH + NH_3 \rightleftharpoons CH_3COO^- + NH_4^+}$$

Both theories easily describe the first reaction: $\mathbf{CH_3COOH}$ acts as an Arrhenius acid because it acts as a source of $\mathbf{H_3O^+}$ when dissolved in water, and it acts as a Brønsted acid by donating a hydron to water. In the second example $\mathbf{CH_3COOH}$ undergoes the same transformation, in this case donating a hydron to ammonia ($\mathbf{NH_3}$), but it cannot be described using the Arrhenius definition of an acid because the reaction does not produce hydronium ions.

To qualify as an Brønsted-Lowry acid, the chemical must either cause, directly or otherwise:

- donate a proton.

Conversely, to qualify as an Brønsted-Lowry base, the chemical must either cause, directly or otherwise:

- accept a proton.

Lewis Acids and Bases

A third concept was proposed in 1923 by Gilbert N. Lewis which includes reactions with acid-base characteristics that do not involve a hydron transfer. A Lewis acid is a species that reacts with a Lewis base to form a Lewis adduct. The Lewis acid accepts a pair of electrons from another species; in other words, it is an electron pair acceptor. Brønsted acid-base reactions involve hydron transfer reactions while Lewis acid-base reactions involve electron pair transfers. All Brønsted acids are Lewis acids, but not all Lewis acids are Brønsted acids.

$$\mathrm{BF_3 + F^- \rightleftharpoons BF_4^-}$$

$$\mathrm{NH_3 + H^+ \rightleftharpoons NH_4^+}$$

In the first example $\mathrm{BF_3}$ is a Lewis acid since it accepts an electron pair from the fluoride ion. This reaction cannot be described in terms of the Brønsted theory because there is no hydron transfer. The second reaction can be described using either theory. A hydron is transferred from an unspecified Brønsted acid to ammonia, a Brønsted base; alternatively, ammonia acts as a Lewis base and transfers a lone pair of electrons to form a bond with a hydrogen ion.

To qualify as an Lewis acid, the chemical must:

- accept an electron pair.

Conversely, to qualify as an Lewis base, the chemical must:

- donate an electron pair.The concept of acids and bases is often associated with the movement of hydrogen ions from one molecule or ion to another. However, a host of acid-base concepts have been developed to help chemists organize and make sense of a wide range of reactions (Table 6.1).

Other Definitions

Lux-Flood

This acid-base theory was a revival of the oxygen theory of acids and bases, proposed by German chemist Hermann Lux in 1939 and further improved by Håkon Flood circa 1947. It is still used in modern geochemistry and for the electrochemistry of molten salts. This definition describes an acid as an oxide ion ($\mathrm{O^{2-}}$) acceptor and a base as an oxide ion donor. For example:

$$\mathrm{MgO\ (base) + CO_2\ (acid) \rightleftharpoons MgCO_3}$$

$$\mathrm{CaO\ (base) + SiO_2\ (acid) \rightleftharpoons CaSiO_3}$$

$$\mathrm{NO_3^-\ (base) + S_2O_7^{2-}\ (acid) \rightleftharpoons NO_2^+ + 2\,SO_4^{2-}}$$

Usanovich

Mikhail Usanovich developed a general theory that does not restrict acidity to hydrogen-containing compounds, and his approach, published in 1938, was even more general than the Lewis theory. Usanovich's theory can be summarized as defining an acid as anything that *accepts negative species, anions or electrons* or *donates positive ones, cations*, and a base as the reverse. This definition could even be applied to the concept of redox reactions (oxidation-reduction) as a special case of acid-base reactions. Some examples of Usanovich acid-base reactions include:

- species exchanged: anion $\mathrm{O^{2-}}$

$$\mathrm{Na_2O\ (base) + SO_3\ (acid) \longrightarrow 2\,Na^+ + SO_4^{2-}}$$

- species exchanged: anion $\mathrm{S^{2-}}$

$$\mathrm{3\,(NH_4)_2S\ (base) + Sb_2S_5\ (acid) \longrightarrow 6\,NH_4^+ + 2\,SbS_4^{3-}}$$

- species exchanged: electron

$$\mathrm{2\,Na\ (base) + Cl_2\ (acid) \longrightarrow 2\,Na^+ + 2\,Cl^-}$$

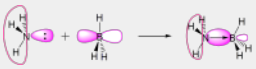
A comparison of the above definitions of Acids and Bases shows that the Usanovich concept encompasses all of the others but some feel that because of this it is too general to be useful.

A Summary of Acid-Base Concepts

Some concepts involve defining acids and bases in particular ways that allow for the understanding of particular types of chemical systems. For example, the familiar Arrhenius and Brønsted acid and base concepts used in general chemistry help chemists make sense of the behavior of compounds which can transfer H^+ ions among themselves, often in aqueous solution. However, the solvent system acid-base concept defines acids and bases in terms of the transfer of a lone-pair bearing group and is particularly useful for conceptualizing the reactivity of main group halides, oxides, and related compounds. Some acid-base definitions seek to encompass an extremely wide range of chemical reactions. For instance, the Lewis acid-base definition encompasses the Arrhenius , Brønsted, and solvent system definitions and has also found wide use in inorganic chemistry owing to the ease with which Lewis acid-base interactions may be described by the Frontier Orbital approach in terms of interacting molecular orbitals on the acid and base.

Table **2.3.1**: A summary of major acid-base models

Definition	Theoretical paradigm and notable features.	Acid	Base	Illustrative sample reactions
Arrhenius (1894)	Interested in what the substance does to the state of an aqueous solution. In particular it assesses proton donation to & removal from water using [H_3O^+] as a proxy. Readily accommodates the pH concept as a measure of the state of a solution.	Increases [H_3O^+]	Decreases [H_3O^+]	$\underset{acid}{HCl} + H_2O \rightarrow H_3O^+ + Cl^-$ $\underset{base}{NH_3} + H_2O \rightarrow NH_4^+ + OH^-$
Brønsted-Lowry (1923)	Envisions acid-base reactivity in terms of the transfer of an H^+ from one substance to another. Allows for conjugate acids and bases and solvent autoionization.	Donates H^+	Accepts H^+	$\underset{acid}{HCl} + \underset{base}{NH_3} \rightarrow \underset{conj.\ acid}{NH_4^+} + \underset{conj.\ base}{Cl^-}$ $\underset{acid}{HOAc} + \underset{base}{NH_3} \rightarrow \underset{conj.\ acid}{NH_4^+} + \underset{conj.\ base}{OAc^-}$ $\underset{amphoteric}{2\ H_2O} \rightarrow \underset{conj.\ acid}{H_3O^+} + \underset{conj.\ base}{OH^-}$
Lux-Flood (1939-~47)	Describes reactions involving oxides and oxyanions in terms of the transfer of oxide ion (O^{2-}). Mainly used in geochemistry, although it also can be used to describe some redox reactions.	Oxide acceptor	Oxide donor	$\underset{acid}{SiO_2} + \underset{base}{CaO} \rightarrow CaSiO_3$ $\underset{base}{H_2O} + \underset{acid}{CO} \rightarrow H_2 + CO_2$
Solvent System	Applies aspects of the Arrhenius , Brønsted-Lowry, and Lux-Flood acid base concepts to solvent cation & anion formation in a generalized reaction. Can be used to describe solution chemistry in nonaqueous solvent systems like BrF_3.	Is a solvent cation or increases the solvent cation concentration, often by receiving a lone pair- bearing group	Is a solvent anion or increases the solvent anion concentration, often by donating a lone pair- bearing group	$\underset{acid}{SbF_5} + \underset{base}{BrF_3} \rightarrow \underset{conj.\ base}{SbF_6^-} + \underset{conj.\ acid}{BrF_2^+}$ $\underset{amphoteric}{2\ BrF_3} \rightarrow \underset{conj.\ acid}{BrF_2^+} + \underset{conj.\ base}{BrF_4^-}$
Lewis (1923)	Envisions acid-base reactivity in terms of electron pair donation. Encompasses the Arrhenius , Brønsted-Lowry, Lux-Flood, and Solvent System definitions and readily	Accepts an electron pair	Donates an electron pair	$\underset{base}{:NH_3} + \underset{acid}{BF_3} \rightarrow H_3N + BF_3$

Definition	Theoretical paradigm and notable features.	Acid	Base	Illustrative sample reactions
	integrates with molecular orbital descriptions of chemical reactivity in Frontier orbital theory.			
Nucleophile-Electrophile	Applies the Lewis concept to organic reactivity. Nucleophiles are Lewis bases which tend to react to form a bond with Lewis acid sites called electrophilic centers.	(The electrophile) Tends to react by receiving an electron pair from a nucleophile, forming a bond in the process	(The nucleophile) Donates an electron pair to form a bond to an electrophile	$\underset{base}{Br^-} + \underset{acid}{CH_3-Cl} \rightarrow Br-CH_3 + Cl^-$
Usanovich (1939)	Extends Lewis theory to include the donation and acceptance of any number of electrons, whether through the formation of an adduct or electron transfer.	Accepts electrons	Donates electrons	$:\underset{base}{NH_3} + \underset{acid}{BH_3} \rightarrow \underset{adduct}{H_3N-BH_3}$ $\underset{acid}{Fe^{2+}} + \underset{base}{Zn^0} \rightarrow Fe^0 + Zn^{2+}$
Frontier Orbital (1960s)	Envisions Lewis Acid-base/Electrophile-nucleophile reactions in terms of the donation and acceptance of electrons between the reactant's frontier orbitals. Specifically, the reaction is envisioned in terms of donation of the base's HOMO electrons into the acid's LUMO level.	Possesses a LUMO capable of forming an occupied bonding MO on mixing with a base's HOMO.	Possesses an electron-bearing HOMO capable of forming a filled bonding MO on mixing with an acid's LUMO.	 base acid adduct

References

Huheey, J. E.; Keiter, E. A.; Keiter, R. L., *Inorganic Chemistry: Principles of Structure and Reactivity. 4th ed.*; HarperCollins: New York, NY, 1993, pg. 318.

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2.4: Arrhenius Concept

The Arrhenius acid-base concept defines acids and bases in terms of how they affect the amount of hydronium ions, $\mathrm{H_3O^+}$, (and by extension hydroxide ions, $\mathrm{OH^-}$) in aqueous solutions. Simply, in the Arrhenius definition an acid is a substance that increases the concentration of hydronium ions when it is dissolved in water. This typically occurs when the acid dissociates by loss of a proton to water according to the general equation:

$$\mathrm{HA\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + A^-\,(aq)} \tag{2.4.1}$$

where A is the deprotonated form of the acid. For example, what hydrochloric and acetic acid, $\mathrm{CH_3CO_2H}$, have in common is that both increase the amount of hydronium ion when they are dissociated in solution.

$$\mathrm{HCl\,(aq) + H_2O\,(l) \longrightarrow H_3O^+\,(aq) + Cl^-\,(aq)}$$

$$\mathrm{CH_3CO_2H\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + CH_3CO_2{}^-\,(aq)}$$

In terms of the Arrhenius definition, the major difference between hydrochloric and acetic acid is that hydrochloric acid dissociates completely in solution to yield stoichiometric amounts of $\mathrm{H_3O^+}$, while acetic acid only partially dissociates. Acids like HCl that completely dissociate in water are classified as strong in the Arrhenius definition, while those like acetic acid that do not are classified as weak.

Although all weak acids incompletely dissociate, the extent of dissociation can vary widely. The relative strengths of weak Arrhenius acids is conveniently expressed in terms of the equilibrium constant for their acid dissociation reaction, K_a.

$$K_a = \frac{[\mathrm{H^+}][\mathrm{A^-}]}{[\mathrm{HA}]}$$

The $\mathrm{pK_a}$ values for selected weak acids are given in Table 2.4.1.

Table 2.4.1: Values of K_a, pK_a, K_b, and pK_b for selected monoprotic acids.

Acid	HA	K_a	pK_a	A^-	K_b	pK_b
sulfuric acid (2nd ionization)	HSO_4^-	1.0×10^{-2}	1.99	SO_4^{2-}	9.8×10^{-13}	12.01
hydrofluoric acid	HF	6.3×10^{-4}	3.20	F^-	1.6×10^{-11}	10.80
nitrous acid	HNO_2	5.6×10^{-4}	3.25	NO_2^-	1.8×10^{-11}	10.75
formic acid	HCO_2H	1.78×10^{-4}	3.750	HCO_2^-	5.6×10^{-11}	10.25
benzoic acid	$C_6H_5CO_2H$	6.3×10^{-5}	4.20	$C_6H_5CO_2^-$	1.6×10^{-10}	9.80
acetic acid	CH_3CO_2H	1.7×10^{-5}	4.76	$CH_3CO_2^-$	5.8×10^{-10}	9.24
pyridinium ion	$C_5H_5NH^+$	5.9×10^{-6}	5.23	C_5H_5N	1.7×10^{-9}	8.77
hypochlorous acid	$HOCl$	4.0×10^{-8}	7.40	OCl^-	2.5×10^{-7}	6.60
hydrocyanic acid	HCN	6.2×10^{-10}	9.21	CN^-	1.6×10^{-5}	4.79
ammonium ion	NH_4^+	5.6×10^{-10}	9.25	NH_3	1.8×10^{-5}	4.75
water	H_2O	1.0×10^{-14}	14.00	OH^-	1.00	0.00
acetylene	C_2H_2	1×10^{-26}	26.0	HC_2^-	1×10^{12}	−12.0
ammonia	NH_3	1×10^{-35}	35.0	NH_2^-	1×10^{21}	−21.0

*The number in parentheses indicates the ionization step referred to for a polyprotic acid.

As can be seen from the table the K_a values for weak acids are less than one (otherwise they would not be weak) and vary over many orders of magnitude. Consequently it is customary to tabulate acid ionization constants as pK_a values:

$$pK_a = -\log K_a$$

Because pK_a values essentially place the K_a values on a negative base ten logarithmic scale, the stronger the weak acid, the lower its pK_a. Weak acids with larger K_a values will have lower pK_a values than weaker acids with smaller K_a. Moreover, each unit increase or decrease in the pK_a corresponds to a tenfold increase or decrease in the corresponding K_a.

While Arrhenius acids increase the concentration of $\mathbf{H_3O^+}$ in aqueous solution, Arrhenius bases decrease $\mathbf{H_3O^+}$. Strong bases do this stoichiometrically. Most are hydroxide salts of alkali metals or quaternary ammonium salts that dissociate completely when dissolved in water:

$$\mathrm{MOH\,(aq) \longrightarrow M^+\,(aq) + OH^-\,(aq)}$$

This added hydroxide decreases the concentration of H_3O^+ by shifting the water autoionization equilibrium towards water.

$$\mathrm{2\,H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + OH^-\,(aq)}$$

In contrast, most weak bases react with water to produce an equilibrium concentration of hydroxide ion according to the base dissociation reaction

$$\mathrm{B\,(aq) + H_2O\,(l) \rightleftharpoons BH^+\,(aq) + OH^-\,(aq)}$$

in which **B** is the weak base. The ionization constant for this reaction, called the **base ionization constant** or K_b, is typically used as a measure of a weak base's strength.

Because both hydroxide and hydronium ion are products of water autoionization, the concentrations of hydronium ion and hydroxide ion in aqueous solution will vary reciprocally with one another. This means that Arrhenius acids can be recognized as substances that decrease the hydroxide concentration and Arrhenius bases as substances that increase it.

Since the Arrhenius acid-base concept is concerned about the state of the water autoionization reaction, Arrhenius acids and bases may also be recognized by their effect on the solution pH. Arrhenius acids decrease the pH and Arrhenius bases will increase it.

NOTE

To qualify as an Arrhenius acid, upon the introduction to water, the chemical must cause, either directly or otherwise:

- an increase in the aqueous hydronium concentration,
- a decrease in the aqueous hydroxide concentration, or
- a decrease in the solution pH.

Conversely, to qualify as an Arrhenius base, upon the introduction to water, the chemical must cause, either directly or otherwise:

- a decrease in the aqueous hydronium concentration,
- an increase in the aqueous hydroxide concentration, or
- an increase in the solution pH.

Because the Arrhenius acid-base model defines acids and bases in terms of their impact on the state of an aqueous solution the Arrhenius concept is unable to describe reactions in nonaqueous solvents, gases, molten liquids, and the solid state. Consequently other models should be used to describe reactions involving the transfer of H^+ and other fragments in nonaqueous media.

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SECTION OVERVIEW

2.5: Brønsted-Lowry Acid-Base Concept

2.5.1: Definitions of Brønsted-Lowry Acids and Bases

2.5.2: Cations Act as Brønsted Acids in Water

2.5.3: Factor Affecting Brønsted Acidity and Basicity

2.5.4: Oxoacids and Oxoanions

2.5.5: Acidity of Binary Hydrides

2.5.6: Brønsted-Lowry Superacids and the Hammett Acidity Function

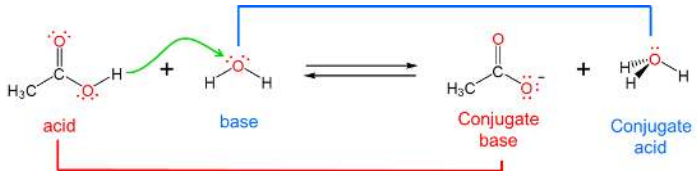
2.5.7: Acid-Base Chemistry in Amphoteric Solvents and the Solvent Leveling Effect

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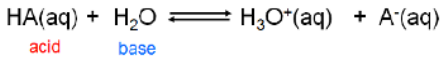
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2.5.1: Definitions of Brønsted-Lowry Acids and Bases

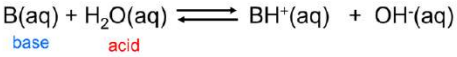
The Brønsted-Lowry acid-base concept overcomes the Arrhenius system's inability to describe reactions that take place outside of aqueous solution by moving the focus away from the solution and onto the acid and base themselves. It does this by redefining acid-base reactivity as involving the transfer of a hydrogen ion, H^+, between an acid and a base. Specifically, a Brønsted acid is a substance that loses an H^+ ion by donating it to a base. This means that a Brønsted base is defined as a substance which accepts H^+ from an acid when it reacts.



Because the Brønsted-Lowry concept is concerned with H^+ ion transfer rather than the creation of a particular chemical species, it is able to handle a diverse array of acid-base concepts. In fact, from the viewpoint of the Brønsted-Lowry concept, Arrhenius acids and bases are just a special case involving hydrogen ion donation and acceptance involving water. Arrhenius acids donate H^+ ion to water, which acts as a Brønsted base in accepting it to give H_3O^+:

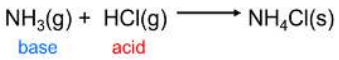


Similarly, Arrhenius bases act as Brønsted bases in accepting a hydrogen ion from the Brønsted acid water:



In this way it can be seen that Arrhenius acids and bases are defined in terms of their causing hydrogen ions to be donated to and abstracted from water, respectively, while Brønsted acids and bases are defined in terms of their ability to donate and accept hydrogen ions to and from anything.

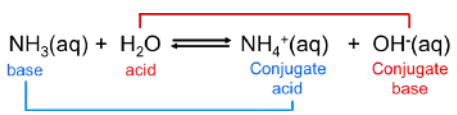
Becasue the Brønsted-Lowry concept can handle any sort of hydrogen ion transfer it readily accommodates many reactions that Arrhenius theory cannot, including those that take place outside of water, such as the reaction between gaseous hydrochloric acid and ammonia:



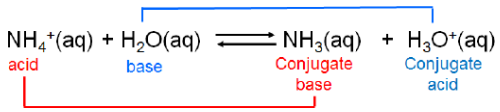
The classification of acids as strong or weak usually refers to their ability to donate or abstract hydrogen ions to or from water to give H_3O^+ and OH^-, respectively, *i.e.*, their Arrhenius acidity and basicity. However, acids and bases may be classified as strong and weak under the Brønsted-Lowry definition based on whether they completely transfer or accept hydrogen ions; it is just that in this case it is important to specify the conditions under which a given acid or base acts strong or weak. For example, acetic acid acts as a weak acid in water but is a strong acid in triethylamine, since in the latter case it completely transfers a hydrogen ion to triethylamine to give triethylammonium acetate. Alternatively, the acidity or basicity of a compound may be specified using a thermodynamic scale like the Hammett acidity.

Conjugate Acids and Bases

By redefining acids and bases in terms of hydrogen ion donation and acceptance, the Brønsted-Lowry system makes it easy to recognize that when an acid loses its hydrogen ion it becomes a substance that is capable of receiving it back again, namely, a base. Consider, for example, the base dissociation of ammonia in water. When ammonia acts as a Brønsted base and receives a hydrogen ion from water, ammonium ion and hydroxide are formed:

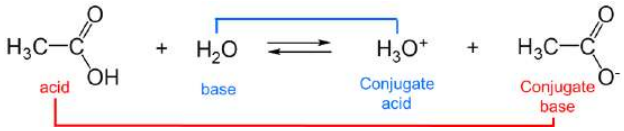


The ammonium ion is itself a weak acid that can undergo dissociation:

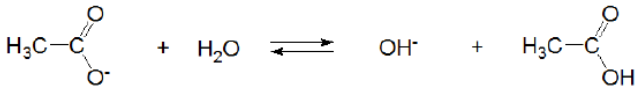


In this case ammonia and ammonium ion are acid-base conjugates. In general acids and bases that differ by a *single ionizable hydrogen ion* are said to be conjugates of one another.

The strengths of conjugates vary reciprocally with one another, so the stronger the acid the weaker the base and vice versa. For example, in water, acetic acid acts as a weak Brønsted acid:



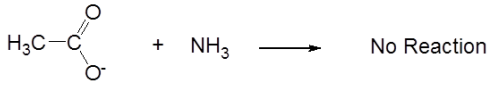
and acetic acid's conjugate base, acetate, acts as a weak Brønsted base.



However, in liquid ammonia acetic acid acts as a strong Brønsted acid:



while its conjugate base, acetate, is neutral.



The reciprocal relationship between the strengths of acids and their conjugate bases has several consequences:

1. Under conditions when an acid or base acts as a weak acid or base its conjugate acts as weak as well. Conversely, when an acid or base acts as a strong acid or base its conjugate acts as a neutral species.
2. When a Brønsted acid and base react with one another, the equilibrium favors formation of the weakest acid-base pair. That is why the acid-base reaction between acetic acid and ammonia in liquid ammonia proceeded to give the weak acid ammonium ion and neutral acetate. This consequence is particularly important for understanding the behavior of acids and bases in nonaqueous solvents, as illustrated by the following example.

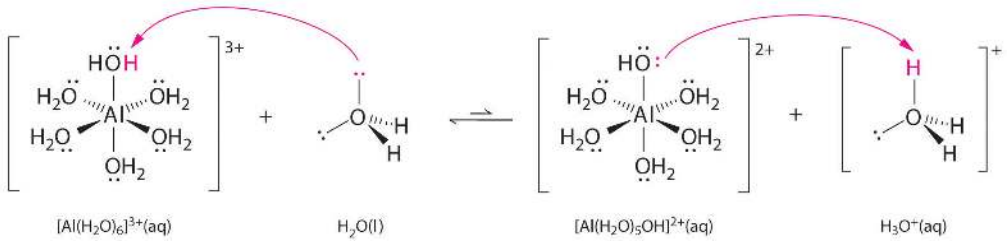
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2.5.2: Cations Act as Brønsted Acids in Water

Metal cations act as acids by polarizing bound water molecules called aqua ligands

Aqueous solutions of simple salts of metal ions can also be acidic, even though a metal ion cannot donate a proton directly to water to produce H_3O^+. Instead, a metal ion can act as a Lewis acid and interact with water, a Lewis base, by coordinating to a lone pair of electrons on the oxygen atom to form a hydrated metal ion.



A water molecule coordinated to a metal ion is more acidic than a free water molecule for two reasons. First, repulsive electrostatic interactions between the positively charged metal ion and the partially positively charged hydrogen atoms of the coordinated water molecule make it easier for the coordinated water to lose a proton.

Second, the positive charge on the Al^{3+} ion attracts electron density from the oxygen atoms of the water molecules, which decreases the electron density in the O–H bonds, as shown in Figure 2.5.2.1*b*. With less electron density between the *O* atoms and the H atoms, the O–H bonds are weaker than in a free H_2O molecule, making it easier to lose an H^+ ion. This is shown schematically in Figure 2.5.2.1.

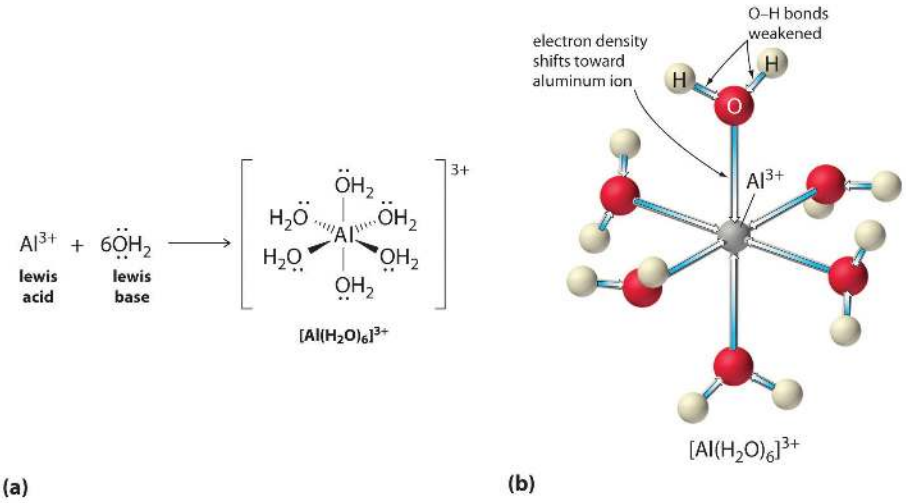


Figure 2.5.2.1: Effect of a Metal Ion on the Acidity of Water (a) Reaction of the metal ion Al^{3+} with water to form the hydrated metal ion is an example of a Lewis acid–base reaction. (b) The positive charge on the aluminum ion attracts electron density from the oxygen atoms, which shifts electron density away from the O–H bonds. The decrease in electron density weakens the O–H bonds in the water molecules and makes it easier for them to lose a proton. (CC BY-NC-SA 3.0; anonymous)

Acidity depends primarily on the charge to size ratio

The degree of acidity of a metal cation depends on the charge on the metal ion and the radius of the metal ion (Figure 2.5.2.2). A divalent ion (M^{2+}) has approximately twice as strong an effect on the electron density in a coordinated water molecule as a monovalent ion (M^+). For metal ions with the same charge, the smaller the ion, the shorter the internuclear distance to the oxygen atom of the water molecule and the greater the effect of the metal on the electron density distribution in the water molecule.

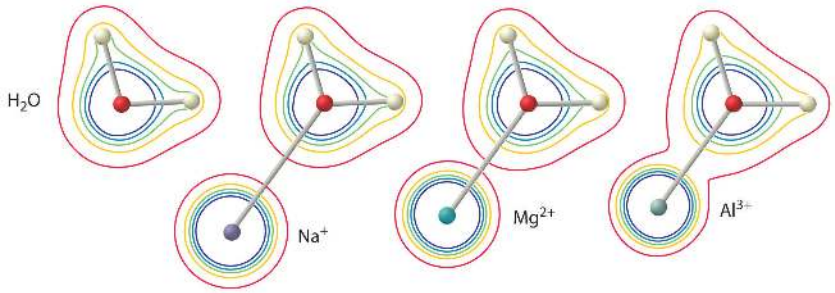


Figure **2.5.2.2**: The effect of the charge and radius of a metal ion on the acidity of a coordinated water molecule. The contours show the electron density on the O atoms and the H atoms in both a free water molecule (left) and water molecules coordinated to Na^+, Mg^{2+}, and Al^{3+} ions. These contour maps demonstrate that the smallest, most highly charged metal ion (Al^{3+}) causes the greatest decrease in electron density of the O–H bonds of the water molecule. Due to this effect, the acidity of hydrated metal ions increases as the charge on the metal ion increases and its radius decreases. (CC BY-NC-SA 3.0; anonymous)

The charge to size ratio explains why most alkali metal cations exhibit little acidity while aqueous solutions of small, highly charged metal ions, such as Al^{3+} and Fe^{3+}, are acidic:

$$[Al(H_2O)_6]^{3+}(aq) \rightleftharpoons [Al(H_2O)_5(OH)]^{2+}(aq) + H^+(aq) \tag{2.5.2.1}$$

The $[Al(H_2O)_6]^{3+}$ ion has a pK_a of 5.0, making it almost as strong an acid as acetic acid. Because of the two factors described previously, the most important parameters for predicting the effect of a metal ion on the acidity of coordinated water molecules are the charge and ionic radius of the metal ion.

A simple empirical equation for predicting the pK_a of metal ions in water has been proposed by Wulfsberg:[1]

$$pK_a = 15.14 - 88.16\ pm\left(\frac{Z^2}{r}\right) \tag{2.5.2.2}$$

where Z is the charge on the metal ion and r its radius. As can be seen from figure **2.5.2.3**, in general the acidity of metal ions increases with $\frac{Z^2}{r}$). Nevertheless a number of ions have considerably lower pK_a values than predicted from this correlation, suggesting that the acidity of metal cations cannot be predicted using a simple electrostatic model alone.

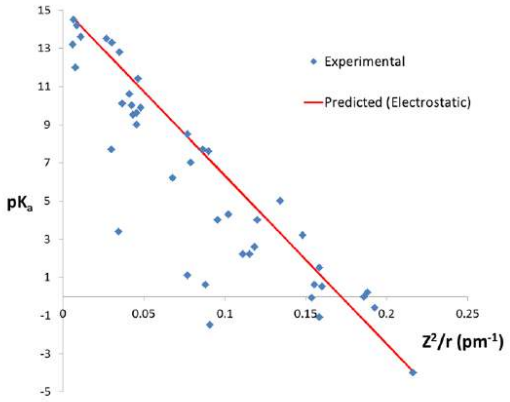


Figure **2.5.2.3**: The pK_a of metal ions (♦) as a function of $\frac{Z^2}{r}$ for 43 metal ions. Drawn using radii listed in reference 1.

Although the charge-to-size ratio is the simplest and most powerful predictor of metal ion acidity in water, three additional factors also can play a role:

Other Factors Affecting Acidity

Electronegativity

All other things being equal, more electronegative elements are better able to withdraw electron density from a bound water ligand and consequently better at enhancing the ability of that water molecule to lose a hydrogen ion. The electrostatic model of ion acidity can be extended to account for electronegativity effects but only needs to be done so for metals with Pauling

electronegativities greater than 1.5. The empirical relationship that has been proposed to account for the effect of electronegativity is:

$$pK_a = 15.14 - 88.16\left(\frac{Z^2}{r} + 0.096(\chi - 1.50)\right) \quad (2.5.2.3)$$

where r is the ion radius in pm and χ is its Pauling electronegativity. As can be seen from figure 2.5.2.4, the electronegativity term accounts for some of the deviations in metal ion acidity predicted from charge and size effects alone.

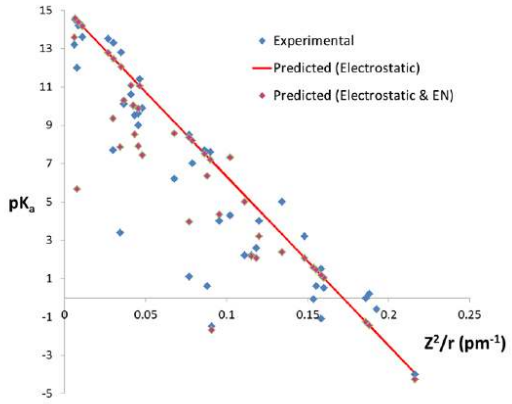


Figure 2.5.2.4: Comparison between the experimental pK_a values (♦) for 43 metal ions and those predicted empirically accounting for size and charge effects (-) and accounting for size, charge, and electronegativity effects (♦). Drawn using radii listed in reference 1.

However, there are still large deviations between the predicted and observed pK_a for a number of ions. In particular, the modified electrostatic model overestimates the pK_a of Al^{3+} and Sn^{4+} and underestimates the pK_a of Hg^{2+}, Sn^{2+}, and Tl^{3+}. While the exact reasons for these discrepancies is not entirely clear, at least some are thought to arise from the impact of the fourth factor that determines metal ion acidity.

Hardness and Softness

Cation hardness or softness is assessed according to Pearson's Hard-Soft Acid Base Principle (HSABP). In general, soft cations are more acidic than hard cations of the same charge and radius, as may be seen from the examples in Table 2.5.2.1. The greater than expected acidity of softer cations is thought to reflect the importance of covalent contributions to the metal-water bond.

Table 2.5.2.1: Comparison of the pK_a values at 25°C of hard and soft cations with approximately the same radius and charge. Based on Gutmann[2] as reported by Burgess.[3]

Cation	Classification	Radius (pm)	pK_a1
K^+	hard	1.33	14
Ag^+	soft	1.26	10
Mg^{2+}	hard	0.65	12.2
Cu^{2+}	soft	0.69	7.3
Ca^{2+}	hard	0.99	12.6
Cd^{2+}	soft	0.97	9.0
Sr^{2+}	hard	1.13	13.1
Hg^{2+}	soft	1.10	3.6

References

1. Wulfsberg, G. *Principles of Descriptive Inorganic Chemistry* University Science Books, 1991, pp. 28-30.
2. (a) Gutmann, V. *Allg. Prakt. Chem.* 1970, *21*, 116. (b) Gutmann, V. *Fortschr. Chem. Forsch.* 1972, *27*, 59.

3. Burgess, J. *Metal Ions in Solution* Ellis Horwood, 1978, pg. 268.

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- **6.3.8: High Charge-to-Size Ratio Metal Ions Act as Brønsted Acids in Water** by Stephen M. Contakes is licensed CC BY 4.0.

2.5.3: Factor Affecting Brønsted Acidity and Basicity

Because the acidity of a given substance depends on the interplay between the relatively large values of its proton affinity and the energy associated with solvation of an acid's conjugate base, it can sometimes be difficult to estimate the strength of an acid in a given solvent in the absence of detailed computations. Nevertheless a variety of simple ideas may be used to roughly estimate the relative strengths of acids. These should never be substituted for a detailed consideration of solvation but can serve as useful aids when thinking about trends and designing new Brønsted acids and bases.

Four Factors Affecting Acidity and Basicity

1. Bond strength effects

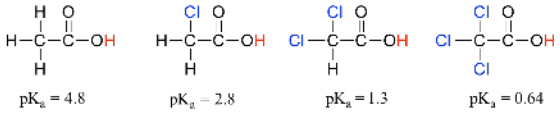
The weaker the bond to the ionizable hydrogen, the stronger the acid. Strongly bonded hydrogen ions are difficult to remove, weakly bonded ones much less so.

2. Inductive effects

Inductive effects involve the donation or withdrawal of electrons from an atom by a group connected to it through bonds. **Electron donating groups** increase the electron density while **electron withdrawing groups** decrease it. Atoms or groups that withdraw electron density away from a center increase its acidity while those which donate electrons to the center decrease its acidity. The reasons for this follow from the heterolytic bond cleavage of acid ionization:

$$E-H \rightarrow E:^- + H^+$$

- When a bond to hydrogen is more polarized away from the H (more like $^{-\delta}E-H^{\delta+}$) it is easier to cleave off the hydrogen ion from that E-H bond. This may be seen from how the pK_a values of acetic acid and its mono-, di-, and tri-chlorinated derivatives decreases with the extent of chlorination of the methyl group.



- Polarized E-H bonds also make for stronger Brønsted acids because the resulting $E:^-$ conjugate base is more stable.

This leads to the third major factor that should be considered when thinking about acid strength.

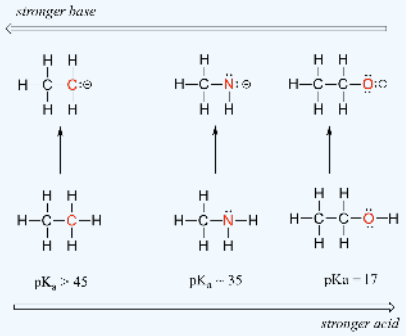
3. Electronegativity Effects, Especially as Seen Using the Conjugate Base Principle

The more stable the acid's conjugate base, the stronger the Brønsted acid. All reactions are in theory reversible, and so when considering the propensity of an acid to donate hydrogen ions, it can be helpful to look at the reverse of hydrogen ion donation, namely, protonation of the acid's conjugate base. If deprotonation of the acid gives a very stable conjugate base then deprotonation of the acid will be more favorable.

Two factors determine the stability of an acid's conjugate base.

- Conjugate bases in which a small amount of charge is on a large atom, spread over a large number of atoms, and on electronegative atoms tend to be more stable. Conjugate bases in which a small amount of charge is spread over a large number of electronegative atoms are especially stable. That is why magic acid, a mixture of HF and SbF_5, is so acidic: the single negative charge on its conjugate base is spread over six F atoms and on Sb in SbF_6^-.
- Groups which tend to inductively polarize E-H bonds also tend to stabilize the conjugate base formed when that bond ionizes. In general, the more electronegative an atom, the better able it is to bear a negative charge. All other things being equal, weaker bases have negative charges on more electronegative atoms; stronger bases have negative charges on fewer electronegative atoms. This is apparent from how inductive effects lead to an increase in the acidity of E-H bonds as the electronegativity of the element to which the acidic hydrogen is bound increases from left to right across a row of the periodic table. This horizontal periodic trend in acidity and basicity is apparent from the homologous series below:

Horizontal periodic trend in acidity and basicity



Notice how the inductive polarization of the E-H bond, which results in greater acidity, contributes to the greater stability of the conjugate base. For the case above, look at where the negative charge ends up in each conjugate base. In the conjugate base of ethane, the negative charge is borne by a carbon atom, while on the conjugate base of methylamine and ethanol the negative charge is located on a nitrogen and an oxygen, respectively. Remember that electronegativity also increases as we move from left to right along a row of the periodic table, meaning that oxygen is the most electronegative of the three atoms, and carbon the least.

Thus, the methoxide anion is the most stable (lowest energy, least basic) of the three conjugate bases, and the ethyl carbanion anion is the least stable (highest energy, most basic). Conversely, ethanol is the strongest acid, and ethane the weakest acid.

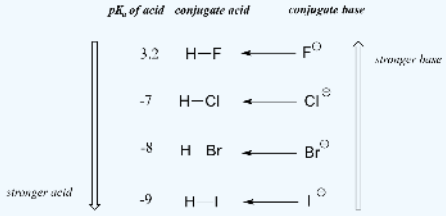
4. Size effects on Bond Strength and Charge Delocalization

There are two classes of size effects to be considered:

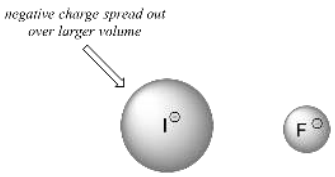
a. The larger the atom to which a H is bound in an E-H bond, the weaker the bond and the stronger the acid.
b. Increased charge delocalization with increasing size. Electrostatic charges, whether positive or negative, are more stable when they are ‘spread out’ over a larger area. The greater the volume over which charge is spread in the acid's conjugate base, the more stable that base and the stronger the acid.

The impact of size effects are readily seen in the increase in acidity of the hydrogen halides, as illustrated by the vertical periodic trend in acidity and basicity below:

Vertical periodic trend in acidity and basicity



On going vertically down the halogen group from F to I the H-X bond strength decreases in the acid, making it easier to ionize, while the charge becomes more diffuse in the resultant X^- ion, making the conjugate base more stable.



The increase in the acidity of the hydrogen halides down a group suggests that size effects are more important than inductive effects. In the case of the hydrogen halides, because fluorine is the most electronegative halogen element, we might expect fluoride to also be the least basic halogen ion. But in fact, it is the *least* stable, and the most basic! It turns out that when moving vertically in the periodic table, the *size* of the atom trumps its electronegativity with regard to basicity. The atomic radius of iodine is approximately twice that of fluorine, so in an iodide ion, the negative charge is spread out over a significantly larger volume.

Contributors and Attributions

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* who expanded this section from a combination of

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https://chem.libretexts.org/Bookshelves/Organic_Chemistry/Book%3A_Organic_Chemistry_with_a_Biological_Emphasis_(Soderberg)/Chapter_07%3A_Organic_compounds_as_acids_and_bases/7.3%3A_Structural_effects_on_acidity_and_basicity

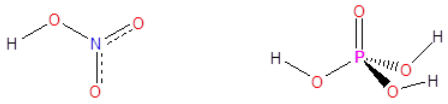
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- **6.3.2: Rules of Thumb for thinking about the relationship between Molecular Structure and Brønsted Acidity and Basicity*** by Stephen Contakes is licensed CC BY 4.0.

2.5.4: Oxoacids and Oxoanions

Oxyacids (also known as *oxoacids*) are compounds of the general formula $\mathbf{H_nEO_m}$, where **E** is a nonmetal or early transition metal and the acidic hydrogens are attached directly to oxygen (not **E**). This class of compounds includes such well-know acids as nitric acid ($\mathbf{HNO_3}$) and phosphoric acid, ($\mathbf{H_3PO_4}$).



Oxoanions are the conjugate base species of oxoacids. Oxoanions behave as bases in solution and have the general formula $\mathbf{MO_x^{y-}}$, where $\mathbf{x}$ is the number of oxo groups and $\mathbf{y^-}$ is the overall charge on the anion. This class of ions includes such well-known anions as nitrate ($\mathbf{NO_3^-}$) and phosphate ($\mathbf{PO_4^{3-}}$). An *oxo group* is a oxygen atom that is bonded to a central atom but makes no other bonds.

The factors affecting basicity of oxoanions and the acidity of oxyacids are discussed below.

Factors Affecting Acidity/Basicity

Electronegativity

Elements in the same group on the periodic table tend to form oxoanions and oxyacids of the same general formulas. For example, chlorine, bromine, and iodine all form oxyacids of formula **HOE**: hypochlorous, hypobromous and hypoiodous acids. The acidity of the oxoacid and the basicity of the corresponding oxoanion are largely determined by the electronegativity of the central element. Central atoms that are better able to inductively pull electron density towards themselves make the acidic oxygen-hydrogen bond more polar, stabilizing the conjugate base, $\mathbf{OE^-}$. Thus, the acid strength in such homologous series increases with the electronegativity of the central atom and basicity of the oxoanion decreases. This may be seen from the data for the hypohalous acids in Table **2.5.4.1**, in which the acid strength increases with the electronegativity of the halogen so that the order of acidity is:

$$\mathbf{HClO > HBrO > HIO}$$

and the order of basicity is:

$$\mathbf{ClO^- < BrO^- < IO^-}$$

Table **2.5.4.1**: Relationship of central atom's electronegativity to acidity and bascity of hypohalous acids and oxoanions

HOX	K_a	Electronegativity of X	OX^-	K_b
HOCl	4.0×10^{-8}	3.0	$^-$OCl	2.5×10^{-7}
HOBr	2.8×10^{-9}	2.8	$^-$OBr	3.6×10^{-6}
HOI	3.2×10^{-11}	2.5	$^-$OI	3.1×10^{-4}

Oxidation State or Number of Oxo Groups

The number of oxo groups bonded to the central atom can vary. Figure **2.5.4.1** shows the examples series perchloric ($\mathbf{ClO_4^-}$), chloric ($\mathbf{ClO_3^-}$), chlorous ($\mathbf{ClO_2^-}$), and hypochlous ($\mathbf{ClO^-}$) acids. As the number of oxo groups increases, the acidity of the oxoacid increases (pKa decreases) and the basicity of the oxoanion decreases (pKb increases). This behavior is the result of the inductive effect, or the ability of the oxygens attached to the central atom to pull electron density across the OH bond. This is seen from the charge density diagram for the chlorine oxoacids shown in Figure **2.5.4.1**, in which the partial positive charge on the acidic hydrogen increases with the number of oxygens present.

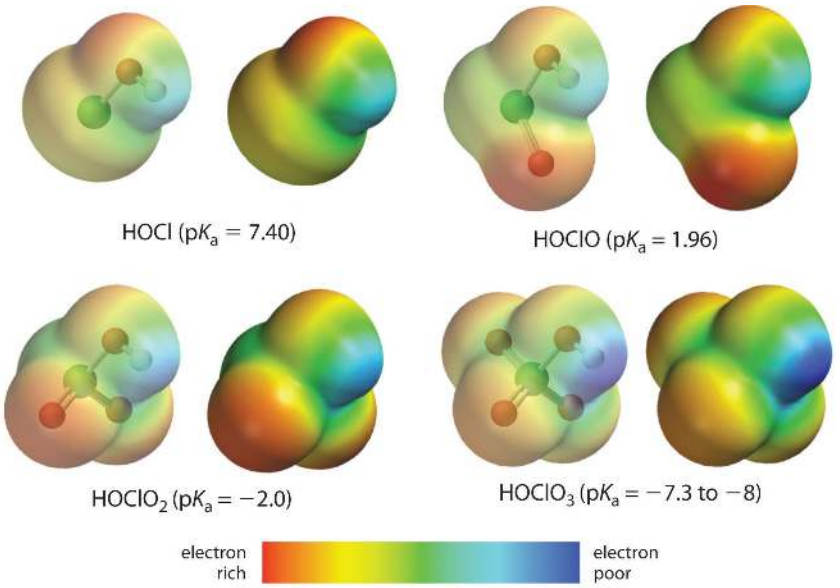


Figure **2.5.4.1**: Increasing the number of oxygens increases K_a, as evidenced by the decreased electron density on the acidic hydrogen (which is most blue in $HClO_4$). Note, $K_a = 10^{-pK_a}$, and so the larger the pK_a, the smaller the K_a. (CC BY-SA-NC; anonymous)

The increase in oxoacid acidity with the number of oxygens bound to the central atom may also be seen by considering the stability of the conjugate oxoanion. The stability of the conjugate base increases with the number of oxygens. The negative charge is spread over more oxygen atoms and becomes increasingly diffuse and, therefore, more stable. The charge distribution diagrams and Lewis bonding models for the chlorine oxyanions are shown in figure **2.5.4.2** .

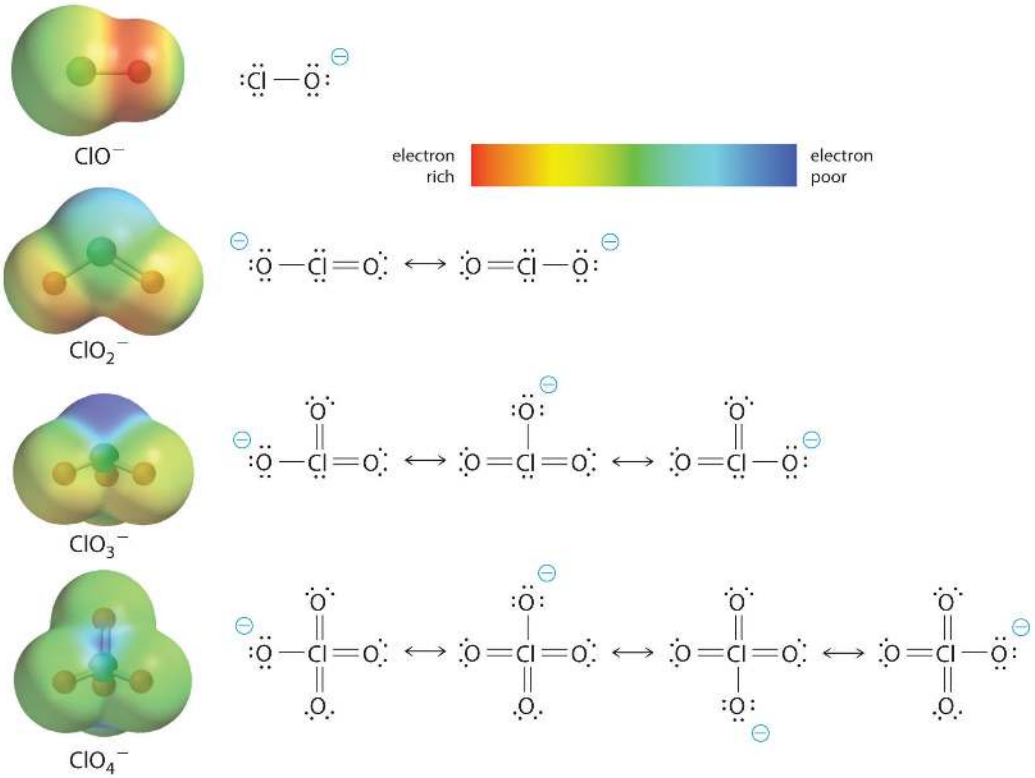


Figure **2.5.4.2**: Increased diffusion of charge in chlorine oxyanions with increasing number of oxygens. The larger the ion the more dispersed the charge and thus the less the charge density, making the perchlorate the most stable anion in the series. Even the simplistic treatment of bonding depicted in the resonance structures correctly shows an increased dispersion of the charge density. (CC BY-SA-NC 3.0; anonymous)

Exercise 2.5.4.1

Sulfur and selenium both forms oxoacids of formula $\mathbf{H_2EO_3}$, where E is either S or Se. These are called sulfurous and selenous acid, respectively. Which oxoacid would you expect to be more acidic: selenous acid or sulfurous acid?

Answer

Sulfurous acid should be more acidic. Since sulfur is more electronegative than selenium sulfur will polarize OH bonds to a greater extent, making them more acidic. This prediction is borne out by a comparison of the pK_a values for the acids:

Acid	pK_{a1}	pK_{a2}
sulfurous acid, H_2SO_3	1.85	7.2
selenous acid, H_2SeO_3	2.62	8.32

For polyprotic oxoacids the acidity decreases as each successive proton is removed

Oxoacids with multiple O-H bonds are called **polyprotic** since they can donate more than one hydrogen ion. In this case hydrogen ions are removed in successive ionization reactions. Examples include phosphoric and carbonic acid:

$$\begin{aligned}
\mathrm{H_3PO_4} &\rightleftharpoons \mathrm{H^+ + H_2PO_4^-} & pK_{a1} &= 2.2\\
\mathrm{H_2PO_4^-} &\rightleftharpoons \mathrm{H^+ + HPO_4^{2-}} & pK_{a2} &= 7.2\\
\mathrm{HPO_4} &\rightleftharpoons \mathrm{H^+ + PO_4^{3-}} & pK_{a3} &= 12.4\\
\mathrm{H_2CO_3} &\rightleftharpoons \mathrm{H^+ + HCO_3^-} & pK_{a1} &= 3.6\\
\mathrm{HCO_3^-} &\rightleftharpoons \mathrm{H^+ + CO_3^{2-}} & pK_{a1} &= 10.3
\end{aligned}$$

The dissociation constants for successive ionization constants decrease by about five orders of magnitude between successive hydrogen ions. This is reflected in Linus Pauling's rules for oxoacids and their oxyanions:

Pauling's Rules

1. The pK_a for an oxyacid of general formula $\mathrm{E(OH)_q(O)_p}$ is given by

$$pK_a = 8 - 5 \times p \tag{2.5.4.1}$$

2. As an oxoacid undergoes successive ionizations the pK_a increases by five each time.

The central theme of Pauling's Rules is that the more oxygens there are on the central atom, the more resonance structures that can be constructed for the conjugate base, which increases its stability and increases the acidity of the acid. However, as the acids successively ionize, they have fewer resonance structures. Pauling's Rules are phenomenological (i.e., not based on a theoretical framework). However, as empirical rules, they often work quite well, but it should be borne in mind that they are approximate.

Exercise 2.5.4.2: How well do Pauling's rules for oxoacids work?

Calculate the theoretical pK_a values for phosphoric and carbonic acid and their dissociation produces and compare the results with the experimental pK_a values.

Answer

For phosphoric acid, Pauling's rules (Equation 2.5.4.1) predict the pK_a values quite well:

$\mathrm{H_3PO_4}$: $p = 3$ and $q = 1$ and

$$pK_{a1,\text{predicted}} = 8 - 5 \times 1 = 3$$

This is slightly greater than the observed value of 2.2. $\mathrm{H_2PO_4^-}$:

$$pK_{a2,\text{predicted}} = pK_{a1,\text{experimental}} + 5 = 7.2$$

This is spot on with experiment. HPO_4^{2-}:

$$pK_{a3,\text{predicted}} = pK_{a2,\text{experimental}} + 5 = 12.2$$

This is slightly less than the experimental value of 12.4.

In some cases discrepancies between experimental pK_a values and those predicted by Pauling's rules suggest that structural rearrangements may be taking place upon ionization or else that the reported pK_a values do not really represent the ionization in question because they do not fully account for all the equilibria taking place in solution. In the case of carbonic acid, however, the reason for the discrepancy between the predicted and experimental pK_{a2} values is not entirely clear.

H_2CO_3: $p = 2$, $q = 1$ and

$$pK_{a1,\text{predicted}} = 8 - 5 \times 1 = 3$$

This is slightly lower than the observed value of 3.6. HCO_3^-:

$$pK_{a2,\text{predicted}} = pK_{a1,\text{experimental}} + 5 = 8.6$$

This is 1.7 units less than the experimental value of 10.3.

For carbonic acid Pauling's rules predict pK_{a1} reasonably well, but pK_{a2} less so:

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- **6.3.7: The Acidity of an Oxoacid is Determined by the Electronegativity and Oxidation State of the Oxoacid's Central Atom*** by Stephen Contakes is licensed CC BY 3.0.

2.5.5: Acidity of Binary Hydrides

The compounds formed between the elements and hydrogen are called binary hydrides. All such compounds can in principle act as Brønsted acids in reactions with a suitably strong base. However, as the electronegativity decreases down a group and increases from left to right across the periodic table, the acidity of binary hydrides increases. In fact, on the left side of the periodic table the hydrides of extremely electropositive alkali and alkaline earth metals are not acidic but basic. They are perhaps best considered to be ionic salts of the hydride ion (H^-). Consequently substances such as **NaH** and **CaH_2** tend to act as Brønsted bases in their reactions.

$$NaH\,(s) + H_2O\,(l) \longrightarrow Na^+\,(aq) + OH^-\,(aq) + H_2\,(g)$$

$$CaH_2\,(s) + 2\,H_2O\,(l) \longrightarrow Ca^{2+}\,(aq) + 2\,OH^-\,(aq) + 2\,H_2\,(g)$$

On the right side of the periodic table the binary hydrides of the nonmetals exhibit appreciable acidity.

$$HBr\,(aq) + H_2O\,(l) \longrightarrow H^+\,(aq) + Br^-\,(aq)$$

For this reason the binary nonmetal hydrides are termed acidic hydrides. Nevertheless not all are equally acidic. The dilute aqueous acid ionization constants for these hydrides are given in Figure **2.5.5.1**. As can be seen from the constants in Table **2.5.5.1**, the ability of the hydrides to transfer a hydrogen to water increases across a period and down a group.

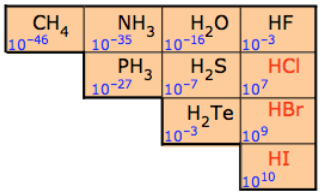


Figure **2.5.5.1**: The acid ionization constants of nonmetal hydrides increase across a period and down a group.

These trends are largely due to changes in the electronegativity and size of the nonmetal atom:

1. Going across a period, the acid strength increases as there is an increase in electronegativity and the molecule gets more polar, with the hydrogen getting a larger partial positive charge. This makes it easier to heterolytically cleave the E-H bond to produce a stable anion.

$$E - H \rightarrow E:^- + H^+$$

2. Going down a group, the acid strength increases because the bond strength decreases as a function of increasing size of the nonmetal, and this has a larger effect than the electronegativity. In fact HF is a weak acid because it is so small that the hydrogen-fluorine bond is so strong that it is hard to break. Remember, the weaker the bond, the stronger the acid strength. This is further illustrated in Table **2.5.5.1**, where the weakest bond has produced the strongest acid.

Table **2.5.5.1** Acid strength as function of bond energy

Relative Acid Strength	HF	<<	HCl	<	HBr	<	HI
H–X Bond Energy (kJ/mol)	570		432		366		298
K_a	10^{-3}		10^{7}		10^{9}		10^{10}

Contributors and Attributions

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* who expanded this section from a combination of

https://chem.libretexts.org/Courses/University_of_Arkansas_Little_Rock/Chem_1403%3A_General_Chemistry_2/Text/16%3A_Acids_and_Bases/16.6%3A_Molecular_Structure%2C_Bonding%2C_and_Acid-Base_Behavior and

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- **6.3.3: The acid-base behavior of binary element hydrides is determined primarily by the element's electronegativity and secondarily by the element-hydrogen bond strength** by Stephen M. Contakes is licensed CC BY 4.0.

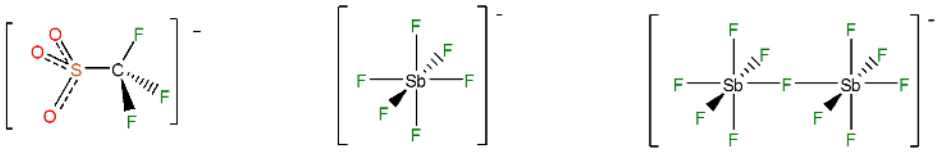
2.5.6: Brønsted-Lowry Superacids and the Hammett Acidity Function

Acids with an acidity greater than that of sulfuric acid are termed superacids.

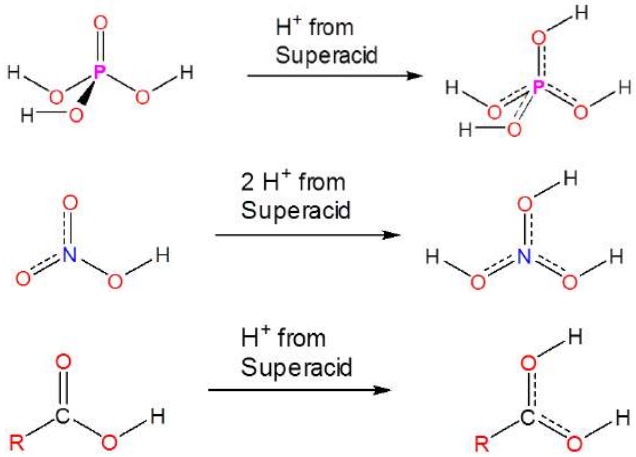
Superacids are able to dissociate completely because when they do so they give an extremely stable anion in which the residual negative charge is distributed among multiple electronegative atoms. For example, in mixtures of **HF** and antimony pentaflouride the dissociation of a hydrogen ion from the **HF** is promoted by the formation of a Lewis acid-base adduct between the **HF** flouride and $\mathbf{SbF_5}$.



This gives extremely stable anions like $\mathbf{SbF_6^-}$ and $\mathbf{Sb_2F_{11}^-}$, in which a single negative charge is delocalized among many electronegative groups and atoms; of these, $\boldsymbol{CF_3}$ and F are particularly common.



Superacids are able to protonate species that would otherwise act as neutral or even acidic species in water or aprotic media. Phosphoric, nitric, carboxylic, and other ordinary acids are all protonated when dissolved in superacids:



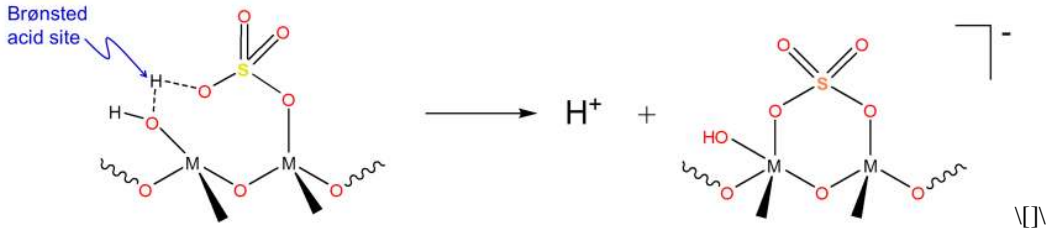
However, superacids also protonate many species that are not usually considered to have acid base properties. Even alkanes can be protonated and, in fact, superacids are used to generate carbocations in a variety of synthetic applications. They do this by protonating alkanes to give unstable species which then decompose to carbocations in further reactions. For example, mixtures of $\mathbf{SbF_5}$ and $\mathbf{FSO_3H}$ called **Magic Acid** can even protonate methane, which gives a $\mathbf{CH_5^+}$ cation:

$$\mathbf{F_5Sb + FSO_3H + CH_4 \longrightarrow F_5Sb{-}OSO_2F^- + CH_5^+}$$

which subsequently decomposes to give an ordinary carbocation

$$\mathbf{CH_5^+ \longrightarrow CH_3^+ + H_2}$$

Since liquid superacids are extremely corrosive and can be costly to separate from reaction mixtures, solid superacids are used industrially instead. The main use for these solid superacids is to generate carbocations for use in hydrocarbon isomerization and alkylation chemistry. Many solid superacids consist of sulfuric acid/sulfates attached to a metal oxide surface to give structures similar to that shown below:



These structures exhibit Hammett acidity parameters in the superacid range. However, the mechanism by which these solid superacids generate carbocations isn't entirely clear since they contain both Brønsted acid sites (at OH) and Lewis acid sites (at M) that could be involved in the carbocation generation process.

The Hammett Acidity Function

The acid ionization constants typically used to measure weak acids' acidity are only valid in dilute aqueous solutions. A more general measure of acidity that in principle is valid for any acid is the Hammett acidity function. The **Hammett acidity function, H_o,** is analogous to the pH used to describe the acidity of aqueous solutions but instead refers to the pure acid:

$$pH = -\log(A_{H^+}) \qquad \text{(for dilute aqueous solutions)}$$

$$H_o = -\log(A_{H^+}) \qquad \text{(for pure acids)}$$

where A_{H^+} is the activity of H^+, which in many dilute solutions is approximately equal to the hydrogen ion concentration (that is why the pH is often defined in terms of $[H^+]$.

At first glance it may seem that the Hammett acidity function is simply a generalization of the pH concept for use in nonaqueous solutions. This is especially so since in water the the pH and H_o do refer to the same quantity. However, the hydrogen ion of the Hammett acidity function is more than a generalization of the pH concept. Its real genius lies in that A_{H^+} does not necessarily represent an actual chemical species of identity H^+ but rather an acid's ability to protonate weak indicator bases, B, specifically via the reaction:

$$H^+ + B \rightleftharpoons BH^+$$

This reaction gives the weak acid BH^+ which can ionize in the reaction that is the reverse of that above:

$$BH^+ \rightleftharpoons B + H^+$$

The extent of this ionization will depend on A_{H^+} according to

$$K_{ion} = \frac{[BH^+]}{A_{H^+}[B]}$$

Taking the negative logarithm of both sides and rearranging gives the Henderson-Hasselbach equation for the indicator base, B:

$$-K_{ion} = -\log A_{H^+} - \log \frac{[BH^+]}{[B]}$$

which can be rearranged to give

$$pK_{ion} = H_o - \log \frac{[BH^+]}{[B]}$$

or

$$H_o = pK_{ion} - \log \frac{[BH^+]}{[B]}$$

From this it is apparent that H_o represents an acid's ability to donate a hydrogen ion, as measured in terms of its ability to shift the equilibrium between B and BH^+ towards BH^+. More negative values of H_o correspond to stronger Brønsted acids with a greater hydrogen ion transfer ability while less negative ones indicate weaker Brønsted acidity.

The value of H_o has been experimentally determined for a number of strong acids by measuring the ratio of BH^+ to B using weakly basic aromatics like 2,4,6-trinitroaniline, various nitrotoluenes, and triflouromethylbenzene as the indicator base, B. Some of these Hammett acidity parameters are shown in Table **2.5.6.1**.

As can be seen from table **2.5.6.1**, sulfuric acid has a Hammett acidity of -12. Since superacids are defined as acids with greater Brønsted acidity than pure sulfuric acid this means that superacids have ($H_o < -12$).

Table **2.5.6.1**: Hammett Acidity for selected strong acids. a. Difficult to estimate reliably. b. Depends on the SF_5 to FSO_3H ratio.

Acid	H_o
Sulfuric acid, H_2SO_4	-12
Perchloric Acid, $HClO_4$	-13.0
Triflic acid (triflouromethanesulfonic acid), CF_3SO_3H	-14.6
Flourosulfonic acid, FSO_3H	-15.6
Magic Acid, $F_5Sb{---}FSO_3H$	-24 to -21[a]
Fluoroantimonic acid, $SbF_5{---}FH$	-24 to -21[a,b]

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1. Gillespie, R. J.; T. E. Peel, T. E.; Robinson, E.A. *J. Am. Chem. Soc.* 1971, *93(20)*, 5083-5087.
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3. Olah, George A. *Superacid chemistry, 2nd ed.* Hoboken, N.J.: Wiley. 2009.

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2.5.7: Acid-Base Chemistry in Amphoteric Solvents and the Solvent Leveling Effect

Amphoteric Protic Solvents Undergo Solvent Autoionization just as Water Does

The Brønsted-Lowry concept allows for an understanding of hydrogen ion transfer chemistry in amphoteric protic solvents. Amphoteric protic solvents are those which can both accept and receive hydrogen ions. From the viewpoint of the Brønsted-Lowry concept, the acid-base chemistry in these solvents is governed by autoionization equilibria analogous to water autoionization.

$$2\,H_2O\,(l) \rightleftharpoons H_3O^+ + OH^- \qquad K_w = 1.0 \times 10^{-14}$$

For example, sulfuric acid ionizes according to the equation:

$$2\,H_2SO_4\,(l) \rightleftharpoons H_3SO_4{}^+ + HSO_4{}^- \qquad K = 4 \times 10^{-4}$$

The magnitude of the solvent autoionization constant in a given amphoteric solvent determines the amount of protonated and deprotonated* solvent present. Since sulfuric acid's autoionization constant is much larger than that of water ($K_w = 10^{-14}$), the concentrations of $H_3SO_4{}^+$ and $HSO_4{}^-$ present in pure sulfuric acid are ~0.02 *M*, much greater than the 10^{-7} *M* H_3O^+ and OH^- present in pure water.

In contrast, ammonia's autoionization constant is much less than that of water and only 10^{-14} *M* $NH_4{}^+$ and $NH_2{}^-$ are present in pure ammonia.

$$2\,NH_3\,(l) \rightleftharpoons NH_4{}^+ + NH_2{}^- \qquad K = 10^{-27}$$

The Solvent Leveling Effect Limits the Strongest Acid or Base that Can Exist

The conjugate acid and base of the solvent are the strongest Brønsted acids and bases that can exist in that solvent. To see why this is the case for acids, consider the reaction between a Brønsted acid (HA) and solvent (S):

$$HA + S \rightleftharpoons HS^+ + A^-$$

This equilibrium will favor dissociation of whichever is a stronger acid - HA or HS^+. If the acid is stronger it will mostly dissociate to give HS^+, while if the solvent's conjugate acid is stronger the acid will be mostly un-ionized and remain as HA.**

Any acid significantly stronger than HS^+ will act as a strong acid and effectively dissociate completely to give the solvent's conjugate acid (HS^+). This also means that the relative acidity of acids stronger than HS^+ cannot be distinguished in solvent S. This is called the **leveling effect** since the solvent "levels" the behavior of acids much stronger than itself to that of complete dissociation. For example, there is no way to distinguish the acidity of strong Arrhenius acids like $HClO_4$ and HCl in water since they both completely dissociate. However, it is possible to distinguish their relative acidities in solvents that are more weakly basic than the conjugate base of the strongest† acid, since then the acids will dissociate to different extents. Such solvents are called differentiating solvents. For example, acetonitrile acts as a differentiating solvent towards $HClO_4$ and HCl. Both $HClO_4$ and HCl partly dissociate in MeCN, with the stronger acid $HClO_4$ dissociating to a greater extent than HCl.

The leveling effect can also occur in basic solutions. The strongest Brønsted base, B, that can exist in a solvent is determined by the relative acidity of the solvent, and the base's conjugate acid, BH^+, determines whether the base will remain unprotonated and able to act as a base in that solvent. If the solvent is represented this time as HS then the relevant equilibrium is:

$$B + HS \rightleftharpoons BH^+ + S^-$$

The position of this equilibrium depends on whether B or S^- is the stronger base. If the solvent's conjugate base, S^-, is stronger, then the base B will remain unprotonated and available to act as a base. However, if B is a stronger base than S^-, it will deprotonate the solvent to give BH^+ and S^-. In this way the strongest base that can exist in a given solvent is the solvent's conjugate base.

The relative strength of Brønsted bases can only be determined in solvents that are more weakly acidic than BH^+; otherwise the bases will all be leveled to S^-.

It is important to consider the leveling effect of protic solvents when performing syntheses that require the use of basic reagents. For instance, hydride and carbanion reagents (lithium aluminum hydride, Grignard reagents, alklyllithium reagents, etc.) cannot be used as nucleophiles in protic solvents like water, alcohols, or enolizable aldehydes and ketones. Since carbanions are stronger

bases than these solvents' conjugate bases, they will instead act as Brønsted bases and deprotonate the solvent. For example if one adds n-butyllithium to water, the result (along with much heat and possibly a fire) will be butane and a solution of lithium hydroxide:

$$Li^+ + {}^- : CH_2CH_2CH_2CH_3 + H_2O\,(l) \longrightarrow Li^+\,(aq) + OH^-\,(aq) + CH_3CH_2CH_2CH_3\,(g)$$

Since hydride and carbanion reagents cannot be used as nucleophiles in protic solvents like water or methanol, they are commonly sold as solutions in solvents such as hexanes (for alklyllithium reagents) or tetrahydrofuran (for Grignard reagents and $LiAlH_4$).

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2.6: 2.5 Lewis Acid-Base Concept

The Brønsted acid-base theory has been used throughout the history of acid and base chemistry. However, this theory is very restrictive and focuses primarily on acids and bases acting as proton donors and acceptors. Sometimes conditions arise where the theory does not necessarily fit, such as in solids and gases. In 1923, G.N. Lewis from UC Berkeley proposed an alternate theory to describe acids and bases. His theory gave a generalized explanation of acids and bases based on structure and bonding. Through the use of the Lewis definition of acids and bases, chemists are now able to predict a wider variety of acid-base reactions. Lewis' theory used electrons instead of proton transfer and specifically stated that an acid is a species that accepts an electron pair while a base donates an electron pair.

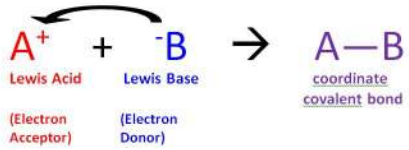


Figure **2.6.1**: A Lewis Base (B) donates it electrons to a Lewis Acid (A) resulting in a coordinate covalently bonded compound, also known as an adduct.

The reaction of a Lewis acid and a Lewis base will produce a coordinate covalent bond (Figure **2.6.1**). A coordinate covalent bond is just a type of covalent bond in which one reactant gives it electron pair to another reactant. In this case the lewis base donates its electrons to the Lewis acid. When they do react this way the resulting product is called an addition compound, or more commonly an adduct.

- Lewis Acid: a species that accepts an electron pair (i.e., an electrophile) and will have vacant orbitals
- Lewis Base: a species that donates an electron pair (i.e., a nucleophile) and will have lone-pair electrons

Lewis Acids

Lewis acids accept an electron pair. Lewis Acids are Electrophilic meaning that they are electron attracting. When bonding with a base the acid uses its lowest unoccupied molecular orbital or LUMO (Figure 2).

- Various species can act as Lewis acids. All cations are Lewis acids since they are able to accept electrons. (e.g., Cu^{2+}, Fe^{2+}, Fe^{3+})
- An atom, ion, or molecule with an incomplete octet of electrons can act as an Lewis acid (e.g., BF_3, AlF_3).
- Molecules where the central atom can have more than 8 valence shell electrons can be electron acceptors, and thus are classified as Lewis acids (e.g., $SiBr_4$, SiF_4).
- Molecules that have multiple bonds between two atoms of different electronegativities (e.g., CO_2, SO_2)

Lewis Bases

Lewis Bases donate an electron pair. Lewis Bases are Nucleophilic meaning that they “attack” a positive charge with their lone pair. They utilize the highest occupied molecular orbital or HOMO (Figure 2). An atom, ion, or molecule with a lone-pair of electrons can thus be a Lewis base. Each of the following anions can "give up" their electrons to an acid, e.g., OH^-, CN^-, CH_3COO^-, $:NH_3$, $H_2O:$, $CO:$. Lewis base's HOMO (highest occupied molecular orbital) interacts with the Lewis acid's LUMO (lowest unoccupied molecular orbital) to create bonded molecular orbitals. Both Lewis Acids and Bases contain HOMO and LUMOs but only the HOMO is considered for Bases and only the LUMO is considered for Acids (Figure **2.6.2**).

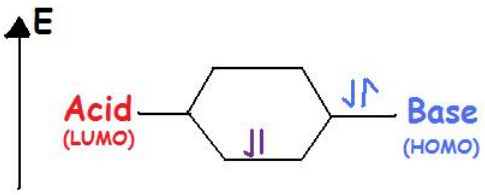


Figure **2.6.2**: Lewis Acids have vacant orbitals so they are in a lower energy level. While lewis bases have lone pair electrons to share and thus occupy a higher energy level.

Complex Ion / Coordination Compounds

Complex ions are polyatomic ions, which are formed from a central metal ion that has other smaller ions joined around it. While Brønsted theory can't explain this reaction Lewis acid-base theory can help. A Lewis Base is often the ligand of a coordination compound with the metal acting as the Lewis Acid (see Oxidation States of Transition Metals).

$$Al^{3+} + 6H_2O \rightleftharpoons [Al(H_2O)_6]^{3+} \tag{2.6.1}$$

The aluminum ion is the metal and is a cation with an unfilled valence shell, and it is a Lewis Acid. Water has lone-pair electrons and is an anion, thus it is a Lewis Base.

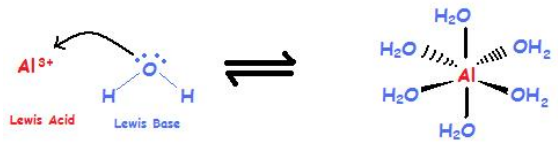


Figure **2.6.3**: Aluminum ion acts as a Lewis acid and accepts the electrons from water, which is acting as a Lewis base. This helps explain the resulting hexaaquaaluminum(III) ion.

The Lewis Acid accepts the electrons from the Lewis Base which donates the electrons. Another case where Lewis acid-base theory can explain the resulting compound is the reaction of ammonia with Zn^{2+}.

$$Zn^{2+} + 4NH_3 \rightarrow [Zn(NH_3)_4]^{4+} \tag{2.6.2}$$

Similarly, the Lewis Acid is the zinc Ion and the Lewis Base is NH_3. Note how Brønsted Theory of Acids and Bases will not be able to explain how this reaction occurs because there are no H^+ or OH^- ions involved. Thus, Lewis Acid and Base Theory allows us to explain the formation of other species and complex ions which do not ordinarily contain hydronium or hydroxide ions. One is able to expand the definition of an acid and a base via the Lewis Acid and Base Theory. The lack of H^+ or OH^- ions in many complex ions can make it harder to identify which species is an acid and which is a base. Therefore, by defining a species that donates an electron pair and a species that accepts an electron pair, the definition of a acid and base is expanded.

Amphoterism

As of now you should know that acids and bases are distinguished as two separate things however some substances can be both an acid and a base. You may have noticed this with water, which can act as both an acid or a base. This ability of water to do this makes it an amphoteric molecule. Water can act as an acid by donating its proton to the base and thus becoming its conjugate acid, OH-. However, water can also act as a base by accepting a proton from an acid to become its conjugate base, H_3O^+.

- Water acting as an Acid:

$$H_2O + NH_3 \rightarrow NH_4^+ + OH^- \tag{2.6.3}$$

- Water acting as a Base:

$$H_2O + HCl \rightarrow Cl^- + H_3O^+ \tag{2.6.4}$$

You may have noticed that the degree to which a molecule acts depends on the medium in which the molecule has been placed in. Water does not act as an acid in an acid medium and does not act as a base in a basic medium. Thus, the medium which a molecule is placed in has an effect on the properties of that molecule. Other molecules can also act as either an acid or a base. For example,

$$Al(OH)_3 + 3H^+ \rightarrow Al^{3+} + 3H_2O \tag{2.6.5}$$

- where $Al(OH)_3$ is acting as a Lewis Base.

$$Al(OH)_3 + OH^- \rightarrow Al(OH)_4^- \tag{2.6.6}$$

- where $Al(OH)_3$ is acting as an Lewis Acid.

Note how the amphoteric properties of the $Al(OH)_3$ depends on what type of environment that molecule has been placed in.

References

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2. Fluorescence Maxima of 10-Methylacridone? Metal Ion Salt Complexes: A Convenient and Quantitative Measure of Lewis Acidity of Metal Ion Salts. Shunichi Fukuzumi and, Kei Ohkubo. *Journal of the American Chemical Society 2002* 124 (35), 10270-10271.
3. Harwood, William S., F. G. Herring, Jeffry D. Madura, and Ralph H. Petrucci. General Chemistry Principles and Modern Applications. 9th ed. New Jersey: Prentice Hall, 2007. 695-96.

Contributors and Attributions

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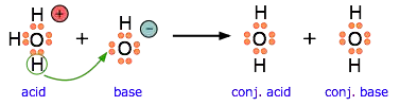
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2.6.1: 2.5.1 Lewis Acid-Base Neutralization

Lewis Acid-Base Neutralization Involving Electron-Pair Transfer

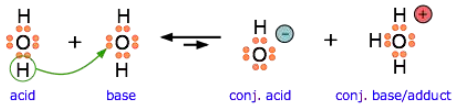
Just as any Arrhenius acid is also a Brønsted acid, any Brønsted acid is also a Lewis acid, so the various acid-base concepts are all "upward compatible". Although we do not really need to think about electron-pair transfers when we deal with ordinary aqueous-solution acid-base reactions, it is important to understand that it is the opportunity for electron-pair sharing that enables proton transfer to take place.



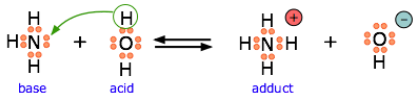
This equation for a simple acid-base neutralization shows how the Brønsted and Lewis definitions are really just different views of the same process. Take special note of the following points:

- The arrow shows the movement of a proton from the hydronium ion to the hydroxide ion.
- Note that the electron-pairs themselves do not move; they remain attached to their central atoms. The electron pair on the base is "donated" to the acceptor (the proton) only in the sense that it ends up being *shared* with the acceptor, rather than being the exclusive property of the oxygen atom in the hydroxide ion.
- Although the hydronium ion is the nominal Lewis acid here, it does not itself accept an electron pair, but acts merely as the source of the proton that coordinates with the Lewis base.

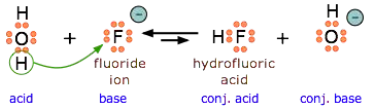
The point about the electron-pair remaining on the donor species is especially important to bear in mind. For one thing, it distinguishes a *Lewis acid-base reaction* from an *oxidation-reduction reaction*, in which a physical transfer of one or more electrons from donor to acceptor does occur. The product of a Lewis acid-base reaction is known formally as an "adduct" or "complex", although we do not ordinarily use these terms for simple proton-transfer reactions such as the one in the above example. Here, the proton combines with the hydroxide ion to form the "adduct" H_2O. The following examples illustrate these points for some other proton-transfer reactions that you should already be familiar with.



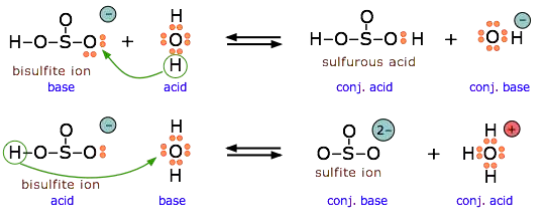
Another example, showing the autoprotolysis of water. Note that the conjugate base is also the adduct.



Ammonia is both a Brønsted and a Lewis base, owing to the unshared electron pair on the nitrogen. The reverse of this reaction represents the *hydrolysis* of the ammonium ion.



Because HF is a weak acid, fluoride salts behave as bases in aqueous solution. As a Lewis base, F^- accepts a proton from water, which is transformed into a hydroxide ion.

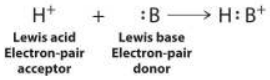


The bisulfite ion is *amphiprotic* and can act as an electron donor or acceptor.

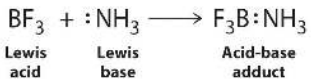
> **Note**
>
> All Brønsted–Lowry bases (proton acceptors), such as OH^-, H_2O, and NH_3, are also electron-pair donors. Thus the Lewis definition of acids and bases does not contradict the Brønsted–Lowry definition. Rather, it expands the definition of acids to include substances other than the H^+ ion.

Lewis Acid-Base Neutralization without Transferring Protons

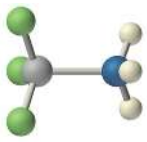
Electron-deficient molecules, such as BCl_3, contain less than an octet of electrons around one atom and have a strong tendency to gain an additional pair of electrons by reacting with substances that possess a lone pair of electrons. Lewis's definition, which is less restrictive than either the Brønsted–Lowry or the Arrhenius definition, grew out of his observation of this tendency. A general Brønsted–Lowry acid–base reaction can be depicted in Lewis electron symbols as follows:



The proton (H^+), which has no valence electrons, is a Lewis acid because it accepts a lone pair of electrons on the base to form a bond. The proton, however, is just one of many electron-deficient species that are known to react with bases. For example, neutral compounds of boron, aluminum, and the other Group 13 elements, which possess only six valence electrons, have a very strong tendency to gain an additional electron pair. Such compounds are therefore potent Lewis acids that react with an electron-pair donor such as ammonia to form an acid–base adduct, a new covalent bond, as shown here for boron trifluoride (BF_3):



The bond formed between a Lewis acid and a Lewis base is a *coordinate covalent bond* because both electrons are provided by only one of the atoms (N, in the case of $F_3B{:}NH_3$). After it is formed, however, a coordinate covalent bond behaves like any other covalent single bond.



Boron trifluoride-ammonia adduct

Species that are very weak Brønsted–Lowry bases can be relatively strong Lewis bases. For example, many of the group 13 trihalides are highly soluble in ethers (R–O–R′) because the oxygen atom in the ether contains two lone pairs of electrons, just as in H_2O. Hence the predominant species in solutions of electron-deficient trihalides in ether solvents is a Lewis acid–base adduct. A reaction of this type is shown in Figure **2.6.1.1** for boron trichloride and diethyl ether:

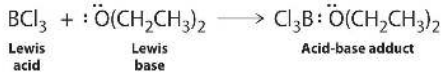
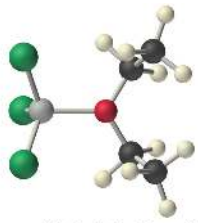


Figure 2.6.1.1: *Lewis Acid/Base reaction of boron trichloride and diethyl ether reaction*

Note

- Electron-deficient molecules (those with less than an octet of electrons) are Lewis acids.
- The acid-base behavior of many compounds can be explained by their Lewis electron structures.

Many molecules with multiple bonds can act as Lewis acids. In these cases, the Lewis base typically donates a pair of electrons to form a bond to the central atom of the molecule, while a pair of electrons displaced from the multiple bond becomes a lone pair on a terminal atom.



Boron trichloride-diethyl ether adduct

Figure 2.6.1.2. The highly electronegative oxygen atoms pull electron density away from carbon, so the carbon atom acts as a Lewis acid. Arrows indicate the direction of electron flow.

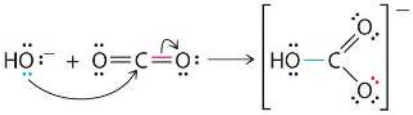


Figure 2.6.1.2: *Lewis Acid/Base reaction of the hydroxide ion with carbon dioxide*

Example 2.6.1.1

Identify the acid and the base in the Lewis acid–base reaction.

$BH_3 + (CH_3)_2S \rightarrow H_3B{:}S(CH_3)_2$

Solution

In each equation, identify the reactant that is electron deficient and the reactant that is an electron-pair donor. The electron-deficient compound is the Lewis acid, whereas the other is the Lewis base.

In BH_3, boron has only six valence electrons. It is therefore electron deficient and can accept a lone pair. Like oxygen, the sulfur atom in $(CH_3)_2S$ has two lone pairs. Thus $(CH_3)_2S$ donates an electron pair on sulfur to the boron atom of BH_3. The Lewis base is $(CH_3)_2S$, and the Lewis acid is BH_3

Example 2.6.1.2

Identify the acid and the base in the Lewis acid–base reaction.

$CaO + CO_2 \rightarrow CaCO_3$

Solution

In each equation, identify the reactant that is electron deficient and the reactant that is an electron-pair donor. The electron-deficient compound is the Lewis acid, whereas the other is the Lewis base.

CO_2 accepts a pair of electrons from the O^{2-} ion in CaO to form the carbonate ion. The oxygen in CaO is an electron-pair donor, so CaO is the Lewis base. Carbon accepts a pair of electrons, so CO_2 is the Lewis acid.

Problems

? Exercise 2.6.1.1

Identify the acid and the base in the Lewis acid–base reaction.

$(CH_3)_2O + BF_3 \rightarrow (CH_3)_2O{:}BF_3$

Answer

Lewis base: $(CH_3)_2O$; Lewis acid: BF_3

? Exercise 2.6.1.2

Identify the acid and the base in the Lewis acid–base reaction.

$H_2O + SO_3 \rightarrow H_2SO_4$

Answer

Lewis base: H_2O; Lewis acid: SO_3

? Exercise 2.6.1.3

Identify the acid and the base in the Lewis acid–base reaction.

$BeCl_2 + 2\ Cl^- \rightarrow BeCl_4^{2-}$

Answer

The chloride ion contains four lone pairs. In this reaction, each chloride ion donates one lone pair to $BeCl_2$, which has only four electrons around Be. Thus the chloride ions are Lewis bases, and $BeCl_2$ is the Lewis acid

? Exercise 2.6.1.4

Here are several more examples of Lewis acid-base reactions that **cannot** be accommodated within the Brønsted or Arrhenius models. Identify the Lewis acid and Lewis base in each reaction.

a. $Al(OH)_3 + OH^- \rightarrow Al(OH)_4^-$
b. $SnS_2 + S^{2-} \rightarrow SnS_3^{2-}$
c. $Cd(CN)_2 + 2CN^- \rightarrow Cd(CN)_4^{2+}$
d. $AgCl + 2NH_3 \rightarrow Ag(NH_3)_2^+ + Cl^-$
e. $Fe^{2+} + NO \rightarrow Fe(NO)^{2+}$
f. $[Ni^{2+} + 6NH_3 \rightarrow Ni(NH_3)_5^{2+}$

Answer a

Lewis base: OH^-; Lewis acid: $Al(OH)_3$

Answer b

Lewis base: S^{2-}; Lewis acid: SnS_2

Answer c

Lewis base: CN^-; Lewis acid: $Cd(CN)_2$

Answer d

Lewis base: NH_3; Lewis acid: AgCl

Answer e

Lewis base: NO; Lewis acid: Fe^{2+}

Answer f

Lewis base: NH_3; Lewis acid: Ni^{2+}

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2.6.2: 2.5.2 Non-Aqueous Acid/Base Systems

We ordinarily think of Brønsted-Lowry acid-base reactions as taking place in aqueous solutions, but this need not always be the case. A more general view encompasses a variety of acid-base *solvent systems*, of which the *water system* is only one (Table **2.6.2.1**). Each of these has as its basis an amphiprotic solvent (one capable of undergoing autoprotolysis), in parallel with the familiar case of water.

The limiting acid in a given solvent is the solvonium ion, such as H_3O^+ (hydronium) ion in water. An acid which has more of a tendency to donate a hydrogen ion than the limiting acid will be a strong acid in the solvent considered, and will exist mostly or entirely in its dissociated form. Likewise, the limiting base in a given solvent is the solvate ion, such as OH^- (hydroxide) ion, in water. A base which has more affinity for protons than the limiting base cannot exist in solution, as it will react with the solvent.

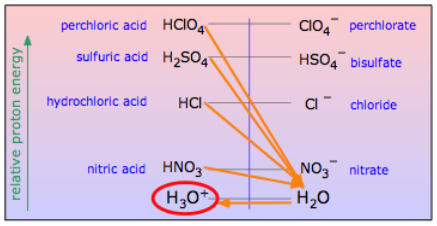


Figure } \PageIndex{3}\): *Use of non-aqueous solvents allows the study of strong acids that are hindered by the "leveling effect" of the solvent.*

The ammonia system is one of the most common non-aqueous system in Chemistry. Liquid ammonia boils at –33° C, and can conveniently be maintained as a liquid by cooling with dry ice (–77° C). It is a good solvent for substances that also dissolve in water, such as ionic salts and organic compounds since it is capable of forming hydrogen bonds. Bases can exist in solution in liquid ammonia which cannot exist in aqueous solution: this is the case for any base which is **stronger** than the hydroxide ion, but **weaker** than the amide ion $\boldsymbol{NH_2^-}$. The limiting acid in liquid ammonia is the ammonium ion, which has a pK_a value in water of 9.25. The limiting base is the amide ion, NH_2^-. This is a stronger base than the hydroxide ion and so cannot exist in aqueous solution. The pK_a value of ammonia is estimated to be approximately 33. Any acid which is a stronger acid than the ammonium ion will be a strong acid in liquid ammonia. This is the case for acetic acid, which is completely dissociated in liquid ammonia solution. The addition of pure acetic acid and the addition of ammonium acetate have exactly the same effect on a liquid ammonia solution: the increase in its acidity: in practice, the latter is preferred for safety reasons.

Note

As with $\boldsymbol{OH^-}$ and $\boldsymbol{H_3O^+}$ in water, the strongest acid and base in $\boldsymbol{NH_3}$ is dictated by the corresponding autoprotolysis reaction of the solvent:

$$\boldsymbol{2NH_3 \rightleftharpoons NH_4^+ + NH_2^-}$$

One use of non-aqueous acid-base systems is to examine the relative strengths of the strong acids and bases, whose strengths are "leveled" by the fact that they are all totally converted into H_3O^+ or OH^- ions in water. By studying them in appropriate non-aqueous solvents which are poorer acceptors or donors of protons, their relative strengths can be determined. Many familiar substances can serve as the basis of protonic solvent systems (Table **2.6.2.1**).

Table 2.6.2.1: Popular Solvent systems

solvent	autoprotolysis reaction	pK_a
water	$2H_2O \rightleftharpoons H_3O^+ + OH^-$	14
ammonia	$2NH_3 \rightleftharpoons NH_4^+ + NH_2^-$	33
acetic acid	$2CH_3COOH \rightleftharpoons CH_3COOH_2^+ + CH_3COO^-$	13
ethanol	$2C_2H_5OH \rightleftharpoons C_2H_5OH_2^+ + C_2H_5O^-$	19
hydrogen peroxide	$2HO-OH \rightleftharpoons HO-OH_2^+ + HO-O^-$	13
hydrofluoric acid	$2HF \rightleftharpoons H^2F^+ + F^-$	10
sulfuric acid	$2H_2SO_4 \rightleftharpoons H3SO_4^+ + HSO_4^-$	3.5

The extreme case is a **superacid**, a medium in which the hydrogen ion is only very weakly solvated. The classic example is a mixture of antimony pentafluoride and liquid hydrogen fluoride:

$$SbF_5 + HF \rightleftharpoons H^+ + SbF_6^- \tag{2.6.2.1}$$

The limiting base, the hexfluoroantimonate anion SbF_6^-, is so weakly attracted to the hydrogen ion that virtually any other base will bind more strongly: hence, this mixture can be used to protonate organic molecules which would not be considered bases in other solvents. It should noted that pH is undefined in aprotic solvents, which assumes presence of hydronium ions. In other solvents, the concentration of the respective solvonium/solvate ions should be used (e.g., $[NH_4^+]$ and $[NH_2^-]$ in $NH_{3(l)}$.

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SECTION OVERVIEW

2.7: The Hard-Soft Acid-Base Concept

Topic hierarchy

2.7.1: Origin of the Hard-Soft Acid-Base Concept

2.7.2: Pearson's Hard-Soft Acid-Base Concept

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2.7.1: Origin of the Hard-Soft Acid-Base Concept

One of the strengths of the Lewis acid-base concept is that it readily illuminates the role of covalent and electrostatic interactions in acid base behavior. Specifically, it explains chemical interactions in terms of the interactions between charged groups as electrons are donated from a base to an acid. However, this theory does little to describe teh extent to which the product of a Lewis acid-base reaction is held together by covalent bonds versus ionic bonds, or when is a product better described as a molecule rather than an ion pair? This question and more are addressed by the conceptual tool, the Hard-Soft acid-base principle.

The **Hard-Soft acid-base principle (HSAB principle)** stems from the recognition that some Lewis acids and bases seem to have a natural affinity for one another.* Consider the following:

- Some metals are commonly found in nature as salts of chloride or as oxide ores, while others are found in combination with sulfur. Geochemists use the Goldschmidtt classification scheme to classify the halide and oxide formers as *lithophiles* and the sulfide formers as *chalcophiles*.
- In living systems small highly charged metals ions like Fe^{3+} are usually found bonded to N and O atoms while larger metals with lower charges such as Zn^{2+} are often found attached to at least one S atom. Similarly, metals prefer to bind to one coordination site over the other when forming complexes with ambidentate ligands. The most well-known instances involve complexes of cyanate and thiocyanate, which can coordinate metals through either the N or chalcogen atom. For instance, Cu^{2+} and Zn^{2+} form *N*-thiocyanato complexes in species like $[Cu(NCS)_2(py)_2]$ and $[Zn(NCS)_4]^{2-}$ while their larger cogeners Au^{3+} and Hg^{2+} preferentially form *S*-thiocyanato complexes, giving species like $[Hg(SCN)_4]^{2-}$.
- The solubility trends for the alklai metal halides and silver halides are opposite, even though both involve salts of formula M^+X^- (salts can be thought of as involving Lewis acid-base adduct formation between the anions and cations). Specifically, although the silver halides are all relatively insoluble in water, the very modest solubility they possess follows the order:

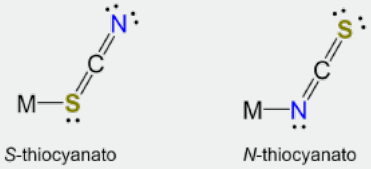
$$X = F >> Cl > Br > I \text{ (for the solubility of AgX)}$$

  In contrast, the much more ample solubility of the alkali metal halides follows the opposite order.** For example, the order for the lithium halides is

$$X = F << Cl < Br << I \text{ (for the solubility of LiX)}$$

Ambidentate ligands

Ambidentate ligands possess multiple coordination sites through which a metal may bind. For instance, thiocyanate may coordinate metals (M) at either the S or N to give *S*-thiocyanato or *N*-thiocyanato complexes.



S-thiocyanato *N*-thiocyanato

Notes

* Despite the fruitfulness of this observation, in general it is important to reduce the potential for observer bias by checking observations like these against compounds reported in the chemical literature and databases like the Inorganic Crystal Structure and Cambridge Crystallographic Databases.

** These are very soluble in water, to the point where some solutions are perhaps better described as solutions of water in the halide.

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- **6.6: Hard and Soft Acids and Bases** by Stephen M. Contakes is licensed CC BY 4.0.

2.7.2: Pearson's Hard-Soft Acid-Base Concept

The Hard-Soft Acid-Base concept is a tool for thinking about patterns of Lewis acid-base reactivity. Arland, Chatt, and Davies' observed that *Lewis acids and bases could be classified into two groups based on their propensity to form stable compounds with one another* (*e.g.* acids in a class tend to form more stable adducts with bases in the same class than they did with bases in the other class).[1] Arland, Chatt, and Davies somewhat boringly termed these groups class a and class b but today they are known by Ralph Pearson's name for them. Pearson called the class a acids and bases *hard* and called the class b acids and bases *soft*. These terms reflect the polarizability of the electron cloud, or how "soft" these substance's electron clouds are towards distortion (Figure **2.7.2.1**). **Soft** acids and bases are relatively polarizable, and **hard** acids and bases are difficult to polarize.

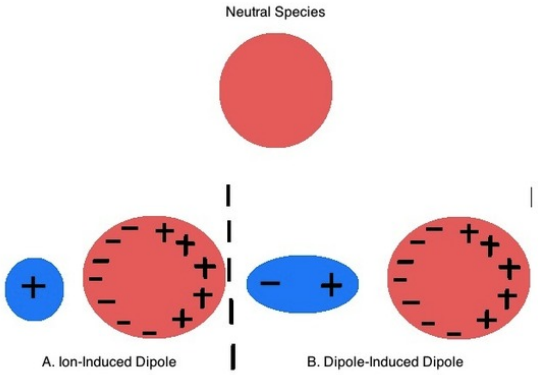


Figure **2.7.2.1**: Polarizability refers to the ease with which a substance's electron cloud may be distorted under the action of an electric field. Polarizability determines the degree to which a neutral species' electron cloud can be distorted to an induced dipole moment by an ion (as shown on the left) or by a polar molecule (as shown on the right). [CC-BY 4.0, LibreText]

Hard and Soft Classification

Hard Species

Hard acids and bases have a high charge density (highly charged relative to size), and polarization is difficult. Low polarizability is attributed to hard acids being relatively electron-poor and hard bases being relatively electron-rich. Low polarizability is also attributed to the localization of charge on an atom with electron-withdrawing substituents (in the case of a hard acid) or electron-donating substituents (in the case of a hard base). It is also observed that hard acids have high oxidation states or large positive formal charges, while hard bases have low oxidation states or negative formal charges.

For hard acids, which possess few valence electrons, polarization involves distorting core (inner shell) electrons, which are difficult to distort because they are close to the nucleus and experience a high nuclear charge. Hard acids tend to be found towards the left side of the periodic table and involve higher oxidation states and/or electron donating substituents

Soft Species

Soft acids and bases posses many valence electrons and are more readily polarized. Soft acids and bases are more likely to be found towards the middle or right of the periodic table. Soft acids and bases also have little charge density and/or are relatively electron rich. Soft acids are more common to the right of the periodic table and involve lower oxidation states and/or electron donating substituents.

Borderline Species

All hard acids and bases are not equally hard, and all soft acids and bases are not equally soft. There is a graduation in hardness and softness, and there are a number of intermediate acids and bases that do not fit neatly in either category. Figure **2.7.2.1** classifies each element as a hard, soft, or **borderline** (intermediate) acid or base. Some borderline acids can be considered hard or soft depending on their oxidation state. The higher oxidation state species can be considered hard acids, and the lower oxidation state species can be considered soft acids. Additional representative examples of hard, soft, and borderline bases are shown in Figure Extra close brace or missing open brace and Figure **2.7.2.3**.

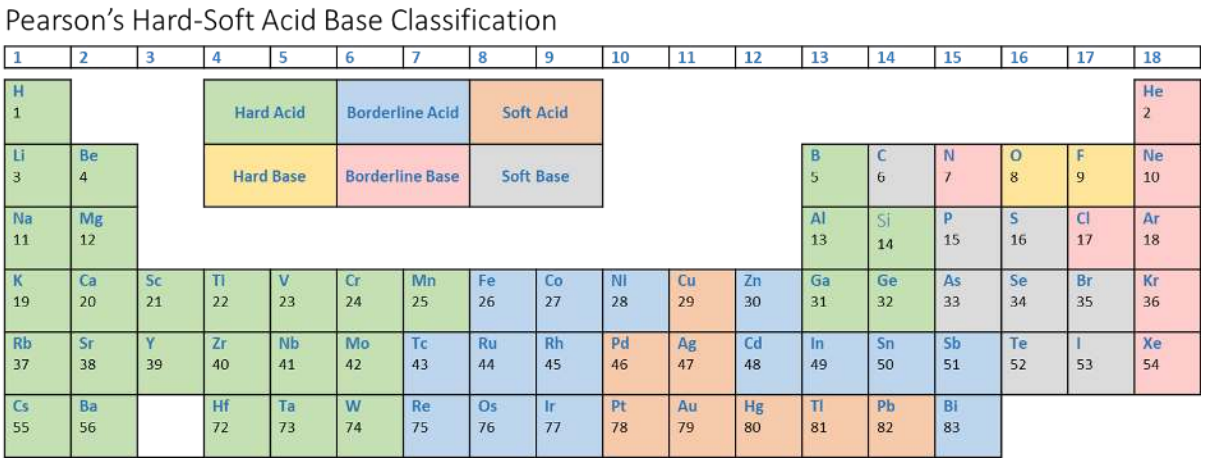


Figure 2.7.2.1: Pearson's Hard-Soft Acid Base Classification of the Elements (CC-BY-NC-SA; Kathryn A. Newton)

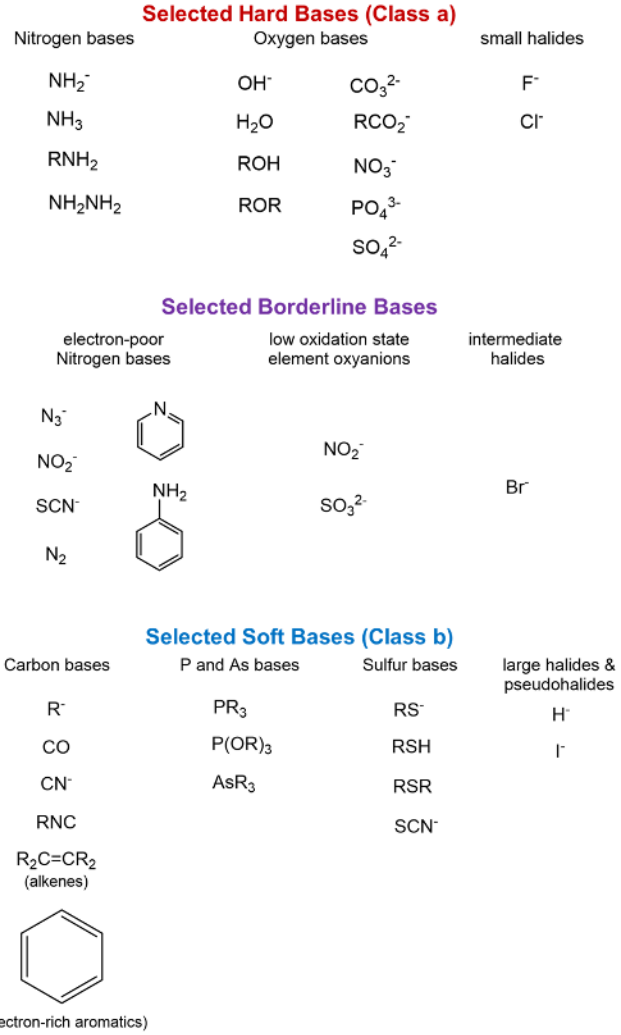


Figure 2.7.2.2: Representative examples of hard, soft, and borderline bases. (LibreText)

Hard Base	Soft Base	Borderline Base	Hard Acid	Soft Acid	Borderline Acid
NR_3 (R = alkyl group) O^{2-} F^- Cl^-	CO CN^- P S As Se Te I NCS^-	Br^- ^-NCS	Ti^{4+} V^{4+} Cr^{3+}, Cr^{6+} $Mn^{2+}, Mn^{4+}, Mn^{7+}$ Fe^{3+} Co^{3+} Ni^{3+}	Cu^+ M^{n-} (−oxidation state)	Fe^{2+} Co^{2+} Ni^{2+} Cu^{2+}

Figure **2.7.2.3**: HSAB classifcation of selected species. (CC-BY-NC-SA; Kathryn A. Newton)

The Hard-Soft Acid-Base Principle (HSAB Principle)

The **Hard-Soft Acid-Base Concept (HSAB Concept)** explains patterns in Lewis acid-base reactivity as a *like reacts with like* preference. Both thermodynamically and kinetically, hard acids prefer hard bases and soft acids soft bases. Specifically,

- Thermodynamically, hard acids form more stable acid-base complexes with hard bases while soft acids form more stable complexes with soft bases.
- Kinetically, hard acids/electrophiles react more quickly with hard bases/nucleophiles while soft acids/electrophiles react more quickly with soft bases/nucleophiles.

The HSAB principle can predict the equilibrium of Lewis acid-base metathesis and displacement reactions. In a Lewis acid-base **metathesis reaction** the acids and bases swap partners:

$$\mathbf{A_1 : B_1 + A_2 : B_2 \overset{k_1,\, K_{eq}}{\rightleftharpoons} A_1 : B_2 + A_2 : B_1}$$

For example, the equilibrium position of the metathesis reaction between $\mathbf{TlF}$ and $\mathbf{K_2S}$ favors the products:

$$\mathbf{2\,TlF + H_2S \rightleftharpoons Tl_2S + 2\,KF}$$

This is consistent with the HSAB's hard-hard and soft-soft preference.



The HSAB principle also allows for prediction of displacement reactions, in which a Lewis acid or base forms an adduct using a base or acid from an existing Lewis acid-base complex. In these reactions, the displacement of acid or base from the reactant complex may be thought of as a sort of metathesis reaction, one in which in the unbound acid or base switches places with one in the complex. For example, the reaction between $\mathbf{HI}$ and methylmercury cation involves displacement of an iodide from $\mathbf{HI}$ to give $\mathbf{CH_3HgI}$. The position of the equilibrium favors $\mathbf{CH_3HgI}$ since both $\mathbf{CH_3Hg^+}$ and $\mathbf{I^-}$ are soft, while $\mathbf{H^+}$ is a hard acid.

$$\mathbf{HI + HgSCH_3^+ \rightleftharpoons CH_3SHgI + H^+}$$



The hard-hard and soft-soft preferences in Lewis acid-base interactions reflect that:

- The lone pair of a hard base is strongly stabilized electrostatically by a hard acid.
- The lone pair of a soft base is strongly stabilized by forming a covalent bond with a soft acid.

- The lone pair of a hard or soft base is comparatively weakly stabilized by an acid opposite to it in hardness or softness since the overall electrostatic and covalent stabilization of the adduct is comparatively weak.

Problems

Exercise 2.7.2.1

Rank the acids or bases in each set in increasing order of expected hardness.

a. Cr^{2+} and Cr^{3+}
b. H^+, Cs^+, and Tl^+
c. SCN^- (acting as a base at N) and SCN^- (acting as a base at S)
d. AlF_3, AlH_3, $AlMe_3$
e. The side chains of the following proteinogenic amino acids

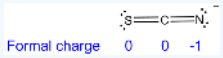


Answer

(a) $Cr^{2+} < Cr^{3+}$ All other things being equal, hardness increases with oxidation state.

(b) $Tl^+ < Cs^+ < H^+$ The order reflects Cs^+ and Tl^+'s larger size relative to H^+ (which doesn't possess any electrons that can be polarized anyway) and that Tl^+ still possesses two valence electrons while Cs^+ possesses none.

(c) SCN^- (acting as a base at S) < SCN^- (acting as a base at N). The order reflects the greater electronegativity of N than S and N's possession of a more negative formal charge of -1.



(d) $AlH_3 < AlMe_3 < AlF_3$. The hardness increases as the substituents on the Lewis acid Al center become less electron donating and more electron withdrawing (and, incidentally, harder bases) as their electronegativity increases in the order H^- < CH_3^- < F^-. Note that the order of electron donating ability for H^- and CH_3^- is the opposite observed for carbocations, for which hyperconjugation plays a larger role.

(e) Sec < Cys < Ser. The hardness increases as the electronegativity of the Lewis base chalcogen increases on going from a selenol to a thiol to an alcohol.

Exercise 2.7.2.2

Predict the position of equilibrium for the following reaction.

$$Fe_2O_3 + 3\,Ag_2S \rightleftharpoons Fe_2S_3 + 3\,Ag_2O$$

Answer

The equilibrium will favor the reactants (K<1) since the hard-hard and soft-soft interactions in the reactants are more stable than the hard-soft interactions in the products.



Exercise 2.7.2.3

Predict whether K for the following equilibria will be <<1, ~1, or >>1.

a. $2\,HF + (CH_3Hg)_2S \rightleftharpoons 2\,CH_3HgF + H_2S$
b. $Ag(NH_3)_2^+ + 2\,PH_3 \rightleftharpoons Ag(PH_3)_2^+ + 2\,NH_3$
c. $Ag(PH_3)_2^+ + 2\,H_3B{-}SH_2 \rightleftharpoons 2\,H_3B{-}PH_3 + Ag(SH_2)_2^+$
d. $H_3B{-}NH_3 + F_3B{-}SH_2 \rightleftharpoons H_3B{-}SH_2 + F_3B{-}NH_3$

Answer

a. K< < 1 since the reactant adducts are hard-hard and soft-soft while the products involve hard-soft interactions.

b. K>>1 since the reactant complex, diamine silver(I), is a complex of a hard base, NH_3, with the soft acid, Ag^+, while the product is a complex of the same soft acid with the soft base phosphine.

c. K~1 since all the adducts amongst the reactants and products involve soft acids and bases.

d. K>>1 since BH_3 is a softer acid than BF_3, so it will form a stronger complex with the softer base H_2S while the harder BF_3 forms a stronger complex with the harder base NH_3.

Exercise 2.7.2.4

Which acid will form the most stable complex with **CO**: BH_3, BF_3, or BMe_3?

Answer

BH_3. Since **CO** forms complexes primarily through its carbon lone pair, it is a soft base and so will form the strongest complex with the softest Lewis acid.

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2. Pearson, R. G., Hard and Soft Acids and Bases. Journal of the American Chemical Society 1963, 85 (22), 3533-3539.

3. Fleming, I., Molecular orbitals and organic chemical reactions. Reference ed.; Wiley: Hoboken, N.J., 2010.

Notes

* Despite the fruitfulness of this observation, in general it is important to reduce the potential for observer bias by checking observations like these against compounds reported in the chemical literature and databases like the Inorganic Crystal Structure and Cambridge Crystallographic Databases.

** These are very soluble in water, to the point where some solutions are perhaps better described as solutions of water in the halide.

2.7.2: Pearson's Hard-Soft Acid-Base Concept is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Kathryn A. Newton, Northern Michigan University.

- **6.6.2: Hard-Hard and Soft-Soft preferences may be explained and quantified in terms of electrostatic and covalent and electronic stabilization on the stability of Lewis acid-base adducts** by Stephen M. Contakes is licensed CC BY 4.0.

CHAPTER OVERVIEW

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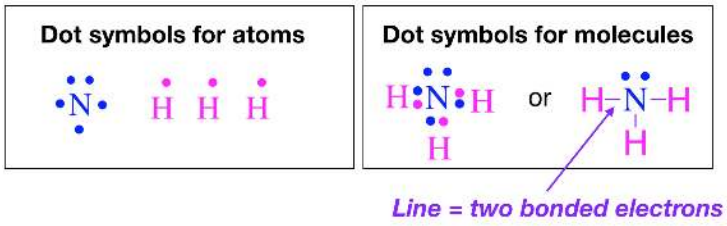
3.4.9: Ionic Compounds and Molecular Orbitals

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3.1: Lewis Electron-Dot Diagrams

In 1916, Gilbert Lewis Newton introduced a simple way to show the bonding between atoms in a molecule though Lewis electron dot diagrams. Creating Lewis diagrams is rather simple and requires only a few steps and some accounting of the valence electrons on each atom. Valence electrons are represented as dots. When two electrons are paired (lone pairs), they are represented by two adjacent dots located on an atom, and when two paired electrons are shared between atoms (bonds), they are shown as lines. For example, below are the electron dot structures of atoms and the Lewis electron dot structures of the molecules.

These diagrams are helpful because they allow us to show how atoms are connected, and when coupled with Valence Shell Electron Repulsion Theory (VSEPR), we can use Lewis structures to predict the shape of the molecule.



The drawing of Lewis electron-dot structures is guided largely by the **octet rule**: that atoms form bonds to achieve eight electrons in their valence shell. For many elements, a full valence shell has an electron configuration of s^2p^6, or eight electrons. A common exception to this rule is the first row elements, H and He. These two elements have $n = 1$ as their valence shell, and so they have only two electrons in a full valence shell ($1s^2$ electron configuration). Although H and He are exceptions to the "octet rule", they still form bonds to achieve a full valence shell. It may be better to think of this as the "full valence" rule of bonding. We will see many more violations to the "octet" rule as we progress through this course. In the case of metals and metalloids, breaking of the rules is particularly common. (CC-BY-NC-SA; Kathryn Haas)

Common violations of the octet rule

- **Less than eight electrons (hypovalency)**: H and He are examples of elements that cannot have more than two electrons in their full valence shell. Additionally, there are cases where a valid Lewis structure contains atoms with ***hypovalency:*** *partially-filled valence shells*. An example of this is a *carbocation, a positively charged carbon with only six electrons in its valence shell.* Carbocations are important intermediates in organic chemistry, and they are highly reactive (unstable) Lewis acids (electrophiles). Another example of hypovalency is the Lewis structure for BH_3, which shows boron with three bonds, and only six electrons in its valence shell. Boron hydride is a strong Lewis Acid. (Side note: the actual chemical form of BH_3 is not well-predicted by the Lewis structure and we'll see more about this in Section 3.1.4.)
- **More than eight electrons (hypervalency)**: This is a case where an element has more than eight electrons in its valence shell. It is common for larger atoms ($n \geq 3$), and it is discussed further in Section 3.1.2.

Pitfall alert! There are different rules for counting electrons depending on the purpose of the counting. These are the rules for counting for "octets". The rules for counting for calculation of an atom's formal charge are different and are described in Section 3.1.3. When an atom is part of a molecule, all electrons that are associated with the atom are counted as contributing to the atom's valence. This includes electrons that are lone pairs on the atoms, and *all* electrons that are shared in bonds. If four electrons are shared between two atoms, it is a double bond. If six electrons are shared between atoms, it is a triple bond.

Electrons in valence (octet) = total unbonded electrons on the atom + total bonded electrons (2 electrons per bond)

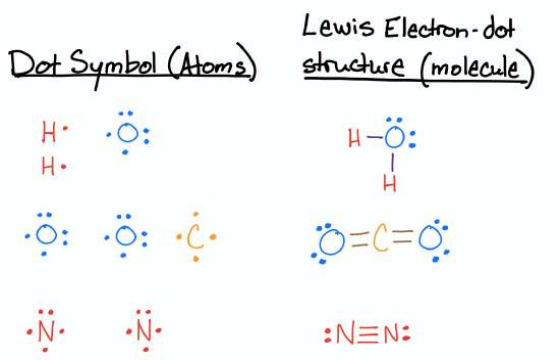
Even if you're an old pro at drawing Lewis structures, it's a good idea to polish up. Please complete the practice exercises below.

Problems

Exercise 3.1.1

Draw the Lewis structures for H_2O, CO_2, and N_2.

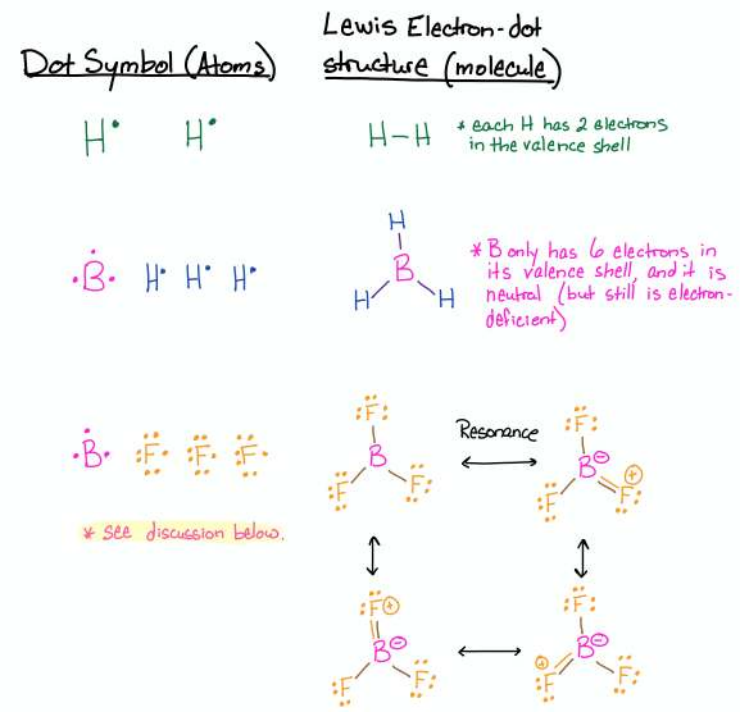
Answer



Exercise 3.1.2

Draw the Lewis structures for H_2, BH_3 and BF_3.

Answer



These three examples include atoms that have less than eight electrons in their valence shell. In the case of H, it is satisfied with only two electrons in its valence, as was discussed earlier in this section. The case of BH_3 was also discussed above. In the Lewis structure of BH_3, the boron can only have six electrons in its octet and it is neutral in charge. The boron is electron deficient even though it has neutral charge.

The case of BF_3 deserves a discussion: If you are unfamiliar with resonance and formal charge, see Sections 3.1.1 (Resonance) and 3.1.3 (Formal Charge) first and come back to this afterward. You might have drawn the BF_3 structure similar to the one that is drawn for BH_3, where boron has three bonds and only six electrons in its valence shell. If you did that, then you are correct; but if you only gave this structure, then your answer is not complete. There are three other correct

ways to draw the structure. Since F has lone pairs of electrons, other valid Lewis structures would each have a double bond to one of the fluorines (three total). All of these structures are called resonance structures, and based on the four of them, we could predict that BF_3 would have B-F bonds that have some double-bond character. If fact, this is the case for BF_3; it has bond lengths that are shorter than single bonds, but longer than double bonds. Read more about it on its Wikipedia page here (click).

Outside Links

- en.Wikipedia.org/wiki/Lewis_structures
- http://www.ausetute.com.au/lewisstr.html
- cost.georgiasouthern.edu/chem...cule/lewis.htm

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3.1.1: Resonance

Resonance structures are a set of two or more Lewis Structures that collectively describe the electronic bonding of a single polyatomic species including fractional bonds and fractional charges. Resonance structures are capable of describing delocalized electrons that cannot be expressed by a single Lewis formula with an integral number of covalent bonds.

Sometimes one Lewis Structure is not Enough

Sometimes, even when formal charges are considered, the bonding in some molecules or ions cannot be described by a single Lewis structure. Resonance is a way of describing delocalized electrons within certain molecules or polyatomic ions where the bonding cannot be expressed by a single Lewis formula. A molecule or ion with such delocalized electrons is represented by several contributing structures (also called resonance structures or canonical forms). Such is the case for ozone ($\mathbf{O_3}$), an allotrope of oxygen with a V-shaped structure and an O–O–O angle of 117.5°.

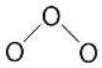
Ozone (O_3)

1. We know that ozone has a V-shaped structure, so one O atom is central:



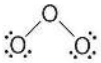
2. Each O atom has 6 valence electrons, for a total of 18 valence electrons.

3. Assigning one bonding pair of electrons to each oxygen–oxygen bond gives



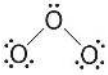
with 14 electrons left over.

4. If we place three lone pairs of electrons on each terminal oxygen, we obtain

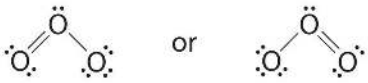


and have 2 electrons left over.

5. At this point, both terminal oxygen atoms have octets of electrons. We therefore place the last 2 electrons on the central atom:

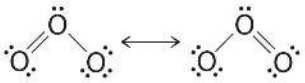


6. The central oxygen has only 6 electrons. We must convert one lone pair on a terminal oxygen atom to a bonding pair of electrons —but which one? Depending on which one we choose, we obtain either



Which is correct? In fact, neither is correct. Both predict one O–O single bond and one O=O double bond. As you will learn, if the bonds were of different types (one single and one double, for example), they would have different lengths. It turns out, however, that both O–O bond distances are identical, 127.2 pm, which is shorter than a typical O–O single bond (148 pm) and longer than the O=O double bond in O_2 (120.7 pm).

Equivalent Lewis dot structures, such as those of ozone, are called **resonance structures**. The position of the *atoms* is the same in the various resonance structures of a compound, but the position of the *electrons* is different. Double-headed arrows link the different resonance structures of a compound:



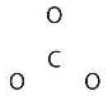
The double-headed arrow indicates that the actual electronic structure is an *average* of those shown, not that the molecule oscillates between the two structures.

> *When it is possible to write more than one equivalent resonance structure for a molecule or ion, the actual structure is the average of the resonance structures.*

The Carbonate (CO_3^{2-}) Ion

Like ozone, the electronic structure of the carbonate ion cannot be described by a single Lewis electron structure. Unlike O_3, though, the actual structure of CO_3^{2-} is an average of *three* resonance structures.

1. Because carbon is the least electronegative element, we place it in the central position:



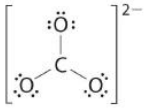
The three oxygens are drawn in the shape of a triangle with the carbon at the center of the triangle.

2. Carbon has 4 valence electrons, each oxygen has 6 valence electrons, and there are 2 more for the −2 charge. This gives 4 + (3 × 6) + 2 = 24 valence electrons.

3. Six electrons are used to form three bonding pairs between the oxygen atoms and the carbon:



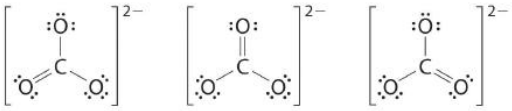
4. We divide the remaining 18 electrons equally among the three oxygen atoms by placing three lone pairs on each and indicating the −2 charge:



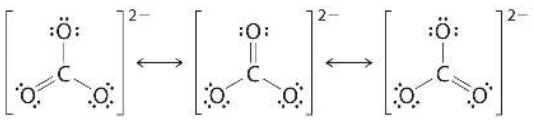
The Lewis dot structure has a central carbon that is bonded to 3 oxygens. Each oxygen has 3 lone pairs. The molecule is inside square brackets and has a charge of minus 2.

5. No electrons are left for the central atom.

6. At this point, the carbon atom has only 6 valence electrons, so we must take one lone pair from an oxygen and use it to form a carbon–oxygen double bond. In this case, however, there are *three* possible choices:



As with ozone, none of these structures describes the bonding exactly. Each predicts one carbon–oxygen double bond and two carbon–oxygen single bonds, but experimentally all C–O bond lengths are identical. We can write resonance structures (in this case, three of them) for the carbonate ion:



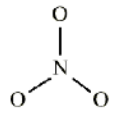
The resonance structure includes all three Lewis dot structures with double headed arrows between them.

The actual structure is an average of these three resonance structures.

The Nitrate (NO_3^-) ion

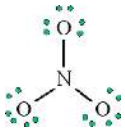
1. Count up the valence electrons: (1*5) + (3*6) + 1(ion) = **24** electrons

2. Draw the bond connectivities:

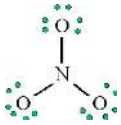


The three oxygens are drawn in the shape of a triangle with the nitrogen at the center of the triangle.

3. Add octet electrons to the atoms bonded to the center atom:

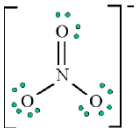


4. Place any leftover electrons (24-24 = **0**) on the center atom:



5. Does the central atom have an octet?

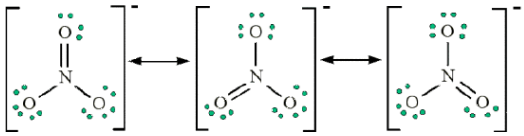
- **NO**, it has 6 electrons
- Add a multiple bond (first try a double bond) to see if the central atom can achieve an octet:



A double bond is added between one oxygen and the central nitrogen. The molecule has a negative charge.

6. Does the central atom have an octet?

- YES
- Are there possible resonance structures? YES



Note: We would expect that the bond lengths in the $\mathbf{NO_3^-}$ ion to be somewhat shorter than a single bond.



Example 3.1.1.1: Benzene

Benzene is a common organic solvent that was previously used in gasoline; it is no longer used for this purpose, however, because it is now known to be a carcinogen. The benzene molecule (C_6H_6) consists of a regular hexagon of carbon atoms, each of which is also bonded to a hydrogen atom. Use resonance structures to describe the bonding in benzene.

Given: molecular formula and molecular geometry

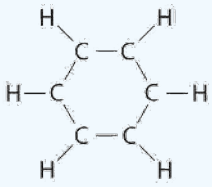
Asked for: resonance structures

Strategy:

A. Draw a structure for benzene illustrating the bonded atoms. Then calculate the number of valence electrons used in this drawing.
B. Subtract this number from the total number of valence electrons in benzene and then locate the remaining electrons such that each atom in the structure reaches an octet.
C. Draw the resonance structures for benzene.

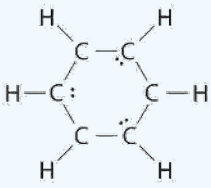
Solution:

A Each hydrogen atom contributes 1 valence electron, and each carbon atom contributes 4 valence electrons, for a total of (6 × 1) + (6 × 4) = 30 valence electrons. If we place a single bonding electron pair between each pair of carbon atoms and between each carbon and a hydrogen atom, we obtain the following:



Each carbon atom in this structure has only 6 electrons and has a formal charge of +1, but we have used only 24 of the 30 valence electrons.

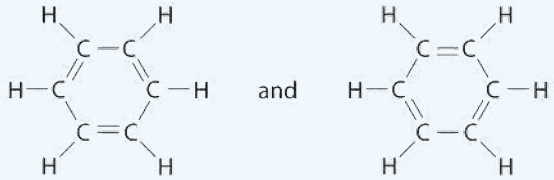
B If the 6 remaining electrons are uniformly distributed pairwise on alternate carbon atoms, we obtain the following:



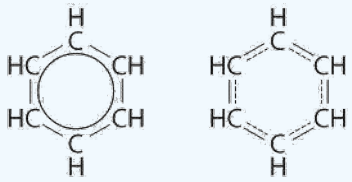
Three carbon atoms now have an octet configuration and a formal charge of −1, while three carbon atoms have only 6 electrons and a formal charge of +1. We can convert each lone pair to a bonding electron pair, which gives each atom an octet of

electrons and a formal charge of 0, by making three C=C double bonds.

C There are, however, two ways to do this:



Each structure has alternating double and single bonds, but experimentation shows that each carbon–carbon bond in benzene is identical, with bond lengths (139.9 pm) intermediate between those typically found for a C–C single bond (154 pm) and a C=C double bond (134 pm). We can describe the bonding in benzene using the two resonance structures, but the actual electronic structure is an average of the two. The existence of multiple resonance structures for aromatic hydrocarbons like benzene is often indicated by drawing either a circle or dashed lines inside the hexagon:



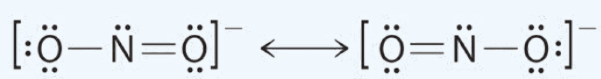
Benzene

Problems

? Exercise 3.1.1.1: Nitrite Ion

The sodium salt of nitrite is used to relieve muscle spasms. Draw two resonance structures for the nitrite ion (NO_2^-).

Answer



There is a double bond between one oxygen and the nitrogen, It can be found on the left oxygen or the right oxygen.

Resonance structures are particularly common in oxoanions of the *p*-block elements, such as sulfate and phosphate, and in aromatic hydrocarbons, such as benzene and naphthalene.

Warning

If several reasonable resonance forms for a molecule exists, the "actual electronic structure" of the molecule will probably be intermediate between all the forms that you can draw. The classic example is benzene in Example 3.1.1.1. One would expect the double bonds to be shorter than the single bonds, but if one overlays the two structures, you see that one structure has a single bond where the other structure has a double bond. The best measurements that we can make of benzene do not show two bond lengths - instead, they show that the bond length is intermediate between the two resonance structures.

Resonance structures is a mechanism that allows us to use all of the possible resonance structures to try to predict what the actual form of the molecule would be. Single bonds, double bonds, triple bonds, +1 charges, -1 charges, these are our limitations in explaining the structures, and the true forms can be in between - a carbon-carbon bond could be mostly single bond with a little bit of double bond character and a partial negative charge, for example.

Summary

Some molecules have two or more chemically equivalent Lewis electron structures, called resonance structures. Resonance is a mental exercise and method within the Valence Bond Theory of bonding that describes the delocalization of electrons within

molecules. These structures are written with a **double-headed arrow** between them, indicating that none of the Lewis structures accurately describes the bonding but that the actual structure is an average of the individual resonance structures. 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.

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- **8.6: Resonance Structures** is licensed CC BY-NC-SA 3.0.

3.1.2: Breaking the octet rule with higher electron counts (hypervalent atoms)

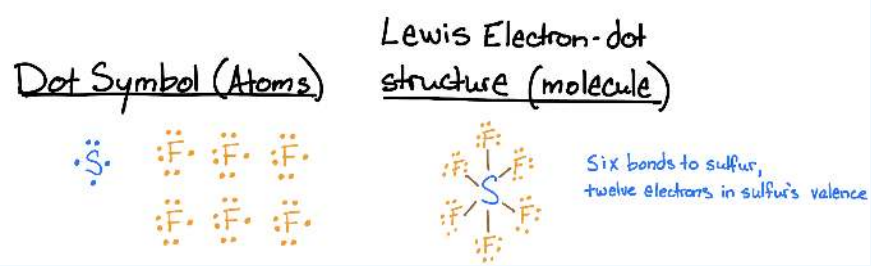
The octet rule applies well to atoms in the second row of the periodic table, where a full valence shell includes eight electrons with an electron configuration of s^2p^6. Even elements in the third and fourth row are known to follow this rule *sometimes*, but not always. In larger atoms, where $n \geq 3$ the valence shell contains additional subshells: the $d, f, g...$ subshells. Therefore, atoms with $n \geq 3$ can have higher valence shell counts by "expanding" into these additional subshells. When atoms contain more than eight electrons in their valence shell, they are said to be **hypervalent**. Hypervalency allows atoms with $n \geq 3$ to break the octet rule by having more than eight electrons. This also means they can have five or more bonds; something that is nearly unheard of for atoms with $n \leq 2$. Complete the exercises below to see examples of molecules containing hypervalent atoms.

? Exercise 3.1.2.1

Draw the Lewis structures for sulfur hexafluoride (SF_6).

Answer

Each fluorine atom has one valence electron and will make one bond each. The sulfur has six valence electrons, and must make six bonds to form a molecule with the six fluorine atoms. The molecular structure has six bonds to sulfur, with twelve valence electrons. The sulfur is hypervalent.

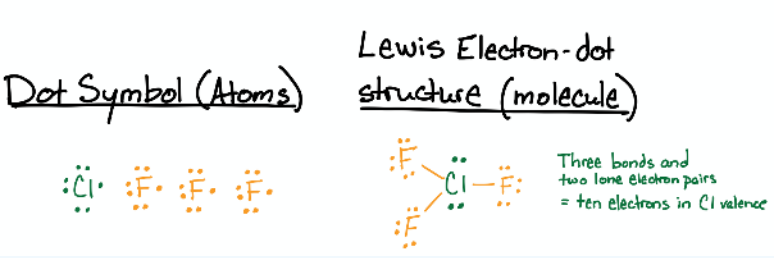


? Exercise 3.1.2.2

Draw the Lewis structure for chlorine trifluoride (ClF_3.

Answer

All atoms are halogens and each has seven valence electrons. Chlorine is capable of hypervalency because it is in the third row of the periodic table; however fluorine cannot have more than eight valence electrons in its valence because it is in the second row. The structure has the three fluorine atoms bonded to a central chlorine atom. The chlorine has a valence of ten electrons due to its three bonds and two lone pairs.



Is hypervalency real? Not exactly. Hypervalency is a concept associated with hybrid orbital theory and Lewis theory. It's useful for some simple things, like predicting how atoms are connected and predicting molecular shape. But the idea that the d-orbitals are involved in bonding isn't accurate according to wave mechanics.

For main group molecules, chemists (like Pauling) thought a long time ago that hypervalence is due to expanded s^2p^6 octets. The consensus is now clear that d orbitals are NOT involved in bonding in molecules like SF_6 any more than they are in SF_4 and SF_2. In all three cases, there is a small and roughly identical participation of d-orbitals in the wavefunctions. This has been established in both MO and VB theory. However, using hybrid orbitals with d-orbital contributions equips us with a language which can pragmatically describe the geometries of highly coordinated substances.

While hybrid orbitals are a powerful tool to describe the geometries and shape of molecules and metal complexes, in "real" molecules their significance may be debated. Often a more realistic molecular orbitals approach is needed. However, from an epistemologically simple point of view, bonding theories can only be judged by their predictions. To the extent that hybridization can explain the shapes of PF_5 and SF_6, valence bond theory is a perfectly good theory. To the extent that if you write out the valence bond wavefunction using hybridized orbitals and calculate energies and other properties à la Pauling (i.e., ionization energy and electron affinities) and find them to be off from experimental results (by tens of kcals/mol), then valence bond theory is not accurate.

> *Bonding theories can only be judged by their predictions.*

A simple explanation that can be given is that molecular wavefunctions constructed out of hybridized atomic orbitals are accurate enough to predict some things, but not others. Predictions of any theory must be compared with empirical evidence to assess when they work and when they fail. When a theory gives the wrong answer, at least one assumption must not hold. In this case, the valence bond wavefunction is not accurate enough to capture some important features of a system's electronic structure. It may not be the most intellectually satisfying answer, but to say more would result in a much more complicated answer and certainly far beyond the level reasonably expected from general chemistry discussions.

3.1.2: Breaking the octet rule with higher electron counts (hypervalent atoms) is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Kathryn A. Newton, Northern Michigan University.

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3.1.3: Formal Charge

The formal charge of an atom in a molecule is the *hypothetical* charge the atom would have if we could redistribute the electrons in the bonds evenly between the atoms. Another way of saying this is that formal charge results when we take the number of valence electrons of a neutral atom, subtract the nonbonding electrons, and then subtract the number of bonds connected to that atom in the Lewis structure.

Calculating Formal Charges

We calculate the formal charge of an atom in a molecule or polyatomic ions as follows:

Formal Charge = (valence electrons of the "free" element) - (unshared electrons) - 1/2 (bonding electrons).

Alternatively:

Formal Charge = (valence electrons of the "free" element) - (unshared electrons) - (bonds).

We can double-check formal charge calculations by determining the sum of the formal charges for the whole structure. The sum of the formal charges of all atoms in a molecule must be zero; the sum of the formal charges in an ion should equal the charge of the ion.

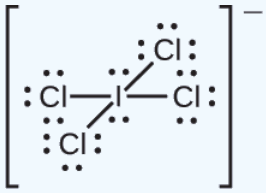
We must remember that the formal charge calculated for an atom is not the *actual* charge of the atom in the molecule. Formal charge is only a useful bookkeeping procedure; it does not indicate the presence of actual charges.

Example 3.1.3.1: ICl_4^-

Assign formal charges to each atom in the interhalogen ion $\mathbf{ICl_4^-}$.

Solution

We divide the bonding electron pairs equally for all **I–Cl** bonds:



We assign lone pairs of electrons to their atoms. Each **Cl** atom now has seven electrons assigned to it, and the I atom has eight.

Subtract this number from the number of valence electrons for the neutral atom:

- I: 7 – 8 = –1
- Cl: 7 – 7 = 0

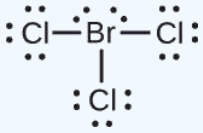
The sum of the formal charges of all the atoms equals –1, which is identical to the charge of the ion (–1).

Example 3.1.3.2: $BrCl_3$

Assign formal charges to each atom in the interhalogen molecule $\mathbf{BrCl_3}$.

Solution

Assign one of the electrons in each Br–Cl bond to the Br atom and one to the Cl atom in that bond:



Assign the lone pairs to their atom. Now each Cl atom has seven electrons and the Br atom has seven electrons.

Subtract this number from the number of valence electrons for the neutral atom. This gives the formal charge:

- Br: 7 – 7 = 0
- Cl: 7 – 7 = 0

All atoms in $BrCl_3$ have a formal charge of zero, and the sum of the formal charges totals zero, as it must in a neutral molecule.

Problems

Exercise 3.1.3.1

Calculate the formal charge for each atom in the carbon monoxide molecule:



Answer

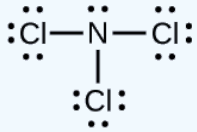
C −1, O +1

Exercise 3.1.3.2

Determine the formal charge for each atom in NCl_3.

Answer

N: 0; all three Cl atoms: 0



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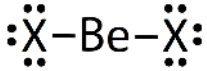
- **7.5: Formal Charges and Resonance** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

3.1.4: Lewis Fails to Predict Unusual Cases - Boron and Beryllium

Two notable cases where Lewis theory fails to predict structure are the cases of beryllium (**Be**) and boron (**B**). These two atoms are in period 2 ($n = 2$) of the periodic table and their atoms have the valence electron configurations of $2s^2$ and $2s^2 2p^1$, respectively.

Beryllium

The Lewis electron dot structures are shown below for BeX_2, where **X** is one of the halogens, **F** or **Cl**.



Each of the structures above would predict a linear geometry for the BeX_2 molecule. Together the three resonance structures suggest partial double-bond character in the Be-X bond, which results in an intermediate bond length between a single and double bond.

There are issues with each of these resonance structures. The structure on the left would predict only four electrons around **Be**; thus, the atom does not fulfill the octet rule. The structure on the left suggests multiple bonds for the halogen (**X**) and high separation of charge with formal charge on each atom. The structure in the middle is a mix of these problems. None of these situations is ideal according to Lewis theory. Further, experimental data is not consistent with any of these structures or their resonance hybrid (except in the case of $BeCl_2$ at very high temperatures).

It turns out that the monomer of BeX_2 does exist, but only at very high temperatures and low pressures. Even under extreme conditions, the monomer is not particularly stable due to the electron deficiency around **Be**.

BeF_2

At ambient temperature and pressure, BeF_2 is a solid that looks similar to quartz (Figure **3.1.4.1**) The Be is four-coordinate with tetrahedral geometry; each F is two-coordinate and the Be-F bond length is 1.54 Å. This structure is possible due to an extended 3-dimensional network in the solid where adjacent BeF_2 units are bonded to one another, as shown in Figure **3.1.4.1**.

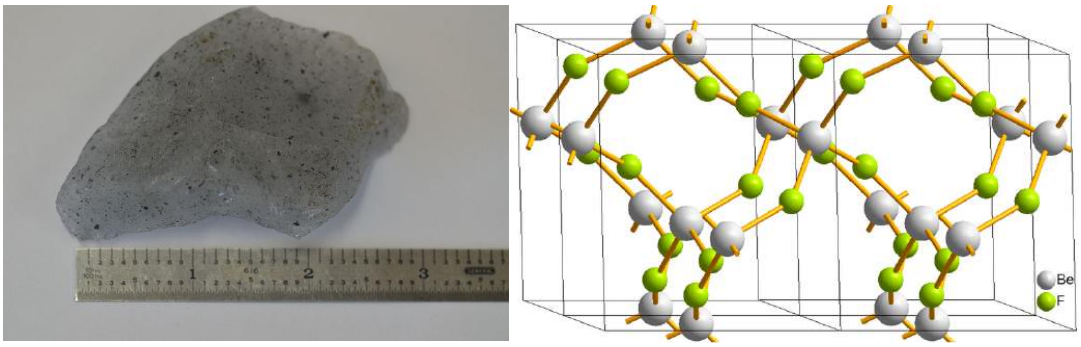


Figure **3.1.4.1**: (left) A nugget of beryllium fluoride obtained from Materion. Black spots are carbon (CC BY-SA 3.0; Bckelleher via Wikipedia). (right) BeF2 structure (CC BY-SA 3.0 Unported; Materialscientist via Wikipedia)

In the liquid phase, BeF_2 has a fluctuating tetrahedral structure where Be and F ions exchange. The vapor phase is reached at temperatures higher than 1000 °C (at ~ 1 atm). In the vapor phase, BeF_2 exists as a monomer with linear geometry and a bond length of 1.43 Å, consistent with a double bond between **Be** and **F**.

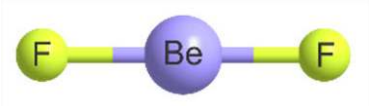


Figure **3.1.4.2**: Geometries of BeF_2. (CC BY; Ibon Alkorta and Anthony C. Legoe via Inorganics)

$BeCl_2$

At ambient temperature and pressure, $BeCl_2$ is a solid. As in BeF_2 described above, $BeCl_2$ has four-coordinate, tetrahedral Be and two-coordinate Cl. In contrast to BeF_2, solid $BeCl_2$ is a 1-dimensional polymer consisting of edge-shared tetrahedral.

In the gas phase, $BeCl_2$ exists as a dimer with two chlorine atoms bridging two Be atoms. In the dimer, the Be atoms are 3-coordinate. Bridging Cl atoms are two-coordinate, while terminal Cl atoms are one-coordinate. At higher temperatures in the vapor phase, the linear monomer also exists.

Boron ($2s^2 2p^1$)

Prediction based on Lewis structures:

Lewis structures of $\mathbf{BH_3}$ and $\mathbf{BF_3}$ were described in Exercise 3.1.2, and are drawn again below for convenience.

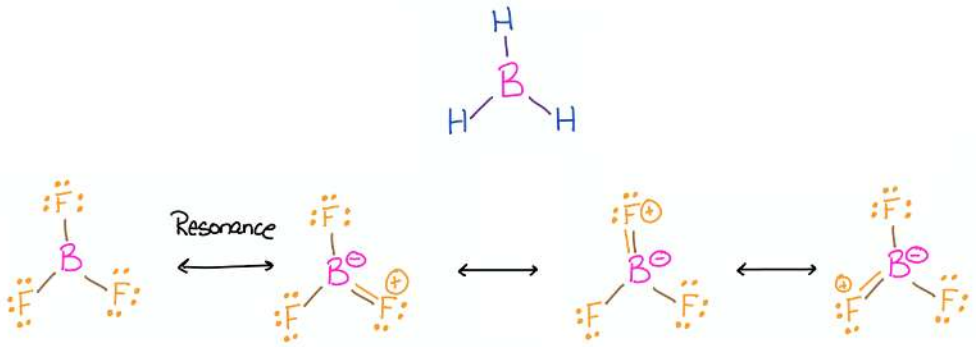


Figure 3.1.4.2: Lewis structures of $\mathbf{BH_3}$ and $\mathbf{BF_3}$. (Kathryn Haas; CC-NC-BY-SA)

Boron trihalides

Boron trihalides, like $\mathbf{BF_3}$, have properties that are largely predicted by Lewis structures and VSEPR theory. The Lewis structure for $\mathbf{BF_3}$ includes several resonance structures. The structure with only single bonds is the most common representation for this molecule because the charge separation shown in the other structures is considered to be unfavorable. The highly polarized B-F bond has a dipole moment that lies opposite to the indicated formal charges shown in the resonance structures with double bonds between boron and fluorine.

The resonance hybrid of $\mathbf{BF_3}$ predicts partial double bond character between boron and fluorine, thus a bond length shorter than a single bond. Using the Lewis structures and VSEPR theory, we would predict a trigonal planar geometry around boron. In fact, the actual structure of $\mathbf{BF_3}$ is a monomer with trigonal planar geometry and with bond length that is shorter than a single bond. The case is similar to structures of other boron trihalides as well.

Boron trihalides are electron deficient at the boron center and react readily with Lewis bases. In other words they are strong Lewis acids (electrophiles).

Boron trihydride (BH_3 is really B_2H_6)

The properties of boron trihydride ($\mathbf{BH_3}$) are not predicted by the simple predictions made through Lewis structures and VSEPR. The monomer, BH_3, is not stable, but when dissolved in the presence of a Lewis base, BH_3 can form a stable acid-base adduct. In its pure form, the compound actually exists as a dimeric gas with a molecular unit of B_2H_6 (try drawing a valid Lewis structure for that!). Its unexpected structure includes two H's that bridge the two boron atoms in 3-center-2-electron bonds. You can read more about B_2H_6 on the Wikipedia page for Diborane(6). The unique bonding observed for boron is described more in Chapter 8 and Chapter 15.

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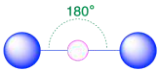
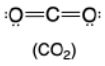
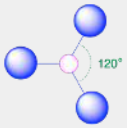
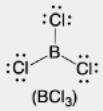
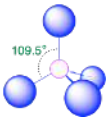
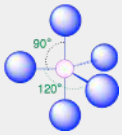
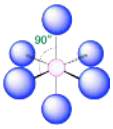
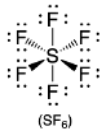
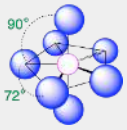
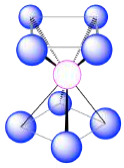
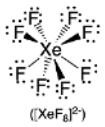
3.2: Valence Shell Electron-Pair Repulsion

Introduction to VSEPR

The **Valence Shell Electron Repulsion (VSEPR)** model can predict the structure of most molecules and polyatomic ions in which the central atom is a nonmetal; it also works for some structures in which the central atom is a metal. VSEPR builds on Lewis electron dot structures (discussed in Section 3.1); Lewis structures alone predict only connectivity while the Lewis structure and VSEPR together can predict the geometry of each atom in a molecule. The main idea of VSEPR theory is that pairs of electrons (in bonds and in lone pairs) repel each other. The pairs of electrons (in bonds and in lone pairs) are called "groups". Because electrons repel each other electrostatically, the most stable arrangement of electron groups (i.e., the one with the lowest energy) is the one that minimizes repulsion. Groups are positioned around the central atom in a way that produces the molecular structure with the lowest energy. In other words, the repulsion between groups around an atom favors a geometry in which the groups are as far apart from each other as possible. Although VSEPR is simplistic because it does not account for the subtleties of orbital interactions that influence molecular shapes, it accurately predicts the three-dimensional structures of a large number of compounds.

We can use the VSEPR model to predict the geometry around the atoms in a polyatomic molecule or ion by focusing on the number of electron pairs (groups) around a *central atom* of interest. Groups include bonded and unbonded electrons; a single bond, a double bond, a triple bond, a lone pair of electrons, or even a single unpaired electron each count as one group. The molecule or polyatomic ion is given an AX_mE_n designation, where **A is the central atom**, **X is a bonded atom**, **E is a nonbonding** valence electron group (usually a lone pair of electrons), and m and n are integers. The number of groups is equal to the sum of m and n. Using this information, we can describe the molecular geometry around a central atom, that is, the arrangement of the *bonded atoms* in a molecule or polyatomic ion. The geometries that are predicted from VSEPR when a central atom has only bonded groups ($n = 0$) are listed below in Table **3.2.1**. The cases where lone pairs contribute to the total groups ($n \geq 1$) are discussed in the next section about lone pair repulsion.

Table 3.2.1. Geometries predicted using VSEPR theory (bonded groups only).

Groups around central atom (m + n)	Geometry Name	Geometry Sketch	Predicted bond Angle	Example
2	linear		180°	
3	trigonal plane		120°	
4	tetrahedron		109.5°	
5	trigonal bipyramid		90° and 120°	
6	octahedron		90°	
7	pentagonal bipyramid		90° and 72°	
8	square antiprism		70.5°, 99.6° and 109.5°	

Practice

VSEPR to predict Molecular Geometry

You can follow these four steps to predict the geometry around an atom using VSEPR:

1. Draw the Lewis electron structure of the molecule or polyatomic ion.
2. For the central atom of interest, assign the AX_mE_n designation and the total number of groups (m+n).
3. Determine the electron group arrangement around the central atom that minimizes repulsions.
4. Describe the molecular geometry.

Use the procedure above to complete the exercises below

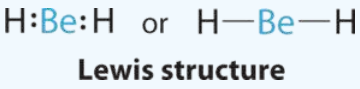
Problems

? Exercise 3.2.1

Predict the geometry around the central atom in BeH_2.

Answer

1. The central atom, beryllium, contributes two valence electrons, and each hydrogen atom contributes one. The Lewis electron structure is



Lewis structure

2. There are two groups around the central atom, and both groups are single bonds. Thus BeH_2 is designated as AX_2.

3. We see from Table **3.2.1** that the arrangement that minimizes repulsions places the groups 180° apart.

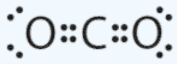
4. From Table **3.2.1** we see that with two bonding pairs, the molecular geometry that minimizes repulsions in BeH_2 is *linear.*

? Exercise 3.2.2

Predict the geometry around the central atom in CO_2.

Answer

1. The central atom, carbon, contributes four valence electrons, and each oxygen atom contributes six. The Lewis electron structure is



2. There are two groups around the central atom, and both groups are double bonds. Thus CO_2 is designated as AX_2.

3. Wee see from the Table **3.2.1** that the arrangement that minimizes repulsions places the groups 180° apart.

4. From Table **3.2.1** we see that with two bonding pairs, the molecular geometry that minimizes repulsions in CO_2 is *linear.*

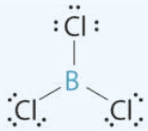
Note: VSEPR only recognizes groups around the *central* atom (the carbon). Thus the lone pairs on the oxygen atoms do not influence the molecular geometry.

? Exercise 3.2.3

Predict the geometry around the central atom in BCl_3 .

Answer

1. The central atom, boron, contributes three valence electrons, and each chlorine atom contributes seven valence electrons. The Lewis electron structure is



Lewis structure

2. There are three groups around the central atom and all are single bonds. The structure is designated as AX_3.

3. To minimize repulsions, the groups are placed 120° apart (Table **3.2.1**).

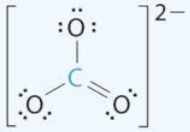
4. From Table **3.2.1** we see that with three bonding pairs around the central atom, the molecular geometry of BCl_3 is *trigonal planar*.

Exercise 3.2.4

Predict the geometry around the central atom in CO_3^{2-}.

Answer

1. The central atom, carbon, has four valence electrons, and each oxygen atom has six valence electrons. The Lewis electron structure of one of three resonance forms is represented as

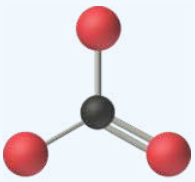


Lewis structure

2. The structure of CO_3^{2-} is a resonance hybrid. It has three identical bonds, each with a bond order of $1\frac{1}{3}$. All electron groups are bonds. With three bonding groups around the central atom, the structure is designated as AX_3.

3. We minimize repulsions by placing the three groups 120° apart (Table **3.2.1**).

4. We see from Table **3.2.1** that the molecular geometry of CO_3^{2-} is trigonal planar with bond angles of 120°.



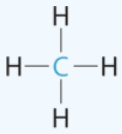
Molecular geometry
(trigonal planar)

Exercise 3.2.5

Predict the geometry around the central atom in CH_4.

Answer

1. The central atom, carbon, contributes four valence electrons, and each hydrogen atom has one valence electron, so the full Lewis electron structure is

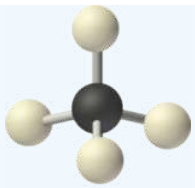


Lewis structure

2. There are four electron groups around the central atom. All electron groups are bonding pairs, so the structure is designated as AX_4.

3. As shown in Table **3.2.1**, repulsions are minimized by placing the groups in the corners of a tetrahedron with bond angles of 109.5°.

4. With four bonding pairs, the molecular geometry of methane is *tetrahedral* (Table **3.2.1**).



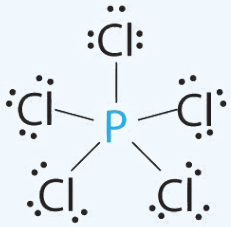
Molecular geometry (tetrahedral)

? Exercise Extra close brace or missing open brace

Predict the geometry around the central atom in PCl_5.

Answer

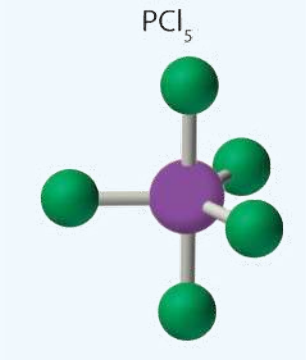
1. Phosphorus has five valence electrons and each chlorine has seven valence electrons, so the Lewis electron structure of PCl_5 is



2. There are five bonding groups around phosphorus, the central atom. All electron groups are bonds, so the structure is designated as AX_5.

3. The structure that minimizes repulsions is a *trigonal bipyramid*, which consists of two trigonal pyramids that share a base (Table **3.2.1**).

4. The molecular geometry of PCl_5 is *trigonal bipyramidal*, as shown below. The molecule has three atoms in a plane in *equatorial* positions and two atoms above and below the plane in *axial* positions. The three equatorial positions are separated by 120° from one another, and the two axial positions are at 90° to the equatorial plane. The axial and equatorial positions are not chemically equivalent.

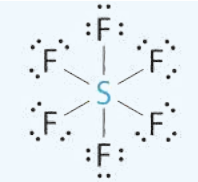


? Exercise 3.2.7

Predict the geometry around the central atom in SF_6.

Answer

1. The central atom, sulfur, contributes six valence electrons, and each fluorine atom has seven valence electrons, so the Lewis electron structure is



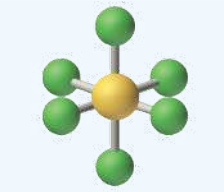
Lewis structure

With an expanded valence, this species is an exception to the octet rule.

2. There are six electron groups around the central atom, each a bonding pair. We see from Figure **3.2.2** that the geometry that minimizes repulsions is *octahedral*.

3. With only bonding pairs, SF_6 is designated as AX_6. All positions are chemically equivalent, so all electronic interactions are equivalent.

4. There are six nuclei, so the molecular geometry of SF_6 is octahedral.



Molecular geometry
(octahedral)

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3.2.1: Lone Pair Repulsion

In the previous section, we saw how to use VSEPR to predict the geometry around a central atom based on the number of groups attached to a central atom. However, our previous discussion was limited to the simple cases where all of the groups were bonded groups (i.e., in the designation AX_mE_n , n=0). When all of the groups are bonds, the geometries can be predicted using information in Table 3.2.1 in the previous section. Now we will consider cases where one or more of these groups are lone pairs.

Lone pairs have stronger repulsive forces than bonded groups.

When one or more of the groups is a lone pair of electrons (non-bonded electrons), the experimentally-observed geometry around an atom is slightly different than in the case where all groups are bonds. The actual bond angles are similar, but not exactly the same, as those predicted based on the *total number of groups* (the "parent" geometry). When there is a mixture of group types (**lone pairs (E)** ***and*** **bonded groups (X)**) there are three different types of angles to consider: bond angles between two bonded atoms (**X-X** angles), angles between a bonded atom and a lone pair (**X-E** angles), and angles between two lone pairs (**E-E** angles). Empirical evidence shows the following trend in the degree of bond angles around atoms with a mixture of group types:

Trend in bond angles:

E-E >**X-E** >**X-X**

Using empirical evidence as a guide, we can predict that lone pairs repel other electron groups more strongly than bonded pairs. The molecular geometry of molecules with lone pairs of electrons is better predicted when we consider that electronic repulsion created by lone pairs is stronger than the repulsion from bonded groups. It is difficult to predict the exact bond angle based on this principle, but we can predict approximate angles, as described and summarized below in Table **3.2.1.1**.

Table **3.2.1.1**: Predictions of molecular geometry and bond angles around atoms with a mixture of bonded (X) and unbonded (E) electron groups.

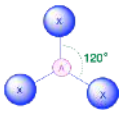
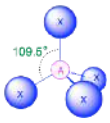
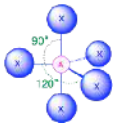
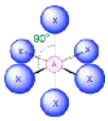
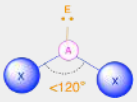
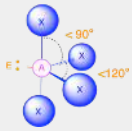
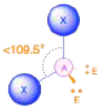
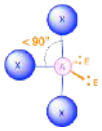
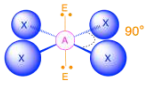
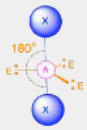
	Electron Groups (m + n)				
	2 (steric number = 2)	**3** (steric number = 3)	**4** (steric number = 4)	**5** (steric number = 5)	**6** (steric number = 6)
Parent Geometry (0 lone pairs) AX_m	 AX_2, linear 180°	 AX_3, trig. plane 120°	 $AX4$, tetrahedron 109.5°	 AX_5, trig. bipyramid 90°, 120°	 AX_6, octahedron 90°
1 lone pair AX_mE_1		 $AX2E_1$, bent <120°	 AX_3E_1, trig. pyramid <109.5°	 AX_4E_1, see-saw <90°, <120°	 AX_5E_1, square pyramid 90°, <90°
2 lone pairs AX_mE_2			 AX_2E_2, bent <109.5°	 AX_3E_2, T-shape <90°	 AX_4E_2, square plane 90°
3 lone pairs AX_mE_3				 AX_2E_3, linear 180°	

Table **3.2.1.1** summarizes the geometries and bond angles predicted for nearest-neighbor bonded groups on central atoms with a mixture of lone pairs and bonded groups. The table does not cover all possible situations; it only includes cases where there are two bonded groups in which an X-X angle is measurable between nearest-neighbors. A more detailed description of some selected cases is given below.

Two Electron Groups (m + n = 2)

(Steric number = 2) In the case that there are only two electron groups around a central atom, those groups will lie 180° from one another. This results in a linear molecular geometry with 180° bond angles.

Three Electron Groups (m + n = 3)

(Steric number = 3) In the case that there are three electron groups around a central atom, those groups will lie approximately 120° from one another in space. This results in an electronic geometry that is approximately **trigonal planar**. There are two different molecular geometries that are possible in this category:

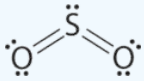
- When all of the electron groups are bonds (m = 3 or AX_3), the molecular geometry is a ***trigonal plane*** with **120°** bond angles.
- When there is one lone pair (m=2, n=1 or AX_2E_1), the molecular geometry is ***bent*** with a bond angle that is slightly **less than 120°**.

Example 3.2.1.1: AX_2E

Predict the geometry and bond angles in SO_2.

Solution

1. The central atom, sulfur, has 6 valence electrons, as does each oxygen atom. With 18 valence electrons, the Lewis electron structure is shown below.



2. There are three electron groups around the central atom: two double bonds and one lone pair. We initially place the groups in a trigonal planar arrangement to minimize repulsions (Table **3.2.1.1**).

3. With two bonding pairs and one lone pair, the structure is designated as AX_2E. This designation has a total of three electron pairs, two X and one E. The lone pair occupies more space around the central atom than a bonding pair (even double bonds!). Bonding pairs and lone pairs repel each other electrostatically in the order BP–BP < LP–BP < LP–LP. In SO_2, we have one BP–BP interaction and two LP–BP interactions.

4. The molecular geometry is described only by the positions of the nuclei, *not* by the positions of the lone pairs. Thus, with two nuclei and one lone pair the shape is *bent*, or *V shaped*, which can be viewed as a trigonal planar arrangement with a missing vertex. The O-S-O bond angle is expected to be *less than* 120° because of the extra space taken up by the lone pair.

Four Electron Groups (m + n = 4)

(Steric number = 4) In the case that there are four electron groups around a central atom, those groups will lie approximately 109.5° from one another in space. This results in an electronic geometry that is approximately **tetrahedral**. There are three different molecular geometries that are possible in this category:

- When all electron groups are bonds (m=4 or AX_4), the molecular geometry is a ***tetrahedron*** with bond angles of **109.5°**.
- When there is one lone pair (m=3, n=1 or AX_3E_1), the molecular geometry is a ***trigonal pyramid*** with bond angles of **slightly less than 109.5°**.
- When there are two lone pairs (m=2, n=2 or AX_2E_2), the molecular geometry is ***bent*** with bond angles of **slightly less than 109.5°**.

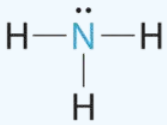
Example 3.2.1.2: AX_3E

Predict the geometry and bond angles in NH_3.

Solution

One of the limitations of Lewis structures is that they depict molecules and ions in only two dimensions. With four electron groups, we must learn to show molecules and ions in three dimensions.

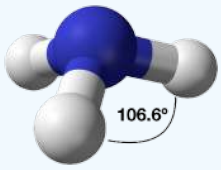
1. In ammonia, the central atom, nitrogen, has five valence electrons and each hydrogen donates one valence electron, producing the Lewis electron structure



Lewis structure

2. There are four electron groups around nitrogen, three bonding pairs and one lone pair. Repulsions are minimized by directing each hydrogen atom and the lone pair to the corners of a tetrahedron.

3. With three bonding pairs and one lone pair, the structure is designated as AX_3E. This designation has a total of four electron pairs, three X and one E. We expect the LP–BP interactions to cause the bonding pair angles to deviate significantly from the angles of a perfect tetrahedron.



The Difference in the Space Occupied by a Lone Pair of Electrons and by a Bonding Pair

As with SO_2, this composite model of electron distribution and negative electrostatic potential in ammonia shows that a lone pair of electrons occupies a larger region of space around the nitrogen atom than does a bonding pair of electrons that is shared with a hydrogen atom.

4. There are three nuclei and one lone pair, so the molecular geometry is *trigonal pyramidal*. In essence, this is a tetrahedron with a vertex missing. However, the H–N–H bond angles are less than the ideal angle of 109.5° because of LP–BP repulsion. The bond angles in ammonia are 106.6°.

Example 3.2.1.3: AX_2E_2

Predict the geometry and in H_2O.

Solution

1. Oxygen has six valence electrons and each hydrogen has one valence electron, producing the Lewis electron structure



2. There are four groups around the central oxygen atom, two bonding pairs and two lone pairs. Repulsions are minimized by directing the bonding pairs and the lone pairs to the corners of a tetrahedron.

3. With two bonding pairs and two lone pairs, the structure is designated as AX_2E_2 with a total of four electron pairs. Due to LP–LP, LP–BP, and BP–BP interactions, we expect a significant deviation from idealized tetrahedral angles.

4. With two hydrogen atoms and two lone pairs of electrons, the structure has significant lone pair interactions. There are two nuclei about the central atom, so the molecular shape is *bent*, or *V shaped*, with an H–O–H angle that is even less than the H–N–H angles in NH_3, as we would expect because of the presence of two lone pairs of electrons on the central atom rather than one. This molecular shape is essentially a tetrahedron with two missing vertices.

Five Electron Groups (m + n = 5)

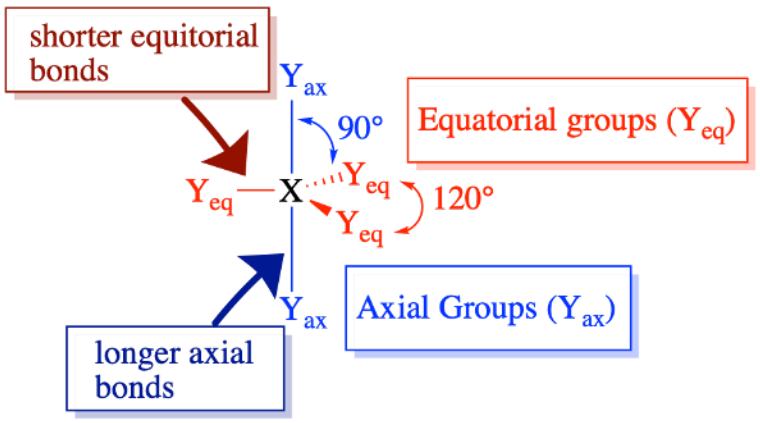


Figure: Trigonal pyramidal molecules (steric number 5) possess different bond angles and lengths for axial (ax) and equatorial (eq) pendant atoms. (CC-BY-NC-SA; Kathryn Haas).

(Steric number = 5) In the case that there are five electron groups around a central atom, there are two different types of positions around the central atom: equatorial positions and axial positions. The three equatorial ligands are 120° from one another and are

90° from each of the two axial ligands. The axial positions have three adjacent groups oriented 90° away in space. Axial groups are thus more crowded than the equatorial positions with only two adjacent groups at 90°. The crowding of axial positions results in slight differences in bond distances; crowded axial groups have longer bonds than the less crowded equatorial groups. Lone pairs of electrons generally prefer to occupy equatorial positions rather than axial positions. The justification for this preference, according to VSEPR theory, is that the lone electron pairs are more repulsive than bonding electron pairs, and thus the lone pairs prefer the less crowded equatorial positions.

The arrangement of five groups around a central atom results in a **trigonal bipyramidal** electronic geometry. There are four different molecular geometries that are possible in this category, depending upon the number of bonded groups and lone pairs of electrons:

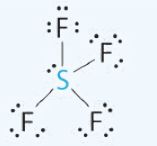
- When all electron groups are bonds (m=5 or AX_5), the molecular geometry is a ***trigonal bipyramid*** with bond angles of **120°** and **90°** between adjacent ligands.
- When there is one lone pair (m=4, n=1 or AX_4E_1), the lone pair occupies one of the equatorial positions. The molecular geometry is called a ***see saw*** with bond angles of **slightly less than 120°** and **slightly less than 90°**.
- When there are two lone pairs (m=3, n=2 or AX_3E_2), each lone pair occupies one of the three equatorial positions. The molecular geometry is ***T-shaped*** with bond angles of **slightly less than 120°** and **slightly less than 90°**.
- When there are three lone pairs (m=1, n=3 or AX_3E_2), the lone pairs occupy the three equatorial positions. The molecular geometry is ***linear*** with bond angles of **180°**.

Example 3.2.1.4: AX_4E

Predict the geometry and bond angles in SF_4.

Solution

1. The sulfur atom has six valence electrons and each fluorine has seven valence electrons, so the Lewis electron structure is



Lewis structure

With an expanded valence, this species is an exception to the octet rule.

2. There are five groups around sulfur, four bonding pairs and one lone pair. With five electron groups, the lowest energy arrangement is a trigonal bipyramid.

3. We designate SF_4 as AX_4E; it has a total of five electron pairs. However, because the axial and equatorial positions are not chemically equivalent, where do we place the lone pair? If we place the lone pair in the axial position, we have three LP–BP repulsions at 90°. If we place it in the equatorial position, we have two 90° LP–BP repulsions at 90°. With fewer 90° LP–BP repulsions, we can predict that the structure with the lone pair of electrons in the *equatorial position is more stable than the one with the lone pair in the axial position*. We also expect a deviation from ideal geometry because a lone pair of electrons occupies more space than a bonding pair.

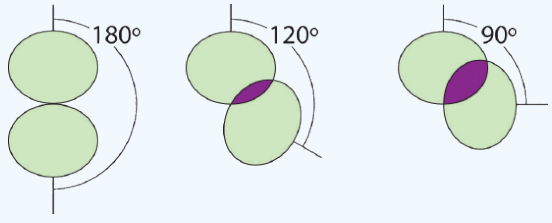
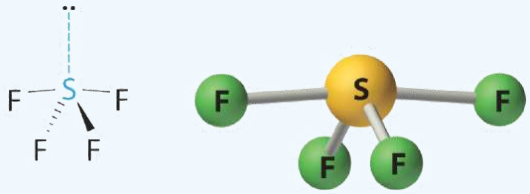


Illustration of the Area Shared by Two Electron Pairs versus the Angle between Them

At 90°, the two electron pairs share a relatively large region of space, which leads to strong repulsive electron–electron interactions.

4. With four nuclei and one lone pair of electrons, the molecular structure is based on a trigonal bipyramid with a missing equatorial vertex; it is described as a *seesaw*. The F_{axial}–S–F_{axial} angle is 173° rather than 180° because of the lone pair of electrons in the equatorial plane.



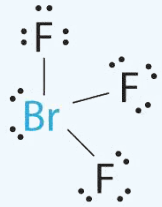
Molecular geometry (seesaw)

Example 3.2.1.5: AX_3E_2

Predict the geometry and bond angles in BrF_3.

Solution

1. The bromine atom has seven valence electrons, and each fluorine has seven valence electrons, so the Lewis electron structure is

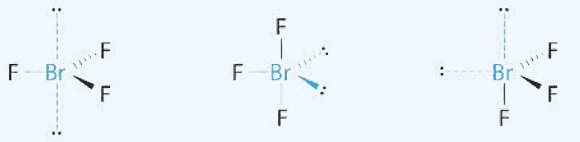


Lewis structure

Once again, we have a compound that is an exception to the octet rule.

2. There are five groups around the central atom, three bonding pairs and two lone pairs. We again direct the groups toward the vertices of a trigonal bipyramid.

3. With three bonding pairs and two lone pairs, the structural designation is AX_3E_2 with a total of five electron pairs. Because the axial and equatorial positions are not equivalent, we must decide how to arrange the groups to minimize repulsions. If we place both lone pairs in the axial positions, we have six LP–BP repulsions at 90°. If both are in the equatorial positions, we have four LP–BP repulsions at 90°. If one lone pair is axial and the other equatorial, we have one LP–LP repulsion at 90° and three LP–BP repulsions at 90°:



	Lone pairs axial (a)	Lone pairs equatorial (b)	Lone pairs axial and equatorial (c)
Interactions			
90° LP–LP	0	0	1
90° LP–BP	6	4	3

Structure (c) can be eliminated because it has a LP–LP interaction at 90°. Structure (b), with fewer LP–BP repulsions at 90° than (a), is lower in energy. However, we predict a deviation in bond angles because of the presence of the two lone pairs of electrons.

4. The three nuclei in BrF_3 determine its molecular structure, which is described as *T shaped*. This is essentially a trigonal bipyramid that is missing two equatorial vertices. The F_{axial}–Br–F_{axial} angle is 172°, less than 180° because of LP–BP repulsions.

Because lone pairs occupy more space around the central atom than bonding pairs, electrostatic repulsions are more important for lone pairs than for bonding pairs.

Example 3.2.1.6: AX_2E_3

Predict the geometry and bond angles in I_3^-.

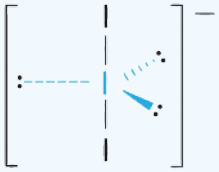
Solution

1. Each iodine atom contributes seven electrons and the negative charge one, so the Lewis electron structure is



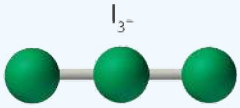
2. There are five electron groups about the central atom in I_3^-, two bonding pairs and three lone pairs. To minimize repulsions, the groups are directed to the corners of a trigonal bipyramid.

3. With two bonding pairs and three lone pairs, I_3^- has a total of five electron pairs and is designated as AX_2E_3. We must now decide how to arrange the lone pairs of electrons in a trigonal bipyramid in a way that minimizes repulsions. Placing them in the equatorial positions eliminates 90° LP–LP repulsions and minimizes the number of 90° LP–BP repulsions.



The three lone pairs of electrons have equivalent interactions with the three iodine atoms, so we do not expect any deviations in bonding angles.

4. With three nuclei and three lone pairs of electrons, the molecular geometry of I_3^- is linear. This can be described as a trigonal bipyramid with three equatorial vertices missing. The ion has an I–I–I angle of 180°, as expected.



Six Electron Groups (m + n = 6)

(Steric number = 6) In the case that there are six electron groups around a central atom, the nearest groups will lie approximately 90° from one another in space. This results in an electronic geometry that is approximately **octahedral**. There are three relevant molecular geometries in this category:

- When all electron groups are bonds (m=6 or AX_6), the molecular geometry is an ***octahedron*** with bond angles of **90°** between adjacent bonds.
- When there is one lone pair (m=5, n=1 or AX_5E_1) we now distinguish between the axial and equitorial positions; the lone pair is considered to be in one of the axial positions, while the bond directly opposite of the lone pair is the axial bond. The molecular geometry is a ***square pyramid*** with bond angles of **90°** between adjacent equatorial bonds and **slightly less than 90°** between the axial bond and equatorial groups.
- When there are two lone pairs (m=4, n=2 or AX_4E_2), the lone pairs are opposite of one another and each occupy an axial position. The molecular geometry is ***square planar*** with bond angles of **90°**.

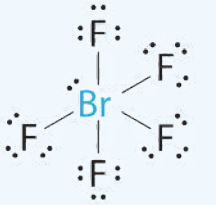
Example 3.2.1.7: AX_5E

Predict the geometry and bond angles in BrF_5.

Solution

AX_5E Molecules: BrF_5

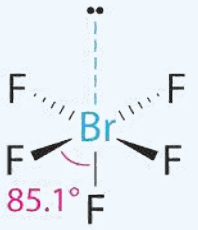
1. The central atom, bromine, has seven valence electrons, as does each fluorine, so the Lewis electron structure is



Lewis structure

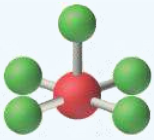
With its expanded valence, this species is an exception to the octet rule.

2. There are six electron groups around the Br, five bonding pairs and one lone pair. Placing five F atoms around Br while minimizing BP–BP and LP–BP repulsions gives the following structure:



3. With five bonding pairs and one lone pair, BrF_5 is designated as AX_5E; it has a total of six electron pairs. The BrF_5 structure has four fluorine atoms in a plane in an equatorial position and one fluorine atom and the lone pair of electrons in the axial positions. We expect all F_{axial}–Br–$F_{equatorial}$ angles to be less than 90° because of the lone pair of electrons, which occupies more space than the bonding electron pairs.

4. With five nuclei surrounding the central atom, the molecular structure is based on an octahedron with a vertex missing. This molecular structure is *square pyramidal*. The F_{axial}–B–$F_{equatorial}$ angles are 85.1°, less than 90° because of LP–BP repulsions.



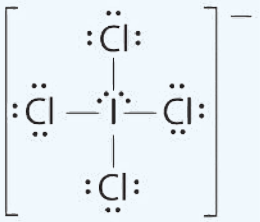
Molecular geometry
(square pyramidal)

Example 3.2.1.8: AX_4E_2

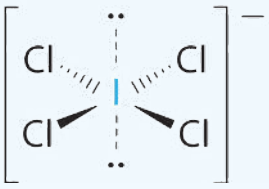
Predict the bond angles in ICl_5^-.

Solution

1. The central atom, iodine, contributes seven electrons. Each chlorine contributes seven, and there is a single negative charge. The Lewis electron structure is

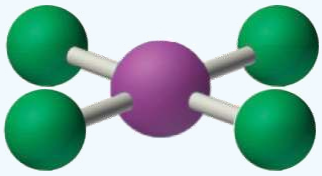


2. There are six electron groups around the central atom, four bonding pairs and two lone pairs. The structure that minimizes LP–LP, LP–BP, and BP–BP repulsions is



3. ICl_4^- is designated as AX_4E_2 and has a total of six electron pairs. Although there are lone pairs of electrons, with four bonding electron pairs in the equatorial plane and the lone pairs of electrons in the axial positions, all LP–BP repulsions are the same. Therefore, we do not expect any deviation in the Cl–I–Cl bond angles.

4. With five nuclei, the ICl4− ion forms a molecular structure that is *square planar*, an octahedron with two opposite vertices missing.



Summary

The arrangement of bonded atoms in a molecule or polyatomic ion is crucial to understanding the chemistry of a molecule, but Lewis electron structures give no information about **molecular geometry**. The **valence-shell electron-pair repulsion (VSEPR) model** allows us to predict which of the possible structures is actually observed in most cases. VSEPR is based on the assumption that pairs of electrons occupy space, and the lowest-energy structure is the one that minimizes repulsions between electron pairs. In the VSEPR model, the molecule or polyatomic ion is given an AX_mE_n designation, where A is the central atom, X is a bonded atom, E is a nonbonding valence electron group (usually a lone pair of electrons), and m and n are integers. Each group around the central atom is designated as a bonding pair (BP) or lone (nonbonding) pair (LP). From the BP and LP interactions we can predict both the relative positions of the atoms and the angles between the bonds, called the **bond angles**. From this we can describe the **molecular geometry**. The VSEPR model can be used to predict the shapes of many molecules and polyatomic ions, but it gives no information about bond lengths and the presence of multiple bonds. A combination of VSEPR and a bonding model, such as Lewis electron structures, is necessary to understand the presence of multiple bonds.

The relationship between the number of electron groups around a central atom, the number of lone pairs of electrons, and the molecular geometry is summarized in Table **3.2.1.1**.

Problems

? Exercise 3.2.1.1

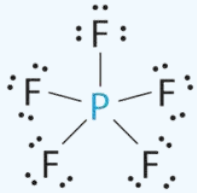
Using the VSEPR model, predict the molecular geometry of PF_5 (a catalyst used in certain organic reactions).

Answer

Strategy:

1. Draw the Lewis electron structure of the molecule or polyatomic ion.
2. Determine the electron group arrangement around the central atom that minimizes repulsions.
3. Assign an AX_mE_n designation; then identify the LP–LP, LP–BP, or BP–BP interactions and predict deviations in bond angles.
4. Describe the molecular geometry.

The central atom, P, has five valence electrons and each fluorine has seven valence electrons, so the Lewis structure of PF_5 is



There are five bonding groups about phosphorus. The structure that minimizes repulsions is a trigonal bipyramid.

All electron groups are bonding pairs, so PF_5 is designated as AX_5. Notice that this gives a total of five electron pairs. With no lone pair repulsions, we do not expect any bond angles to deviate from the ideal.

The PF_5 molecule has five nuclei and no lone pairs of electrons, so its molecular geometry is trigonal bipyramidal.



? Exercise 3.2.1.2

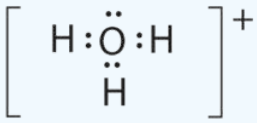
Using the VSEPR model, predict the molecular geometry of H_3O^+ (hydronium ion).

Answer

Strategy:

1. Draw the Lewis electron structure of the molecule or polyatomic ion.
2. Determine the electron group arrangement around the central atom that minimizes repulsions.
3. Assign an AX_mE_n designation; then identify the LP–LP, LP–BP, or BP–BP interactions and predict deviations in bond angles.
4. Describe the molecular geometry.

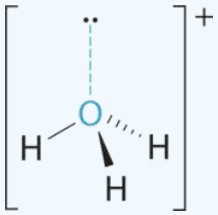
The central atom, O, has six valence electrons, and each H atom contributes one valence electron. Subtracting one electron for the positive charge gives a total of eight valence electrons, so the Lewis electron structure is



There are four electron groups around oxygen, three bonding pairs and one lone pair. Like NH_3, repulsions are minimized by directing each hydrogen atom and the lone pair to the corners of a tetrahedron.

With three bonding pairs and one lone pair, the structure is designated as AX_3E and has a total of four electron pairs (three X and one E). We expect the LP–BP interactions to cause the bonding pair angles to deviate significantly from the angles of a perfect tetrahedron.

There are three nuclei and one lone pair, so the molecular geometry is *trigonal pyramidal*, in essence a tetrahedron missing a vertex. However, the H–O–H bond angles are less than the ideal angle of 109.5° because of LP–BP repulsions:



? Exercise 3.2.1.3

Using the VSEPR model, predict the molecular geometry of XeO_3.

Answer a

trigonal pyramidal

? Exercise 3.2.1.4

Using the VSEPR model, predict the molecular geometry of PF_6^-.

Answer

octahedral

? Exercise 3.2.1.5

Using the VSEPR model, predict the molecular geometry of NO_2^+.

Answer

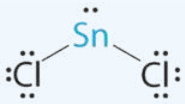
linear

? Exercise 3.2.1.6

Predict the molecular geometry of $SnCl_2$.

Answer

The tin atom donates 4 valence electrons and each chlorine atom donates 7 valence electrons. With 18 valence electrons, the Lewis electron structure is



There are three electron groups around the central atom, two bonding groups and one lone pair of electrons. To minimize repulsions the three groups are initially placed at 120° angles from each other.

From B we designate $SnCl_2$ as AX_2E. It has a total of three electron pairs, two X and one E. Because the lone pair of electrons occupies more space than the bonding pairs, we expect a decrease in the Cl–Sn–Cl bond angle due to increased LP–BP repulsions.

With two nuclei around the central atom and one lone pair of electrons, the molecular geometry of $SnCl_2$ is bent, like SO_2, but with a Cl–Sn–Cl bond angle of 95°. The molecular geometry can be described as a trigonal planar arrangement with one vertex missing.

? Exercise 3.2.1.7

Predict the molecular geometry of XeF_2.

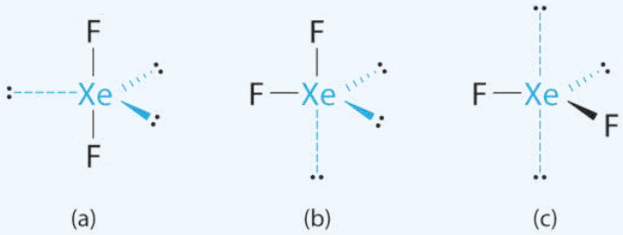
Answer

Xenon contributes eight electrons and each fluorine seven valence electrons, so the Lewis electron structure is



There are five electron groups around the central atom, two bonding pairs and three lone pairs. Repulsions are minimized by placing the groups in the corners of a trigonal bipyramid.

From B, XeF_2 is designated as AX_2E_3 and has a total of five electron pairs (two X and three E). With three lone pairs about the central atom, we can arrange the two F atoms in three possible ways: both F atoms can be axial, one can be axial and one equatorial, or both can be equatorial:



Interactions			
90 LP–LP	0	2	2

The structure with the lowest energy is the one that minimizes LP–LP repulsions. Both (b) and (c) have two 90° LP–LP interactions, whereas structure (a) has none. Thus both F atoms are in the axial positions, like the two iodine atoms around the central iodine in I_3^-. All LP–BP interactions are equivalent, so we do not expect a deviation from an ideal 180° in the F–Xe–F bond angle.

With two nuclei about the central atom, the molecular geometry of XeF_2 is linear. It is a trigonal bipyramid with three missing equatorial vertices.

? Exercise 3.2.1.8

Predict the molecular geometry of SO_3.

Answer

trigonal planar

? Exercise 3.2.1.9

Predict the molecular geometry of XeF_4.

Answer

square planar

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3.2.2: Multiple Bonds

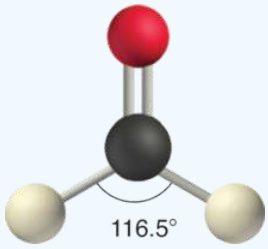
In the previous sections, we saw how to predict the approximate geometry around an atom using VSEPR theory, and we learned that lone pairs of electrons slightly distort bond angles from the "parent" geometry. This page discusses the effect of multiple (double and triple) bonds between bonded atoms.

Double and triple bonds are more repulsive than single bonds

VSEPR theory predicts that double and triple bonds have stronger repulsive forces than single bonds. Like lone pairs of electrons, multiple bonds occupy more space around the central atom than a single bond. The result is that bond angles are slightly distorted compared to the parent geometry. Since a multiple bond has a higher electron density than a single bond, its electrons occupy more space than those of a single bond. Double and triple bonds distort bond angles in a way similar to what lone pairs do. Due to the stronger repulsion, double and triple bonds occupy positions similar to those of lone pairs in groups with 5 and 6 electron groups.

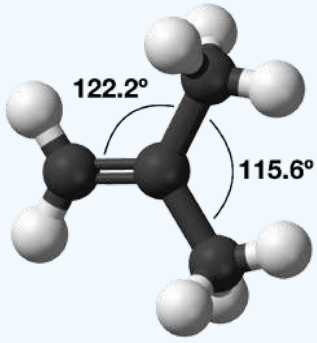
Example 3.2.2.1: CH_2O

In a molecule such as CH_2O (AX_3), whose structure is shown below, the double bond repels the single bonds more strongly than the single bonds repel each other. This causes a deviation from ideal geometry (an H–C–H bond angle of 116.5° rather than 120°).



Example 3.2.2.2: 2-Methylbutene

In the molecule, $CH_2C(CH_3)_2$, the methyl—C—methyl bond angle is 115.6°, which is less than the 120° bond angle that would be expected of the parent geometry. On the other hand, the acetyl—C—methyl bond angle is greater than 120°, with an actual bond angle of 122.2°.



Atoms with both lone pairs and multiple bonds

In general, we expect that a lone pair has slightly greater repulsive force than a multiple bond, and that a multiple bond has slightly greater repulsive force than a single bond. The **order of expected repulsive force** is:

$$\text{lone pair} > \text{double or triple bond} > \text{single bond}$$

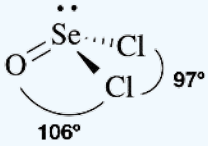
Example 3.2.2.3: $IO_2F_2^-$

With five electron groups, the IO_2F_2 molecule has an approximately trigonal bipyramidal electronic (parent) geometry. The central iodine atom has a single bond to each of the fluorine atoms, a double bond to each oxygen, and a lone pair. The lone pair and the double bonds will occupy more space around iodine than each of the single bonds. Thus, we expect the lone pair and double bonds to occupy equatorial positions around the central iodine. The O=I=O bond angle is 102° (*much* smaller than the 120° angle expected from the parent geometry). This dramatically smaller angle is a result of the increased repulsion between the lone pair and the double bond.



Example 3.2.2.4: $SeOCl_2$

With four electron groups, the $SeOCl_2$ molecule has four electron groups and approximately tetrahedral electronic (parent) geometry. It has both a lone pair and a double bond on the central selenium atom. The two chlorine atoms are singly bonded to selenium, while the oxygen is double bonded. The lone pair is most repulsive, followed by the double bonded oxygen, and then the chlorine bonds. This gives a Cl—Se—Cl bond angle of 97° and a Cl—Se—O bond angle of 106°; both angles are less than the 109.5° angles expected for the ideal tetrahedral geometry.



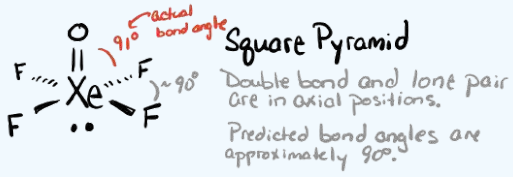
Problems

Exercise 3.2.2.1

Use VSEPR theory to predict the geometries and draw the structures of $XeOF_4$.

Answer

This molecule has six electron groups around the central Xe atom (steric number 6), and thus has an approximately octahdral electronic (parent) geometry. There is a double bond to O and a lone pair, both of which are more strongly repulsive than the single bonds to F. The double bond and lone pair will be directly opposite to each other, designated as axial positions. The result is a square pyramidal molecular geometry. VSEPR theory predicts F—Xe—F bond angles of 90°. As a general rule, lone pairs are slightly more repulsive than multiple bonds, and so we might expect the O—Xe—F bond angles to be <90°; *however in this case the actual O—Xe—F bond angle is observed to be 91°* (you could not have predicted the latter).



Exercise 3.2.2.2

Use VSEPR theory to predict the geometries and draw the structures of NO_2^-.

Answer

This molecule has three electron groups around the central atom: one lone pair and two double bonds to oxygen atoms. This results in an approximately trigonal planar electronic (parent geometry). We expect the lone pair to be slightly more repulsive than double bonds, and so we expect the O—N—O bond angle to be slightly less than 120°. *The actual O—N—O angle is 115°.*

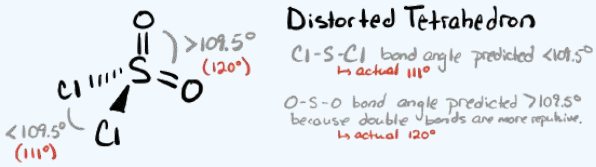


Exercise 3.2.2.3

Use VSEPR theory to predict the geometries and draw the structures of $SOCl_2$.

Answer

This molecule has four electron groups (steric number 4) with an approximately tetrahedral electronic (parent) geometry. Each double bonded oxygen will take up more space around the central S than the single bonded Cl atoms. We should expect the double bonds to repel each other more strongly than they repel each single bond, with the least repulsive interaction being between the two single bonds. The bond angle for Cl—S—Cl is expected to be <109.5° according to VSEPR theory (however, it is actually 111°). We would expect the bond angle for O—S—O to be larger than the angle for Cl—S—Cl and for Cl—S—O. The O—S—O bond angle is predicted to be >109.5° (and the actual bond angle is 120°). The molecular geometry is a distorted tetrahedron.

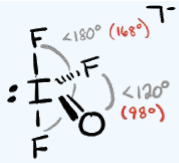


Exercise 3.2.2.4

Use VSEPR theory to predict the geometries and draw the structures of IOF_3^-.

Answer

This molecule has five electron groups (steric number 5) with an approximately trigonal bipyramidal electronic (parent) geometry. There is one lone pair, a double bond to O, and three single bonds to F atoms around the central I atom. The lone pair and double bond are most repulsive, and should occupy the less crowded equatorial positions rather than the more crowded axial positions. This results in a seesaw molecular geometry. With the more repulsive lone pair and the strongest equatorial repulsive force being between the double bond and lone pair, we should expect the $F_{equatorial}$—I—O bond angle to be less than the 120° angle expected for the parent geometry (*it is actually much less, at 98°*). Due to repulsion between the axial F atoms and both the lone pair and double bond, we should expect the F—S—F bond angles to be compressed. The F_{axial}—I—F_{axial} is actually 168°.



Distorted see saw

Lone pair and double bond in equitorial positions.

Predicted bond angles:

F-I-O <120° /actual 98°

F_{axial}-I-F_{axial} <180° /actual 168°

References

- Miessler, G.; Fischer, P.J.; Tarr, D. (2014). Inorganic Chemistry. New Jersey: Prentice-Hall. pp. 55

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3.3: Valence Bond Theory - Hybridization of Atomic Orbitals

The geometrical shape and the inherent physical/chemical properties seen in molecules can be attributed to atomic and molecular orbitals. Features of molecular structure can be explained by taking into consideration (1) how orbitals interact within a single atom to form hybrid atomic orbitals and (2) how atomic orbitals between different atoms interact, giving rise to molecular orbitals. This module will serve as a reminder of the fundamental concepts of bonding as they relate to molecular structure, as well as an investigation into the complexities of hybridized atomic orbitals.

Orbitals and Hybridization

Valence Bond theory describes the formation of a chemical bond in terms of overlapping between atomic orbitals. Atomic orbitals within the same atom are considered to interact and give rise to *hybrid* atomic orbitals. Linear combinations of atomic orbitals yield an equal number of hybrid orbitals in the correct orientations to account for observed bond angles. Molecular orbital theory dictates that the number of hybrid orbitals produced must equal the sum of the orbitals that underwent hybridization.

The degree of orbital hybridization is governed by the number of attachments (ligands) found on a central atom, includign lone pairs. Table **3.3.1** provides a summary of orbital hybridization wherein the number of ligands attached to a central molecule corresponds to the electron geometry.

Table **3.3.1**: Summary of hybridization

Steric Number	Hybridization	Electron Geometry	Bond Angles(s)
2	sp	linear	180°
3	sp^2	trigonal planar	120°
4	sp^3	tetrahedral	109.5°
5	sp^3d	trigonal bipyramidal	120°, 90°
6	sp^3d^2	octahedral	90°

sp Hybridization

Combining an *s* orbital and a *p* orbital yields two *sp* hybrid orbitals pointed in opposite directions. These two *sp* hybrid orbitals generate a bond angle of 180˚, yielding linear electron geometry.

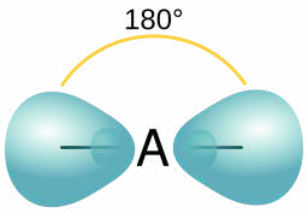


Figure **3.3.1**: Two sp hybrid orbitals oriented at 180˚ angles. (CC-BY-NC-SA; Wikipedia)

sp^2 Hybridization

The sp^2 hybridization is the mixing of one *s* and two *p* atomic orbitals. The combination of these atomic orbitals creates three sp^2 hybrid orbitals that are equal in energy. The hybrid orbitals are higher in energy than the *s* orbital but lower in energy than the *p* orbitals and are closer in energy to the *p* orbitals because they contain more *p* orbital charcter. The sp^2 hybrid orbitals generates a bond angle of 120˚, yielding trigonal planar electron geometry.

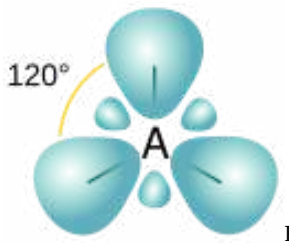


Figure **3.3.2**: Three sp^2 hybrid orbitals oriented at 120˚ angles. (CC-BY-NC-SA; Wikipedia)

sp^3 Hybridization

The sp^3 hybridization is the mixing of one *s* orbital and three *p* orbitals to yield four hybrid sp^3 orbitals that are equal in energy. The hybrid orbitals are higher in energy than the *s* orbital but are lower in energy than the *p* orbitals and are closer in energy to the *p* orbitals due to having more *p* orbital character. The sp^3 hybrid orbitals generate a bond angle of 109.5˚, yielding tetrahedral electron geometry.

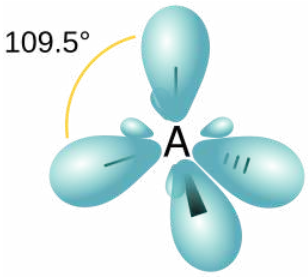


Figure **3.3.3**: Four sp^3 hybrid orbitals oriented at 109.5˚ angles. (CC-BY-NC-SA; Wikipedia)

Other Hybrid Orbitals

Additional hybrid orbitals can conceptualized by including d orbitals into the mix of orbitals. Incorporation of d orbitals can be used to explain hypervalency and molecular geometries for steric numbers 5 and greater.

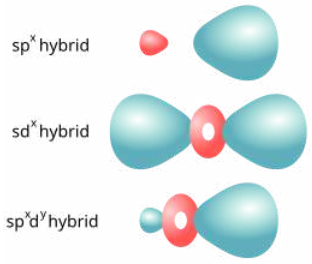


Figure **3.3.4**: General hybrid orbitals that include contributions from d orbitals. (CC-BY-NC-SA; Wikipedia)

Problems

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- Quynh Nhu Nguyen

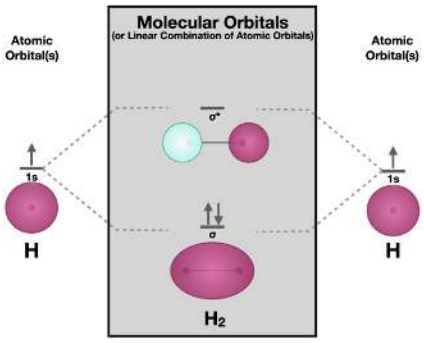
3.3: Valence Bond Theory - Hybridization of Atomic Orbitals is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Kathryn A. Newton, Northern Michigan University.

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SECTION OVERVIEW

3.4: Molecular Orbital Theory

Molecular Orbital Theory



Molecular Orbital (MO) Theory is a sophisticated bonding model. It is generally considered to be more powerful than *Lewis* and *Valence Bond Theories* for predicting molecular properties; however, this power comes at the price of complexity. In its full development, MO Theory requires complex mathematics, though the ideas behind it are simple. Atomic orbitals (AOs) that are localized on individual atoms combine to make molecular orbitals (MOs) that are distributed over the molecule. The simplest example is the molecule dihydrogen (H_2), in which two independent hydrogen 1s orbitals combine to form the σ bonding MO and the σ antibonding MO of the dihydrogen molecule (see figure). The MO's are also called Linear Combinations of Atomic Orbitals (LCAO).

Types of Bonds

Inorganic compounds use s, p, and d orbitals (and more rarely f orbitals) to make bonding and antibonding combinations. These combinations result in **σ, π,** and **δ** bonds (and antibonds).

In inorganic chemistry, π bonds can be made from p- and/or d-orbitals. δ bonds are more rare and occur by face-to-face overlap of d-orbitals, as in the ion $Re_2Cl_8^{2-}$. The fact that the Cl atoms are eclipsed in this anion is evidence of δ bonding.

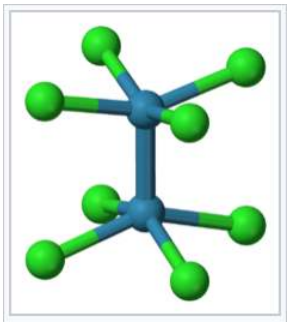
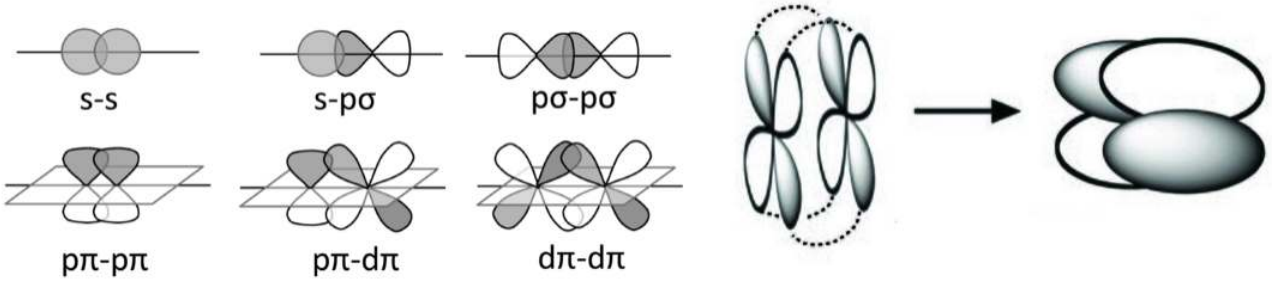


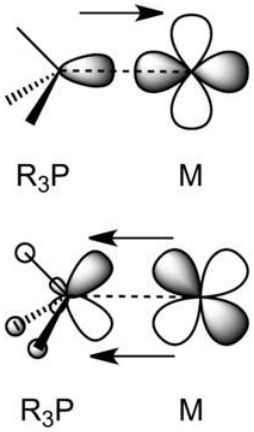
Figure **3.4.1**: The octachlorodirhenate(III) anion, $[Re_2Cl_8]^{2-}$, which has a quadruple Re-Re bond.[3]

Some possible σ (top row), π (bottom row), and δ bonding combinations (right) of s, p, and d orbitals are sketched below. In each case, we can make bonding or antibonding combinations, depending on the signs of the AO wavefunctions. Because pπ-pπ bonding involves sideways overlap of p-orbitals, it is most commonly observed with second-row elements (C, N, O). π-bonded compounds of heavier elements are rare because the larger cores of the atoms prevent good π-overlap. For this reason, compounds containing C=C double bonds are very common, but those with Si=Si bonds are rare. δ bonds are generally quite weak compared to σ and π bonds. Compounds with metal-metal δ bonds occur in the middle of the transition series.

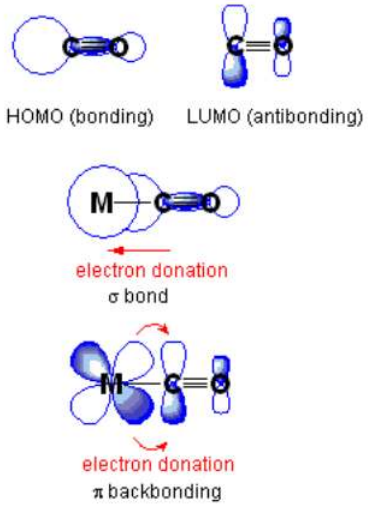


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Transition metal d-orbitals can also form σ bonds, typically with s-p hybrid orbitals of appropriate symmetry on ligands. For example, phosphines (R_3P:) are good σ donors in complexes with transition metals, as shown below.



pπ-dπ bonding is also important in transition metal complexes. In metal carbonyl complexes such as $Ni(CO)_4$ and $Mo(CO)_6$, there is sideways overlap between filled metal d-orbitals and the empty π-antibonding orbitals (the LUMO) of the CO molecule, as shown in the figure below. This interaction strengthens the metal-carbon bond but weakens the carbon-oxygen bond. The C-O infrared stretching frequency is diagnostic of the strength of the bond and can be used to estimate the degree to which electrons are transferred from the metal d-orbital to the CO π-antibonding orbital.



The same kind of backbonding occurs with phosphine complexes, which have empty π orbitals, as shown at the right. Transition metal complexes containing halide ligands can also have significant pπ-dπ bonding, in which a filled pπ orbital on the ligand donates electron density to an unfilled metal dπ orbital. We will encounter these bonding situations in Chapter 5.

Attributions

- 2.4: σ, π, and δ orbitals, Chemistry 310, Penn State University, CC-BY-SA 4.0
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3.4.1: Formation of Molecular Orbitals from Atomic Orbitals

3.4.2: Molecular Orbitals from s Orbitals

3.4.3: Molecular Orbitals from p Orbitals

3.4.4: Molecular orbitals from d orbitals

3.4.5: Nonbonding Orbitals and Other Factors

3.4.6: Features of Molecular Orbital Diagrams

3.4.7: Diatomic Molecules of the First and Second Periods

3.4.8: Molecular Orbitals of Heteronuclear Diatomic Molecules

3.4.9: Ionic Compounds and Molecular Orbitals

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3.4.1: Formation of Molecular Orbitals from Atomic Orbitals

Molecular orbital theory extends from quantum theory and the atomic orbital wavefunctions (ψ) described by the Schrödinger equation. While the Schrödinger equation defines a wavefunction for electrons in individual atoms, we can approximate what the molecular wavefunction Ψ would look like if we combined the atomic orbital wavefunctions of individual atoms. The addition or subtraction of wavefunctions is termed **linear combination of atomic orbitals** (LCAO). Molecular orbital theory is applied to LCAO to describe bonding.

The LCAO for the wavefunction of two atoms (ψ_a and ψ_b) is represented by the general expression below. The coefficients c_a and c_b quantify the contribution of each atomic orbital wavefunction to the molecular orbital wavefunction.

$$\Psi = c_a\psi_a + c_b\psi_b$$

For two atomic ψs to form a bond, three conditions must be satisfied:

- First, the **distance between the atoms** must be small enough to provide good overlap. This is because the two orbitals must be able to overlap using regions of ψ^2 where the probability of finding electrons is significant. If atoms are not close enough, ψ_a and ψ_b cannot interact productively. At the same time, the atoms must be far enough apart that their nuclei do not repel each other.
- The **symmetry of the orbitals** must be compatible such that regions of ψ_a and ψ_b with the same sign constructively interfere more than regions with opposite sign destructively interfere. In other words, for a productive interaction, there must be a relatively high probability of finding an electron between the two nuclei, and this depends on the symmetry (and sign of the ψ) of the atomic orbitals.
- Third, the **energies of the atomic orbitals** must be similar. Orbitals with similar energy combine to make the most stable bonding molecular orbitals. Atomic orbitals with very different energies form less stable bonding interactions, and the larger the difference in the atomic orbitals, the weaker the bonding interaction will be.

Atomic orbitals combine to form molecular orbitals when these three conditions are met. The result is a set of bonding molecular orbitals that are lower in energy than the original atomic orbital energies.

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3.4.2: Molecular Orbitals from s Orbitals

Sigma Bonding with s-orbitals (ex: Dihydrogen)

In the case of the hydrogen molecule, two atomic orbitals are combined to form two molecular orbitals. These new molecular orbitals have different wavelengths than the two atomic orbitals: one has a longer wavelength and is a little lower in energy, while the other has a shorter wavelength and is a little higher in energy. If we take into account the energy of the two original atomic wavefunctions, and compare them to the total energy of the two new molecular wavefunctions, there is no change overall.

We started with two atomic orbitals, and by combining them we produced two molecular orbitals. The average energy of the orbitals has remained almost constant, and the number of wavefunctions has remained constant.

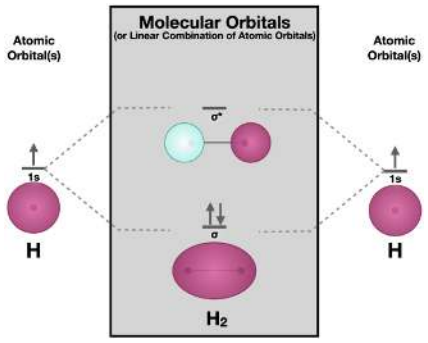


Figure **3.4.2.1**: Molecular Orbital Diagram for H_2 [LibreText]

Of course, from the point of view of the two real electrons, some remarkable changes have occurred. Both of these electrons have adopted a longer wavelength and a lower energy and that has made all the difference. There is an occupied molecular orbital and an unoccupied molecular orbital; only the occupied orbital makes a real energetic contribution to the overall stability of the molecule. The unoccupied orbital is completely imaginary. The electrons have a lower kinetic energy in the bond than they had before bonding; lectronic energy has decreased. A stable bond has formed.

A bonding picture of He_2 would look exactly the same because it would also involve the overlap of 1s electrons on one atom with 1s electrons on the other atom. However, there would be a difference in the electronic energy because each He has two valence electrons: both the bonding and antibonding orbitals would be occupied. Having both orbitals fully occupied results in no net gain in stability, which makes the helium-helium bond unlikely to form.

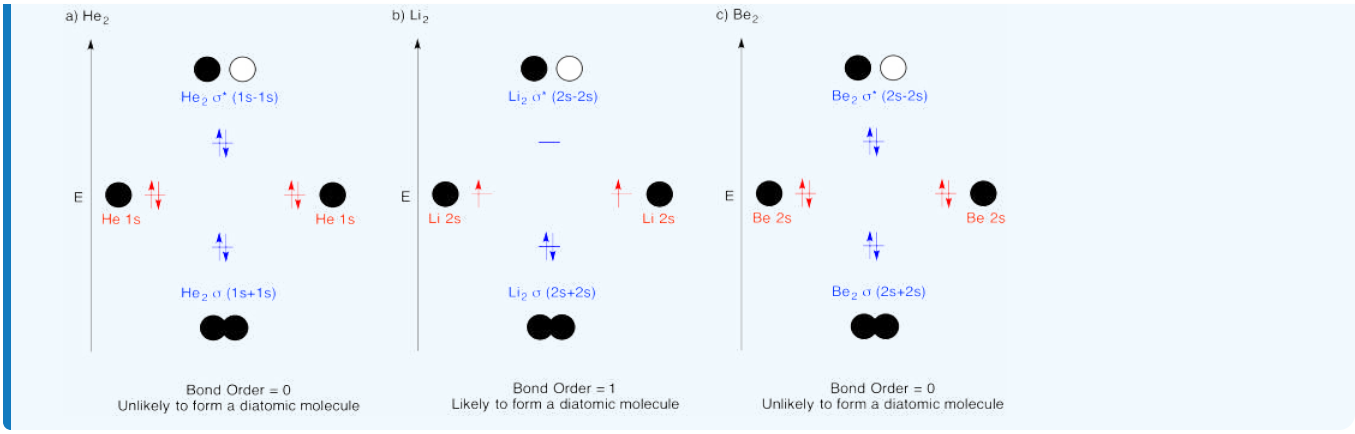
Problems

? Exercise 3.4.2.1

Construct molecular orbital diagrams for the following diatomic species and discuss the likelihood of bond formation in each case.

a. He_2.
b. Li_2.
c. Be_2.

Answer



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3.4.3: Molecular Orbitals from p Orbitals

Some Assumptions

Other diatomic molecules can be constructed in a similar way to that of H_2. Consider dinitrogen, N_2.

Nitrogen has five valence electrons, and these electrons are found in the 2s and 2p levels. There are three possible atomic orbitals in the 2p level where some of these electrons could be found: p_x, p_y and p_z. We need to look at the interaction between the s and p_x, p_y and p_z orbitals on one nitrogen atom with the s and p_x, p_y and p_z orbitals on the other nitrogen. That process could be extremely complicated, but is simplified because orbital interactions are governed by symmetry. Orbitals interact most easily with other orbitals that have the same element of symmetry. For now, we can simplify this idea and say that orbitals on one atom only interact with the same type of orbitals on the other atom.

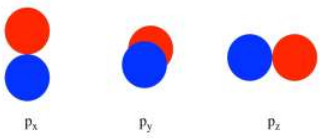
- s orbitals interact with s orbitals. We can already see how that will work out in dinitrogen, because that is what happened in dihydrogen.
- p_x orbitals interact with p_x orbitals.
- p_y orbitals interact with p_y orbitals.
- p_z orbitals interact with p_z orbitals.

Another complication here is that the s and p orbitals do not start out at the same energy level. When the orbitals mix, one combination goes up in energy and one goes down. Does the s antibonding combination go higher in energy than the combinations from p orbitals? Do the p bonding combinations go lower in energy than the combinations from s orbitals? We will **simplify** and **assume** that the s and p levels remain completely separate from each other. This is not always true, but the situation varies depending on what atoms we are dealing with.

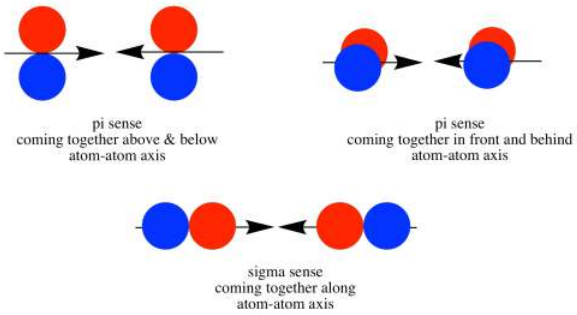
- The combination of one s orbital with another is just like in hydrogen. Two original orbitals will combine and rearrange to produce two new orbitals.
- There is a bonding combination in which the orbitals are in phase. The new orbital produced has a longer wavelength than the original orbital. It is lower in energy.
- There is an antibonding combination in which the orbitals are out of phase. The new orbital produced has a shorter wavelength than the original orbital. It is higher in energy.

Sigma bonding with p-orbitals

In considering the interaction of two p orbitals, we have to keep in mind that p orbitals are directional. A p orbital lies along a particular axis: x, y or z. The three p orbitals on nitrogen are all mutually perpendicular (or orthogonal) to each other. That situation is in contrast to s orbitals, which are spherical and thus look the same from any direction.

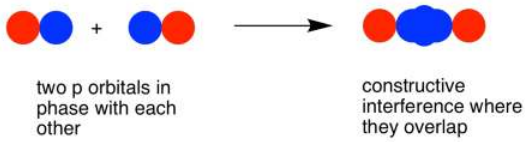


We first need to define one axis as lying along the N-N bond. It does not really matter which one. However, by convention we say the N-N bond lies along the z axis. The p_z orbitals have a different spatial relationship to each other compared to the p_y and p_x. The p_z orbitals lie along the bond axis, whereas the p_y and p_x are orthogonal (perpendicular) to it.

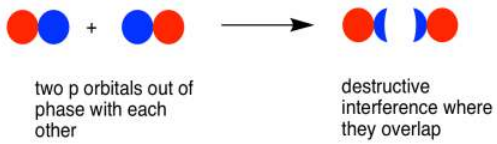


As the nitrogen atoms are brought together, one lobe on one p_z orbital overlaps strongly with one lobe on the other p_z orbital. The other lobes point away from each other and do not interact in any obvious way.

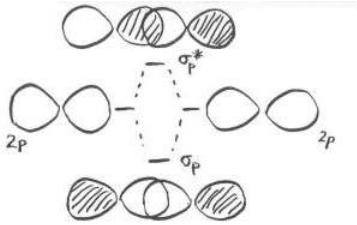
As with the s orbital, the p_z orbitals can be in-phase or out-of-phase. The in-phase combination results in constructive interference. (Here, "in-phase" means the lobes that overlap are in-phase; for that to happen the two p orbitals are actually completely out-of-phase with each other mathematically, so that one orbital is the mirror image of the other.) This combination is at a longer wavelength than the original orbital. It is a lower energy combination.



The out-of-phase combination (meaning in this case that the overlapping lobes are out-of-phase) results in destructive interference. This combination is at shorter wavelength than the original orbital. It is a higher energy combination.



As a result, we have two different combinations stemming from two different p orbitals coming together in two different ways. We get a low-energy, in-phase, bonding combination and a high-energy, out-of-phase, antibonding combination.



Pi-bonding with p-orbitals

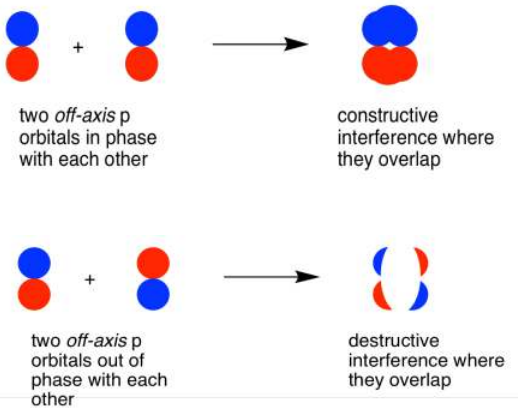
As the nitrogen atoms are brought together, one lobe on one p_z orbital overlaps strongly with one lobe on the other p_z orbital. The other lobes point away from each other and do not interact in any obvious way.

As with the s orbital, the p_z orbitals can be in-phase or out-of-phase. The in-phase combination results in constructive interference. (Here, "in-phase" means the lobes that overlap are in-phase; for that to happen the two p orbitals are actually completely out-of-phase with each other mathematically, so that one orbital is the mirror image of the other.) This combination is at a longer wavelength than the original orbital. It is a lower energy combination.

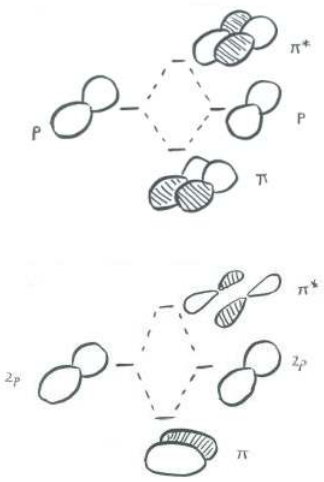
As the nitrogen atoms are brought together, the parallel (but not collinear), p orbitals can also interact with each other. The p_x orbital on one atom will interact with the p_x orbital on the other atom. The p_y orbital on one atom will interact with the p_y orbital

on the other atom. As the two atoms approach along the internuclear axis (z axis), the orbitals would approach each other side by side, with their lobe interacting above and below the bond axis between the two atoms. Although the p_x and p_y orbitals can be close enough to each other to overlap, they do not overlap as strongly as p_z orbitals lying along the bond axis.

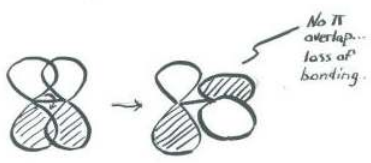
The interaction of a pair of p_x (or p_y) orbitals produces a bonding and an antibonding combination. The in-phase combination (bonding) is shown below, followed by the out-of-phase combination. The resulting orbitals contain nodes along the bond axis, and the electron density is found above and below the bond axis. This bond is called a p (pi) bond.



The illustration above is for one set of p orbitals that are orthogonal to the bond axis. The second picture shows the result of the constructive (or destructive) interference. A similar picture could be shown for the other set of p orbitals.



An important consequence of the spatial distribution or "shape" of a p orbital is that it is not symmetric with respect to the bond axis. An s orbital is not affected when the atom at one end of the bond is rotated with respect to the other. A p orbital is affected by such a rotation. If one atom turns with respect to the other, the p orbital would have to stretch to maintain the connection. The orbitals would not be able to overlap, so the connection between the atoms would be lost.

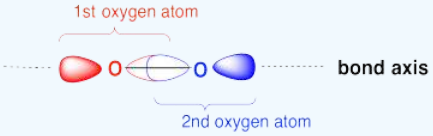


Problems

Exercise 3.4.3.1

Draw an MO cartoon of a sigma bonding orbital formed by the overlap of two p orbitals between two oxygen atoms. Label the positions of the oxygen nuclei with the symbol "O". Label the O-O bond axis.

Answer



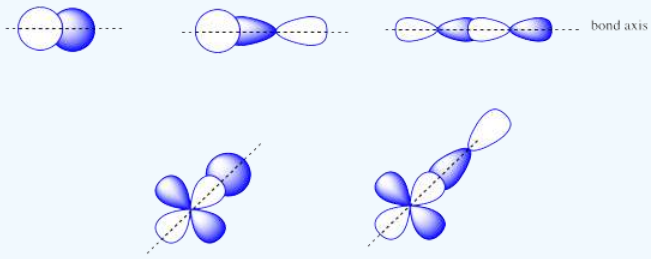
Exercise 3.4.3.2

The combinations of _____ atomic orbitals leads to σ orbitals.

Draw pictures.

Answer

The combinations of s + s; s + p; p + p; s + d; p + d atomic orbitals can lead to σ orbitals.



Exercise 3.4.3.3

The combinations of _____ atomic orbitals leads to π orbitals.

Draw pictures.

Answer

The combinations of side by side p + p or p + d atomic orbitals leads to π orbitals.



Exercise 3.4.3.4

Which molecular orbital is typically the highest in energy?

a. p
b. σ
c. π*
d. π
e. σ*

Answer

e. σ*

? Exercise 3.4.3.5

Why would a *core* 1s orbital not interact with a *valence* 2s orbital?

Hint: Why is a Li_2O bond stronger than a K_2O bond?

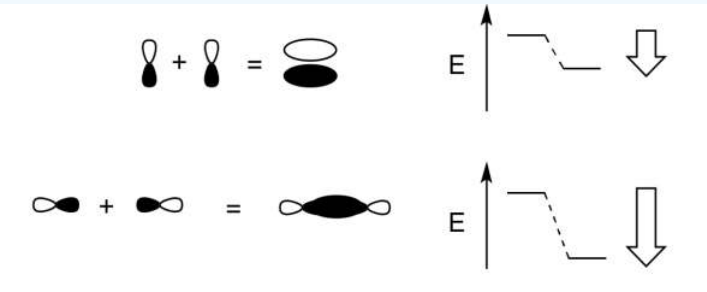
Answer

Li^+ and O^{2-} are more similar in size than K^+ and O^{2-}, so the bond between Li^+ and O^{2-} is stronger.

The energy difference between any core orbitals and valence orbitals is too large, so they cannot interact. In order for orbitals to interact, the orbitals need to have the same symmetry, be in the same plane, and be similar in energy.

? Exercise 3.4.3.6

Add a few words to explain the ideas conveyed in these drawings.



Answer

When two parallel p orbitals combine out-of-phase, destructive interference occurs.

There is a node between the atoms.

The energy of the electrons increases.

When two parallel p orbitals combine in-phase, constructive interference occurs.

There is no node between the atoms; the electrons are found above and below the axis connecting the atoms.

The energy of the electrons decreases.

Attribution

Chris P Schaller, Ph.D., (College of Saint Benedict / Saint John's University)

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3.4.4: Molecular orbitals from d orbitals

In transition metals and other heavier elements, the d orbitals may combine with other orbitals of compatible symmetry (and energy) to form molecular orbitals. Generally, there are three types of bonding and antibonding interactions that may occur with d orbitals: sigma (σ), pi (π), and delta (δ) bonds.

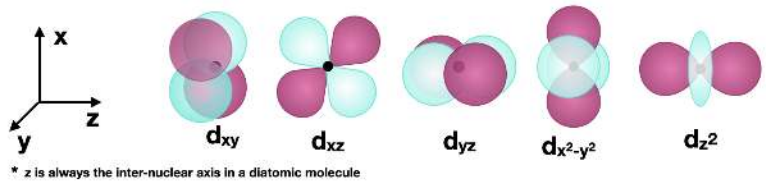


Figure 3.4.4.1: The five 3d orbitals are shown. The orientation of the axes is consistent and the z axis is horizontal for convenience in drawing bonding along the z axis (see examples below). (CC-BY-SA; Kathryn Haas)

Sigma (σ) bonding with d orbitals

σ bonds are symmetric with respect to the inter-nuclear axis (in a diatomic molecule, this is the z axis). An example of a σ bond formed by d orbitals is that of two d_{z^2} orbitals (see Figure 3.4.4.2). If a bonded atom is in a position other than on the z axis (in an octahedral geometry, for example), σ bonds can also form. For example, two $d_{x^2-y^2}$ orbitals on atoms bonded along the x or y axes could also form a σ bond.

d orbitals can also form σ bonds with other types of orbitals with the appropriate symmetry. Examples of orbitals with appropriate symmetry are the s orbital and certain p orbitals on another atom, as shown below in Figure 3.4.4.2.

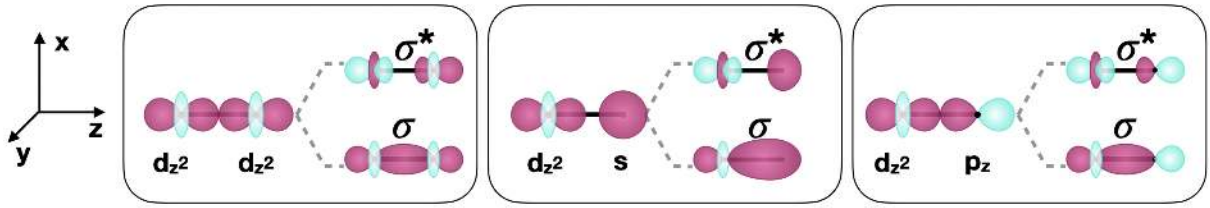


Figure 3.4.4.2: Selected examples of σ bonds involving d orbitals along the z internuclear axis (shown as a bold horizontal line) between two atoms. (CC-BY-SA; Kathryn Haas)

Pi (π) bonding with d orbitals

π bonds are those with one node that is in-plane with the internuclear axis. A π bond can form between two d orbitals or between d orbitals and other types of orbitals with comparable symmetry. An example of a π bond between two d orbitals is that formed by two d_{xz} orbitals along the z axis (shown in Figure 3.4.4.3). d orbitals can also form π bonds using p orbitals with compatible symmetry, as shown in Figure 3.4.4.3.

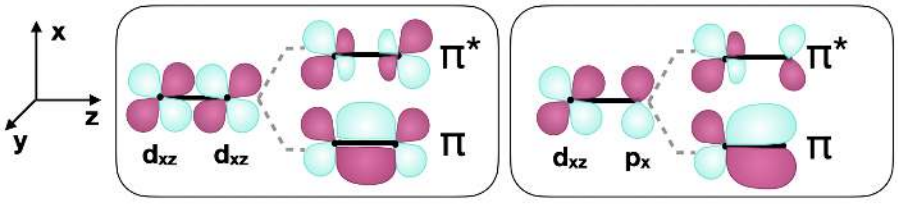


Figure 3.4.4.3: Selected examples of π bonds involving d orbitals along the z internuclear axis (shown as a bold horizontal line) between two atoms. (CC-BY-SA; Kathryn Haas)

Delta (δ) bonding with d orbitals

δ bonds are those with two nodes that are in-plane with the internuclear axis. δ bonds can form between two d orbitals with appropriate symmetry. For example, when two atoms bond along the z axis, the d_{xy} orbitals and the two $d_{x^2-y^2}$ orbitals can form δ bonds (Figure 3.4.4.4).

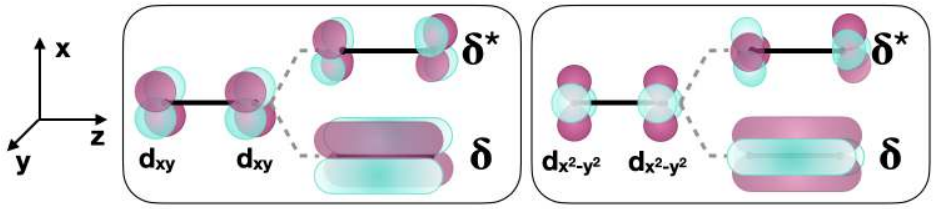


Figure **3.4.4.4**: Selected examples of δ bonds involving d orbitals along the z internuclear axis (shown in bold horizontal line) between two atoms. (CC-BY-SA; Kathryn Haas)

Incompatible orbitals

In the descriptions above, we focused on how bonds (and antibonds) can be formed with d orbitals. All bonding and non-bonding interactions require that orbitals have compatible symmetry to form productive interactions. It is worth mentioning that orbitals with symmetry that is incompatible with the d orbitals will not have bonding or antibonding interactions with d orbitals. The figure below shows several sets of orbitals that are incompatible for bonding.

Curated or created by Kathryn Haas

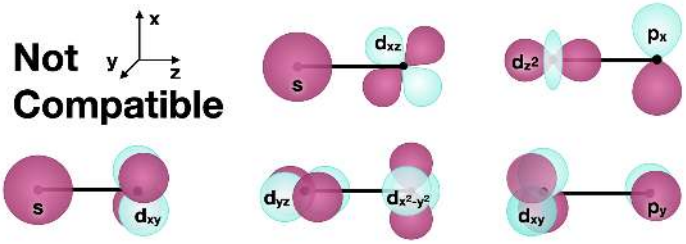


Figure **3.4.4.5**: Several incompatible pairs of orbitals. (CC-BY-SA; Kathryn Haas)

3.4.4: Molecular orbitals from d orbitals is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Kathryn A. Newton, Northern Michigan University.

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3.4.5: Nonbonding Orbitals and Other Factors

The simplest case is when there is an even number of atomic orbitals that all combine to form strong bonding and antibonding orbitals. But what if there is an uneven number of atomic orbitals? Or what if there are some orbitals that don't meet the criteria for bonding? Or what if the bonding interactions are weak? In these cases, there will be molecular orbitals on the molecule that have non-bonding character.

It is important to note that the bonding, non-bonding, and antibonding nature of orbitals exist on a spectrum. Some bonding and anti-bonding orbitals may have some non-bonding character depending on where their energies lie with respect to the original atomic orbital energies. When molecular orbitals have energies similar to their original atomic orbitals, they will have some non-bonding character. The closer the energies of atomic and molecular orbitals, the more non-bonding the molecular orbitals.

Differences in symmetry

The MO picture for a molecule gets complicated when many valence AOs are involved. We can simplify the problem enormously by noting (without proof here) that orbitals of different symmetry do not interact. Here we will take a simple approach understanding the symmetry of orbitals based on their **nodal symmetry**. Note, a more rigorous approach to the symmetry classes of bonds aand orbitals is defined by **group theory** and is the topic of advanced inorganic courses.

To form a molecular orbital, atomic orbitals must have the same **nodal symmetry** or their overlap is zero. This means that two orbitals must have the same symmetry with respect to the bonding axis in order to form a molecular orbital. Figure \PageIndes1 shows a hydrogen 1s orbital and a chlorine $3p_y$ orbital. The H 1s orbital is symmetric about the bonding axis; the sign of the orbital is unchanged by a 180° rotation about the bond axis. However, the Cl $3p_y$ orbital is antisymmetric about the bonding axis; the same rotation inverts the sign of the Cl $3p_y$ wavefunction. Because these two orbitals have different symmetries, the Cl $3p_y$ orbital is **nonbonding** and doesn't interact with the H 1s. The same is true of the Cl $3p_x$ orbital. The p_x and p_y orbitals have π symmetry (nodal plane containing the bonding axis) and are labeled π_{nb} in the MO energy level diagram shown in Figure **3.4.5.2**. In contrast, the H 1s and Cl $3p_z$ orbitals both have σ symmetry so they can make the bonding and antibonding combinations.

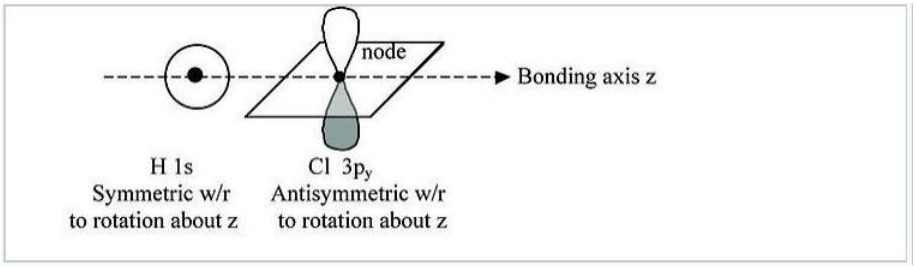


Figure **3.4.5.1**: Orbitals of σ and π symmetry do not interact.

The MO diagram of HCl that includes all the valence orbitals of the Cl atom is shown in Figure **3.4.5.2**. Two of the Cl valence orbitals ($3p_x$ and $3p_y$) have the wrong symmetry to interact with the H 1s orbital. The Cl 3s orbital has the same σ symmetry as H 1s, but it is much lower in energy so there is little orbital interaction. The energy of the Cl 3s orbital is thus affected only slightly by forming the molecule. The pairs of electrons in the π_{nb} and σ_{nb} orbitals are therefore **nonbonding**.

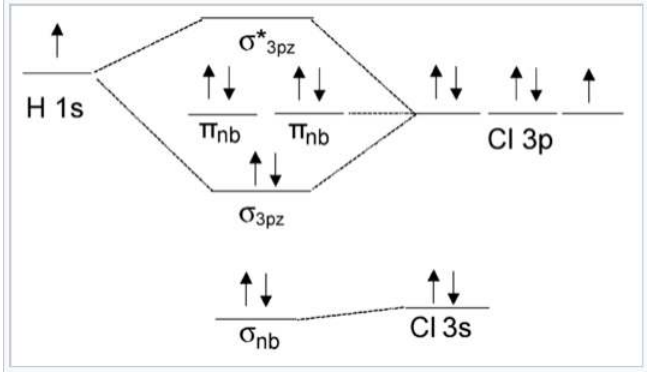


Figure **3.4.5.2**: Energy level diagram of the HCl molecule showing MOs derived from the valence AOs.

Note that the MO result in Figure **3.4.5.2** (1 bond and three pairs of nonbonding electrons) is the same as we would get from valence bond theory for HCl. The nonbonding orbitals are localized on the Cl atom, just as we would surmise from the valence bond picture. In order to differentiate it from the σ bonding orbital, the σ antibonding orbital, which is empty in this case, is designated with an asterisk.

Differences in energy

Combination of orbitals with different energies may lead to orbitals with non-bonding character. Atomic orbitals that have similar energies will have the strongest interactions, and result in bonding molecular orbitals with much lower energies than the component atomic orbitals. On the other hand, atomic orbitals with very unequal energies have a weaker interaction because the molecular orbitals are closer in energy to the atomic orbital energies, thus there is less energy benefit to putting electrons in the bonding molecular orbitals (Figure **3.4.5.3**). When bonding or antibonding orbitals are close to the energies of the contributing atomic orbitals, those molecular orbitals may have some non-bonding character.

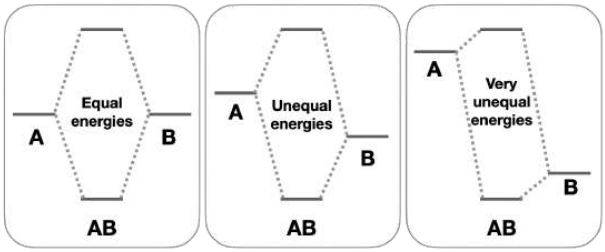


Figure **3.4.5.3**. This figure illustrates how relative energies of atomic orbitals result in molecular orbitals that are more or less favorable. The greater the energy difference between atomic orbitals and the bonding molecular orbital, the more enereticaly favorable it is for bonding to occur. (CC-BY-NC-SA, Kathryn Haas)

Uneven number of atomic orbitals

In the case that there is an uneven number of atomic orbitals with compatible symmetry, orbitals with non-bonding character will form. For example, in the case where three atomic orbitals combine, the most common result is formation of a low-energy bonding orbital, a high energy antibonding orbital, and a non-bonding orbital of intermediate energy (Figure **3.4.5.4**).

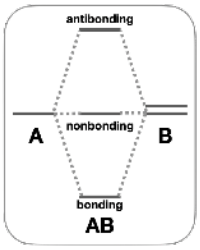


Figure **3.4.5.4**. This figure illustrates the most common case for three atomic orbitals that combine to form three molecular orbitals; formation of one low-energy bonding, one high-energy antibonding, and one intermediate energy non-bonding molecular orbital. (CC-BY-NC-SA, Kathryn Haas)

Problems

Exercise 1

What will most likely lead to the smallest covalent interaction?

a) Overlap of a small and a large orbital.

b) Overlap of two small orbitals.

c) Overlap of two large orbitals.

Answer

a) Overlap of a small and a large orbital.

Exercise 2

What will most likely lead to the largest covalent interaction?

a) orbital overlap in sigma-fashion

b) orbital overlap in pi-fashion

c) orbital overlap in delta-fashion

Answer

a) orbital overlap in sigma-fashion

Exercise 4

Decide by “inspection” which of the following combinations of orbitals have the “right” symmetries to form molecular orbitals.

a) The $2p_x$ orbital of the first N atom and the $2p_y$ orbital of the second N atom in the molecule N_2. The z axis is defined as the bond axis in N_2.

b) The F $2p_x$ and the H 1s orbital in the HF molecule. The z axis is defined as the bond axis.

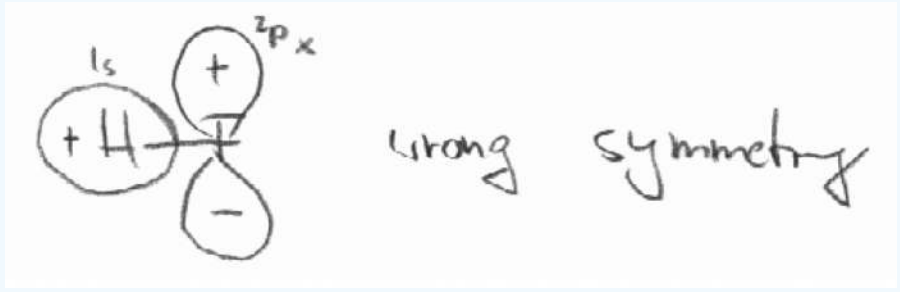
c) The $2p_z$ orbital of F and the 1s orbital in the HF molecule. The z axis is defined as the bond axis.

Answer

a)



b)



c)



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3.4.6: Features of Molecular Orbital Diagrams

There are several cases where our more elementary models of bonding (like Lewis Theory and Valence Bond Theory) fail to predict the actual molecular properties and reactivity. A classic example is the case of O_2 and its magnetic properties. At very cold temperatures, O_2 is attracted to a magnetic field, and thus it must be paramagnetic (unpaired electrons give rise to magnetism). Watch the video below!



The magnetic properties of O_2 are easily rationalized by its **molecular orbital diagram**, which shows the relative energies and identities of each molecular orbital in a molecule. Figure 3.4.6.1 shows a simplified and generic molecular orbital diagram for a second-row homonuclear diatomic molecule. The diagram is simplified in that it assumes that interactions are limited to degenerate orbitals from two atoms.

There are some things you should note as you inspect Figure 3.4.6.1 (and keep these in mind as you draw your own diagrams!). First, notice that there are the **same number of molecular orbitals as there are atomic orbitals**. Second, the diagram in Figure 3.4.6.1 lacks electrons (because it is generic for any second-row diatomic molecule). If this were a *complete* molecular orbital diagram it would **include the electrons for each atom and for the molecule**. Electrons in molecular orbitals are filled in the same way an atomic orbital diagram would be filled, following Hund's Rule and the Aufbau principle, where electrons occupy lower energy orbitals before higher energy orbitals, and electrons occupy empty degenerate orbitals before pairing.

A complete molecular orbital diagram would show whether the molecule is diamagnetic or paramagnetic. It can also be used to calculate the bond order of the molecule (the number of bonds between atoms) using the formula below:

$$\text{Bond order } = \frac{1}{2}\left[\left(\begin{array}{c}\text{number of electrons}\\ \text{in bonding orbitals}\end{array}\right) - \left(\begin{array}{c}\text{number of electrons}\\ \text{in antibonding orbitals}\end{array}\right)\right]$$

In general, non-valence (core) electrons can be ignored because they contribute nothing to the bond order. In fact, many molecular orbital diagrams will ignore the core orbitals, as they are insignificant for bonding interactions and reactivity.

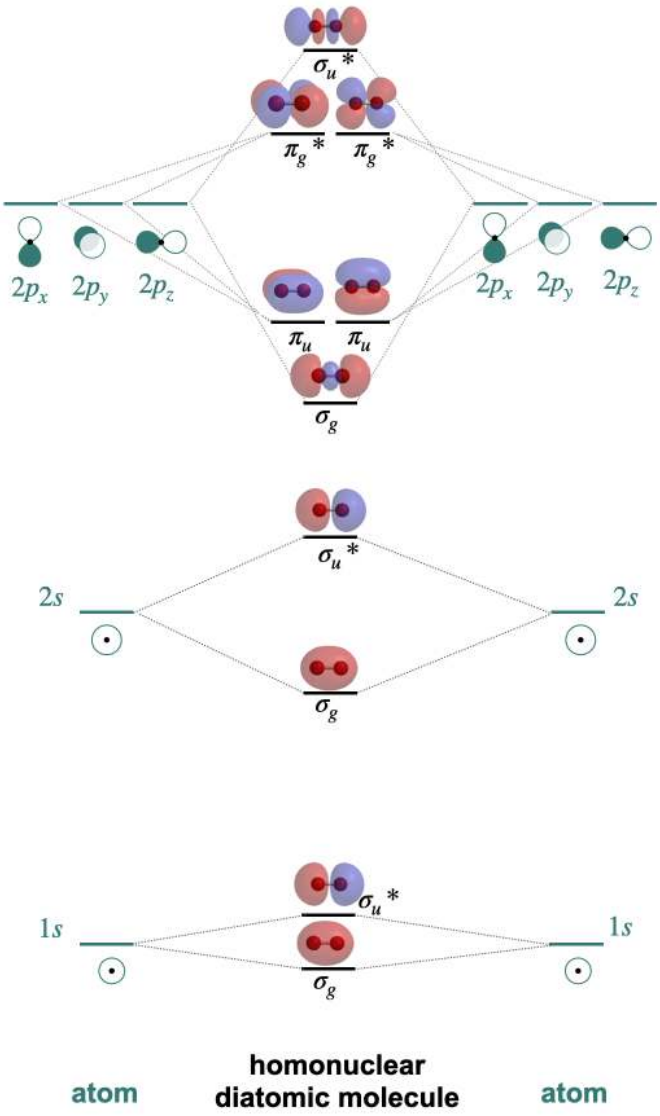


Figure **3.4.6.1**: A generic molecular orbital diagram for a homonuclear diatomic molecule of second-row elements assuming no orbital mixing (interactions are formed by orbitals of the same energy from each atom). (CC-BY-NC-SA, Kathryn Haas)

Now, to see how this molecular orbital diagram can explain the magnetic behaviour of O_2, complete the example below.

✔ Example **3.4.6.1**

Let's change Figure **3.4.6.1** to make it specific for O_2. Re-draw the MO diagram (no need to draw the shapes of orbitals). Fill in the correct number of electrons for each oxygen atom on either side of the diagram. Then, fill in the total molecular electrons in the center. Calculate the bond order and determine whether it is diamagnetic or paramagnetic.

Solution

The diagram in Figure **3.4.6.1** includes core orbitals (the 1s) and valence electrons (2s, 2p). Therefore, we will consider all the electrons in an oxygen atom and a dioxygen molecule. An oxygen atom has eight total electrons. So we fill eight electrons into the atomic orbitals for the oxygen atom on the right, and eight electrons into the atomic orbitals for oxygen on the left. The total number of electrons for the molecule is sixteen, so fill in 16 electrons into the molecular orbitals, being sure to apply Hund's rule and the Aufbau principle. The result is a diagram that looks like the one drawn below in Figure **3.4.6.2**.

The bond order is calculated using the molecular orbitals (we can ignore atomic orbitals). There are 10 electrons in binding orbitals and 6 electrons in antibonding orbitals). This gives a bond order of $\frac{1}{2}(10-6)=2$. This bond order is consistent with valence bond theory!

This diagram indicates that dioxygen is paramagnetic; it has two unpaired electrons in the π^* orbitals. This paramagnetic electron configuration explains why dioxygen is attacted to magnetic fields!

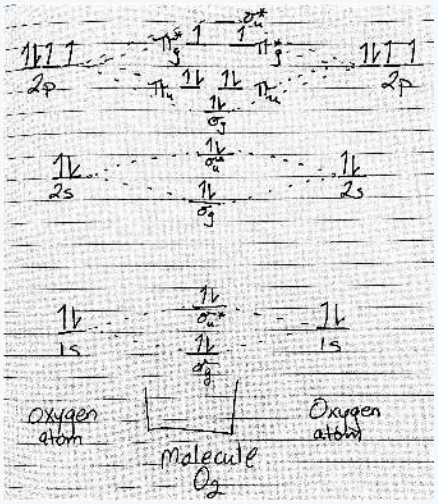


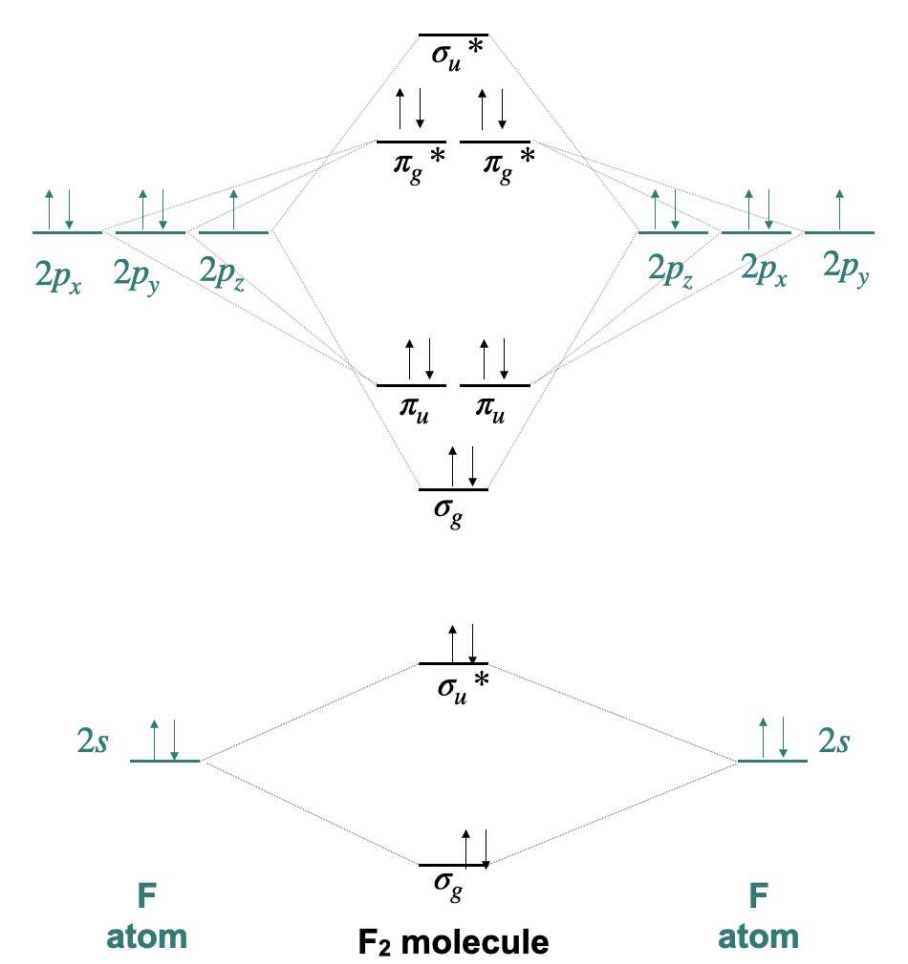
Figure 3.4.6.2: Hand-drawn molecular orbital diagram for dioxygen. (CC-BY-SA; Kathryn Haas)

? Exercise 3.4.6.2

Draw the molecular orbital diagram for F_2; be sure to label your orbitals with the appropriate symmetry and count your orbitals to make sure that the total number of atomic orbitals and molecular orbitals is the same. As a shortcut, include only the valence orbitals and electrons. What is the bond order? Is the molecule diamagnetic or paramagnetic?

Answer

The valence orbitals on an F atom are 2s and 2p. And, there are seven valence electrons in F. This gives fourteen total valence electrons. The MO diagram of the valence molecular orbitals can be constructed by combining the valence 2s and valence 2p orbitals from each F atom. The bond order is 1 and the molecule is diamagnetic.



Exercise 3.4.6.3

A Molecular Orbital Diagram for a diatomic molecule (two atoms) always has the same basic pattern.

- Draw a picture of the levels.
- Label each level with σ, σ*, π, π*

Answer

—— σ*

—— —— π*

—— —— π

—— σ

—— σ*

—— σ

Exercise 3.4.6.4

A Molecular Orbital Diagram for a diatomic molecule (two atoms) varies in the number of electrons. How do you populate the electrons?

Answer

- Count the valence electrons on the molecule. That's the number of valence electrons on each atom, adjusted for any charge on the molecule. (eg C_2^{2-} has 10 valence electrons: 4 from each carbon -- that's 8 -- and two more for the 2- charge).
- Fill electrons into the lowest energy orbitals first.
- Pair electrons after all orbitals at the same energy level have one electron.

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3.4.7: Diatomic Molecules of the First and Second Periods

First Period Homonuclear Diatomic Molecules

In the first row of the periodic table, the valence atomic orbitals are $1s$. There are two possible homonuclear diatomic molecules of the first period:

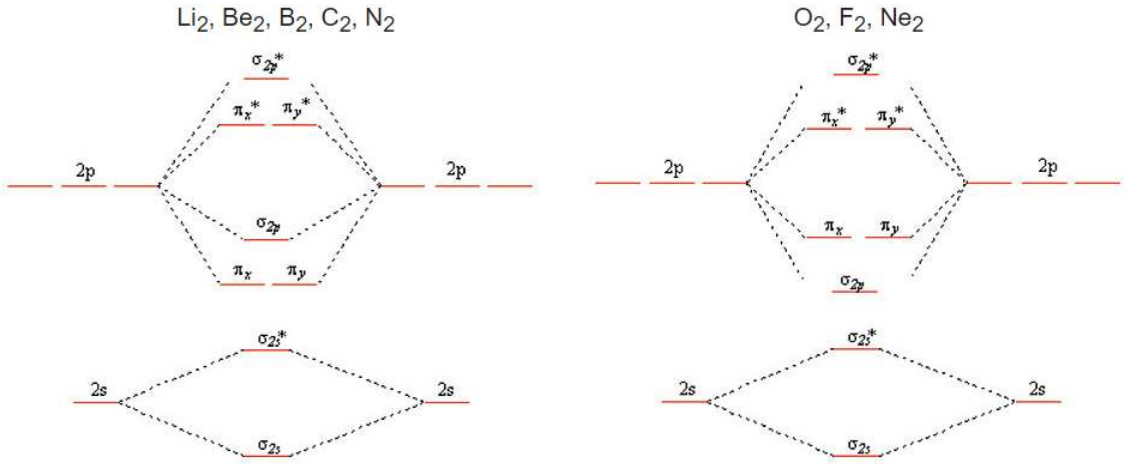
Dihydrogen, H_2 [$\sigma_g^2(1s)$]: This is the simplest diatomic molecule. It has only two molecular orbitals (σ_g and σ_u^*), two electrons, a bond order of 1, and is diamagnetic. Its bond length is 74 pm. MO theory would lead us to expect bond order to decrease and bond length to increase if we either add or subtract one electron. The calculated bond length for the H_2^+ ion is approximately 105 pm.[1]

Dihelium, He_2 [$\sigma_g^2\sigma_u^{*2}(1s)$]: This molecule has a bond order of zero due to equal number of electrons in bonding and antibonding orbitals. Like other noble gases, He exists in the atomic form and does not form bonds at ordinary temperatures and pressures.

Second Period Homonuclear Diatomic Molecules

The second period elements span from Li to Ne. The valence orbitals are 2s and 2p. In their molecular orbital diagrams, non-valence orbitals (1s in this case) are often disregarded in molecular orbital diagrams.

Valence bond theory fails for a number of the second row diatomics, most famously for O_2, where it predicts a diamagnetic, doubly bonded molecule with four lone pairs. O_2 does have a double bond, but it has two unpaired electrons in the ground state, a property that can be explained by the MO picture. We can construct the MO energy level diagrams for these molecules as follows

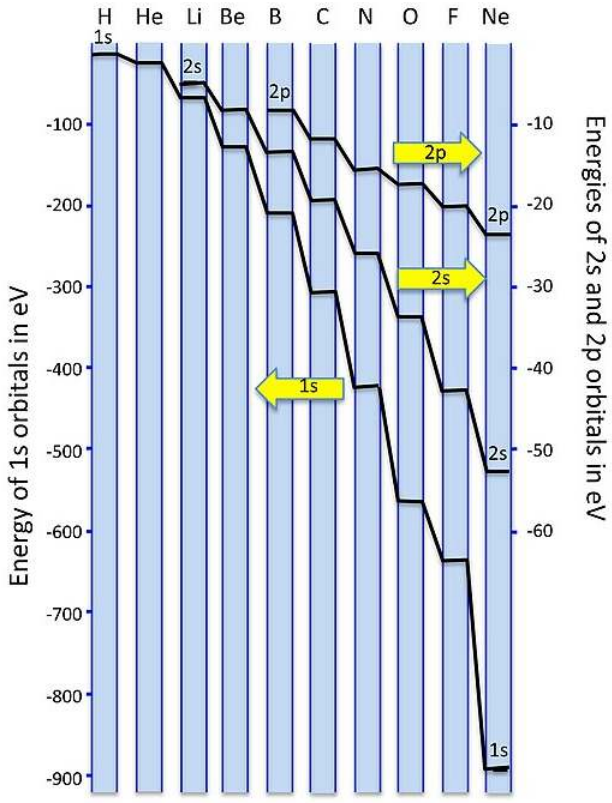


We get the simpler diatomic MO picture on the right when the 2s and 2p atomic orbitals are well separated in energy, as they are for O, F, and Ne. The picture on the left results from **mixing** of the σ_{2s} and σ_{2p} molecular orbitals, which are close in energy for Li_2, Be_2, B_2, C_2, and N_2. Mixing has two effects: 1 - to push the σ_{2s}* down in energy; and 2 - to push the σ_{2p} up in energy to the point where the pπ orbitals are below the σ_{2p}.

Mixing does not occur for O_2 and F_2 because of the energies of the σ_{2s} and σ_{2p} molecular orbitals, which are not drawn to scale in the simple picture above. As we move across the second row of the periodic table from Li to F, we are progressively adding protons to the nucleus. The 2s orbital, which has finite amplitude at the nucleus, "feels" the increased nuclear charge more than the 2p orbital. This means that as we progress across the periodic table (and also when we move down the periodic table), the **energy difference between the s and p orbitals increases**. As the 2s and 2p energies become farther apart in energy, there is less interaction between the orbitals (i.e., less mixing).

A plot of orbital energies is shown below. Because of the very large energy difference between the 1s and 2s/2p orbitals, we plot them on different energy scales, with the 1s to the left and the 2s/2p to the right. For elements at the left side of the 2nd period (Li, Be, B) the 2s and 2p energies are only a few eV apart. The energy difference becomes very large - more than 20 electron volts - for O and F. Since single bond energies are typically about 3-4 eV, this energy difference would be very large on the scale of our MO

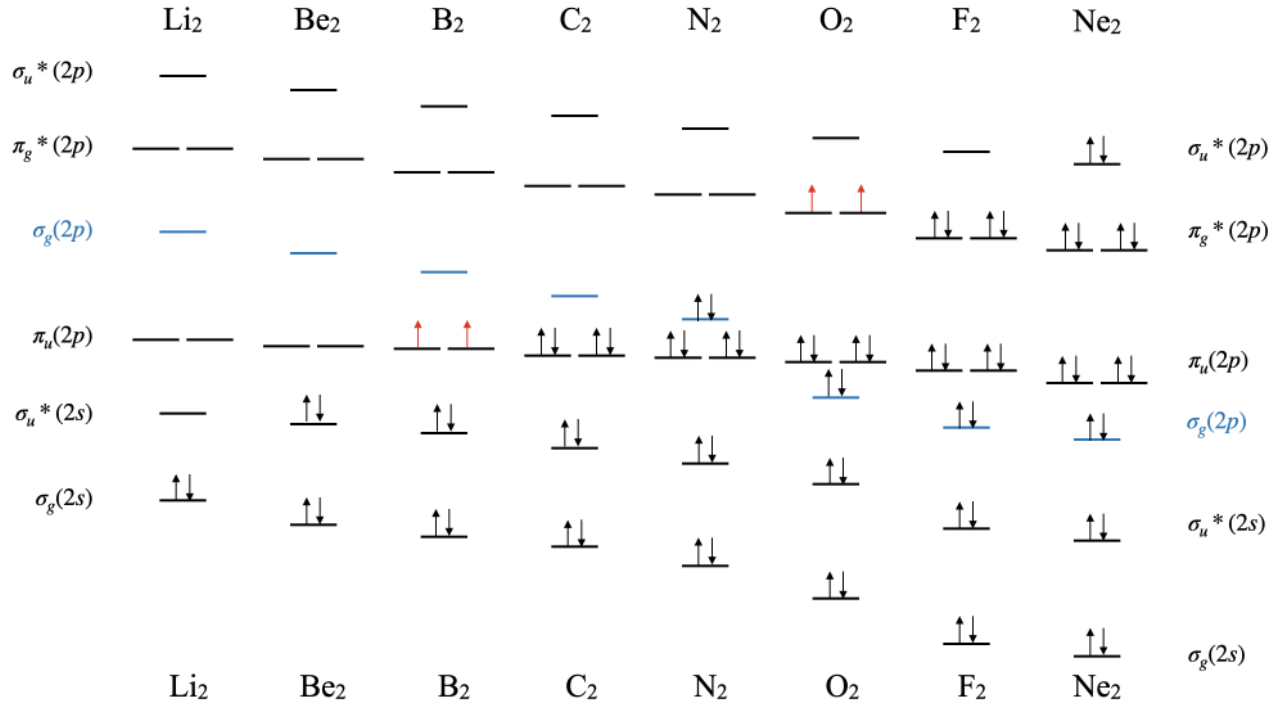
diagrams. For all the elements in the 2nd row of the periodic table, the 1s (core) orbitals are very low in energy compared to the 2s/2p (valence) orbitals, so we don't need to consider them in drawing our MO diagrams.



Period 1 and 2 Elements (CC-BY-SA 4.0, Chemistry 310)

Figure **3.4.7.1**: Energies of 1s, 2s, and 2p atomic orbitals for

Orbital mixing has significant consequences for the magnetic and spectroscopic properties of second period homonuclear diatomic molecules because it affects the order of filling of the $\sigma_g(2p)$ and $\pi_u(2p)$ orbitals. Early in period 2 (up to and including nitrogen), the $\pi_u(2p)$ orbitals are lower in energy than the $\sigma_g(2p)$ (see Figure **3.4.7.1**). However, later in period 2, the $\sigma_g(2p)$ orbitals are pulled to a lower energy. This lowering in energy of $\sigma_g(2p)$ is not unique; all of the σ orbitals in the molecule are pulled to lower energy due to the increasing positive charge of the nucleus. The π orbitals in the molecule are also affected, but to a much lesser extent than σ orbitals. The reason has to do with the high penetration of s atomic orbitals compared to p atomic orbitals. The σ molecular orbitals have more s character and thus their energy is more influenced by increasing nuclear charge. As nuclear charge increases, the energy of the $\sigma_g(2p)$ orbital is lowered significantly more than the energy of the $\pi_u(2p)$ orbitals (Figure **3.4.7.1**).



	Li_2	Be_2	B_2	C_2	N_2	O_2	F_2	Ne_2
Unpaired e⁻	0	0	2	0	0	2	0	0
Bond Order	1	0	1	2	3	2	1	0
Experimental* Bond Length (pm)	267.3	246.0	159.0	124.3	109.8	120.8	141.2	310.0

*Experimental bond lengths from "List of Experimental Diatomic Bond Lengths", NIST, https://cccbdb.nist.gov/diatomicexpbondx.asp

Figure 3.4.7.1: Molecular orbital energy-level diagrams for the diatomic molecules of the period 2 elements. Unlike earlier diagrams, *only the valence molecular orbital energy levels for the **molecules** are shown here (atomic orbitals not shown for simplicity).* For Li_2 through N_2, the $\sigma_g(2p)$ orbital is higher in energy than the $\pi_u(2p)$ orbitals. In contrast, from O_2 onward, the $\sigma_g(2p)$ orbital is *lower* in energy than the $\pi_u(2p)$ orbitals because the nuclear charge increases across the row. The experimental bond lengths correlate with the calculated bond order. (CC-BY-NC-SA, Kathryn Haas)

Dilithium, Li_2 $[\sigma_g^2(2s)]$: This molecule has a bond order of one and is observed experimentally in the gas phase to have one Li-Li bond.

Diberylium, Be_2 $[\sigma_g^2\sigma_u^{*2}(2s)]$: This molecule has a bond order of zero due to the equal number of electrons in bonding and antibonding orbitals. Although Be_2 does not exist under ordinary conditions, it can be produced in a laboratory and its bond length measured (Figure 3.4.7.2). Although the bond is very weak, its bond length is surprisingly ordinary for a covalent bond of the second period elements.[2]

Diboron, B_2 $[\sigma_g^2\sigma_u^{*2}(2s)\pi_u^1\pi_u^1(2p)]$: The case of diboron is one that is much better described by molecular orbital theory than by Lewis structures or valence bond theory. This molecule has a bond order of one. The molecular orbital description of diboron also predicts, accurately, that diboron is paramagnetic. The paramagnetism is a consequence of orbital mixing, resulting in the σ_g orbital's being at a higher energy than the two degenerate π_u^* orbitals.

Dicarbon, C_2 $[\sigma_g^2\sigma_u^{*2}(2s)\pi_u^2\pi_u^2(2p)]$: This molecule has a bond order of two. Molecular orbital theory predicts two bonds with π symmetry, and no σ bonding. C_2 is rare in nature because its allotrope, diamond, is much more stable.

Dinitrogen, N_2 $[\sigma_g^2\sigma_u^{*2}(2s)\pi_u^2\pi_u^2\sigma_g^2(2p)]$: This molecule is predicted to have a triple bond. This prediction is consistent with its short bond length and bond dissociation energy. The energies of the $\sigma_g(2p)$ and $\pi_u(2p)$ orbitals are very close, and their relative energy levels have been a subject of some debate (see next section for discussion).

Dioxygen, O_2 [$\sigma_g^2\sigma_u^{*2}(2s)\sigma_g^2\pi_u^2\pi_u^2\pi_g^{*1}\pi_g^{*1}(2p)$]: This is another case where valence bond theory fails to predict actual properties. Molecular orbital theory correctly predicts that dioxygen is paramagnetic, with a bond order of two. Here, the molecular orbital diagram returns to its "normal" order of orbitals where orbital mixing could be somewhat ignored, and where $\sigma_g(2p)$ is lower in energy than $\pi_u(2p)$.

Difluorine, F_2 [$\sigma_g^2\sigma_u^{*2}(2s)\sigma_g^2\pi_u^2\pi_u^2\pi_g^{*2}\pi_g^{*2}(2p)$]: This molecule has a bond order of one and like oxygen, the $\sigma_g(2p)$ is lower in energy than $\pi_u(2p)$.

Dineon, Ne_2 [$\sigma_g^2\sigma_u^{*2}(2s)\sigma_g^2\pi_u^2\pi_u^2\pi_g^{*2}\pi_g^{*2}\sigma_u^{*2}(2p)$]: Like other noble gases, Ne exists in the atomic form and does not form bonds at ordinary temperatures and pressures. Like Be_2, Ne_2 is an unstable species that has been created in extreme laboratory conditions and its bond length has been measured (Figure **3.4.7.2**).

Bond Lengths in Homonuclear Diatomic Molecules

The trends in experimental bond lengths are predicted by molecular orbital theory, specifically by the calculated bond order. The values of bond order and experimental bond lengths for the second period diatomic molecules are given in Figure **3.4.7.1**, and shown in graphical format on the plot in Figure **3.4.7.2**. From the plot, we can see that bond length correlates well with bond order, with a minimum bond length occurring where the bond order is greatest ($\mathbf{N_2}$). The shortest bond distance is at $\mathbf{N_2}$ due to its high bond order of 3. From $\mathbf{N_2}$ to $\mathbf{F_2}$ the bond distance increases despite the fact that atomic radius decreases.

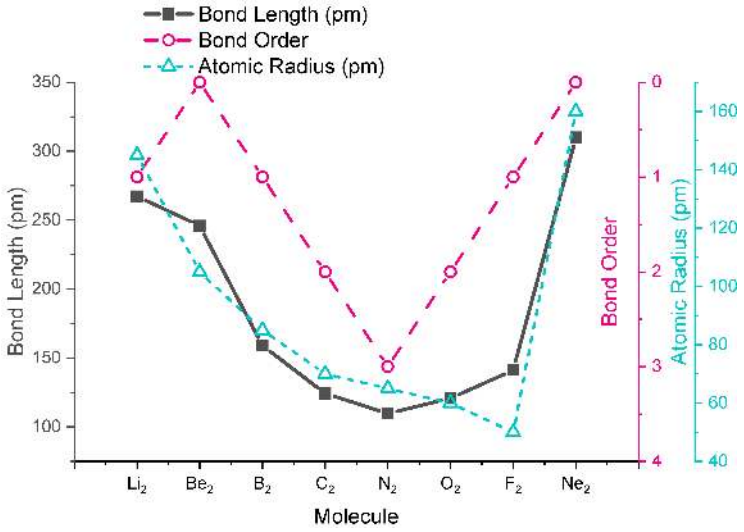


Figure **3.4.7.2**: Overlayed plots of bond length (black squares), bond order (pink circles), and atomic radius (teal triangles) versus atomic number for second period homonuclear diatomic molecules. (CC-BY-NC-SA; Kathryn Haas)

Problems

? Exercise 3.4.7.2

Draw the complete molecular orbital diagrams for $\mathbf{H_2}$ and for $\mathbf{He_2}$. Include sketches of the atomic and molecular orbitals.

Answer

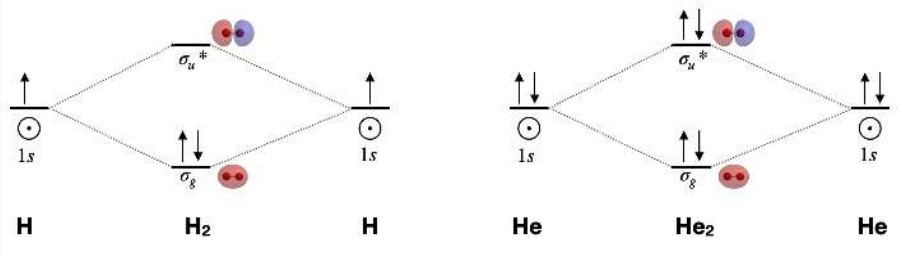


Figure for Exercise **3.4.7.1**: Molecular orbital diagrams for dihydrogen and dihelium. Molecular orbital surfaces calculated using Spartan software. (CC-BY-NC-SA; Kathryn Haas)

A complete molecular orbital diagram includes all atomic orbitals and molecular orbitals, their symmetry labels, and electron filling.

Exercise 3.4.7.2

Draw the complete molecular orbital diagram for O_2. Show calculation of its bond order and tell whether it is diamagnetic or paramagnetic.

Answer

O_2 is paramagnetic with a bond order of 2. Its $\sigma_g(2p)$ molecular orbital is lower in energy that the set of $\pi_u(2p)$ orbitals.

$$\text{Bond order} = \frac{1}{2}\left[\left(\begin{array}{c}\textbf{8 electrons in}\\ \textbf{valence bonding orbitals}\end{array}\right) - \left(\begin{array}{c}\textbf{4 electrons in}\\ \textbf{valence antibonding orbitals}\end{array}\right)\right]$$

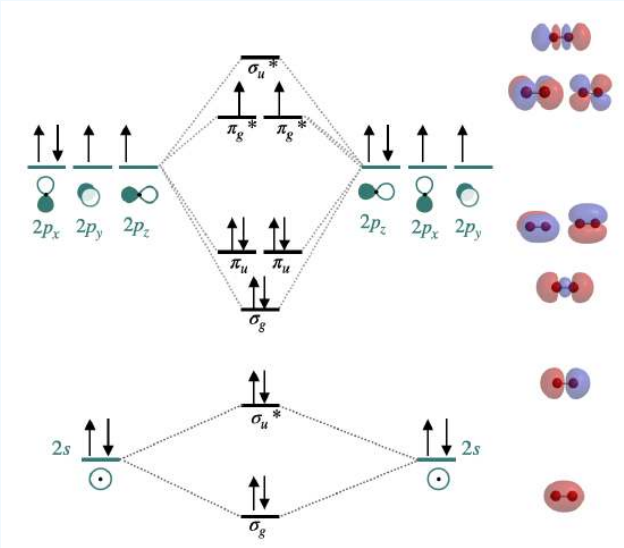


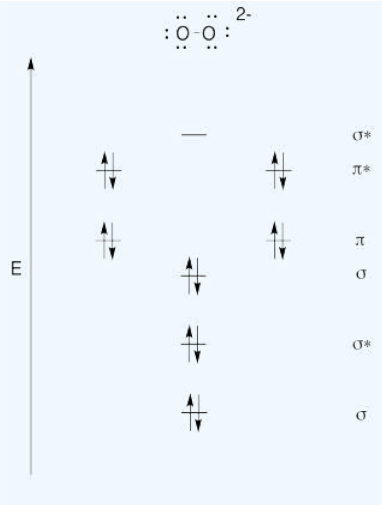
Figure for Exercise **3.4.7.2**. Molecular orbital diagram of O_2. (CC-BY-NC-SA, Kathryn Haas)

Exercise 3.4.7.3: The Peroxide Ion

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

This diagram looks similar to that of $\mathbf{O_2}$, except that there are two additional electrons.
$(\sigma_g(2s))^2\,(\sigma_u^*(2s))^2\,(\sigma_g(2p))^2\,(\pi_u(2p))^4\,(\pi_g(2p))^4$; bond order of 1; no unpaired electrons.

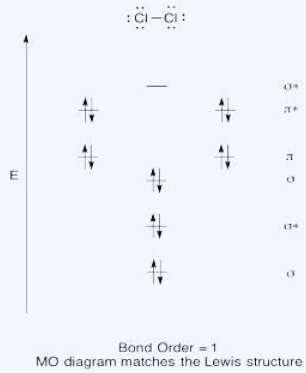


Bond Order = 1
MO diagram matches the Lewis structure. Both predict a Bond Order of 1 and 6 lone pairs of electrons. The addition of two electrons to O_2 to O_2^{2-} would be possible.

Exercise 3.4.7.4

Construct a qualitative molecular orbital diagram for chlorine, Cl_2. Compare the bond order to that seen in the Lewis structure (remember that an electron in an antibonding orbital cancels the stabilization due to bonding of an electron in a bonding orbital).

Answer

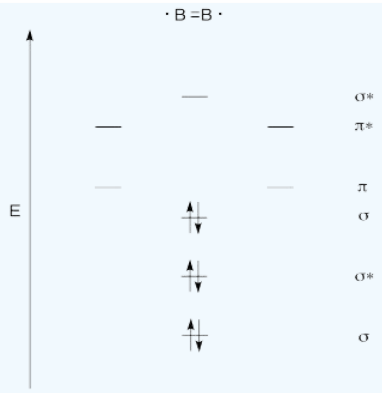


Bond Order = 1
MO diagram matches the Lewis structure

Exercise 3.4.7.5

Construct a qualitative molecular orbital diagram for diboron, B_2. Do you think boron-boron bonds could form easily, based on this picture?

Answer

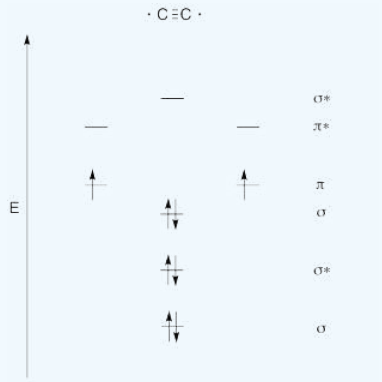


Bond Order = 1
Boron-Boron bonding should be possible

Exercise 3.4.7.6

a. Construct a qualitative molecular orbital diagram for dicarbon, C_2.
b. Compare the bond order to that seen in the Lewis structure.
c. How else does this MO picture of oxygen compare to the Lewis structure? What do the two structures tell you about electron pairing?

Answer

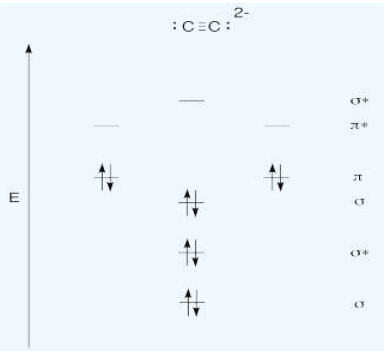


Bond Order = 2
MO diagram does not match the Lewis structure.
However, the MO diagram does concur about the
2 unpaired electrons.

Exercise 3.4.7.7

a. Construct a qualitative molecular orbital diagram for acetylide anion, C_2^{2-}.
b. Compare the bond order to that seen in the Lewis structure.
c. How else does this MO picture of oxygen compare to the Lewis structure? What do the two structures tell you about electron pairing?
d. Based on molecular orbital pictures, how easily do you think dicarbon could be reduced to acetylide (through the addition of two electrons)?

Answer

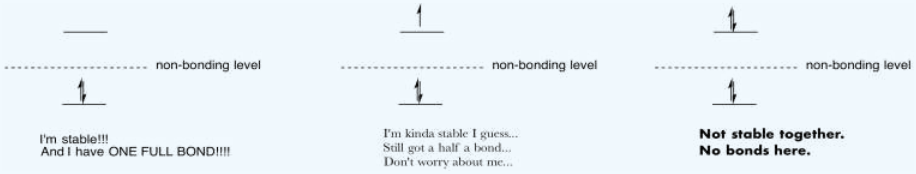


Bond Order = 3
MO diagram matches the Lewis structure. Both predict a Bond Order of 3 and 2 lone pairs of electrons. The addition of two electrons to C_2 to C_2^{2-} would be possible.

Exercise 3.4.7.8

Make drawings and notes to summarize the effect of populating antibonding orbitals.

Answer

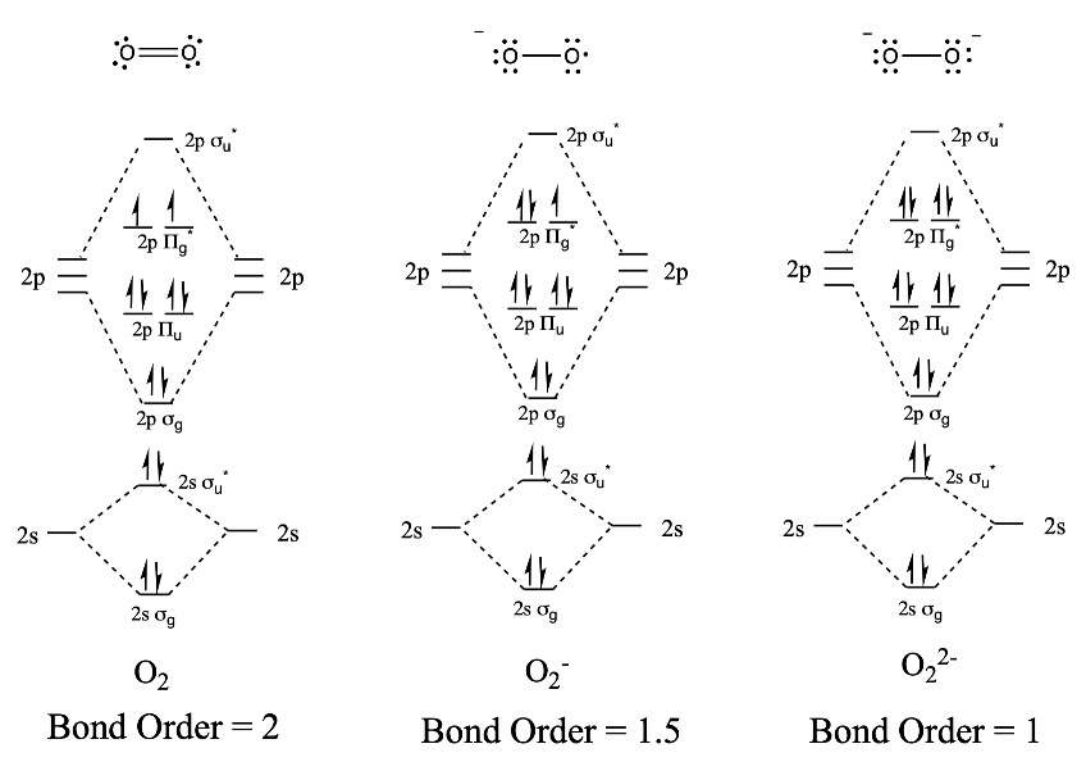


Exercise 3.4.7.9

Draw and compare the molecular orbital diagrams to the Lewis structure diagrams for O_2, O_2^-, and O_2^{2-}.

Answer

The Lewis structures and MO diagrams are shown below. In general, the bond order derived from the MO diagram agrees with the Lewis structure for each species. In the case of the two ions, the number of unpaired electrons from MO theory and the Lewis structure also agrees. In the case of dioxygen, however, there is an inconsistency between the Lewis representation and the MO diagram. While the Lewis structure would lead us to believe that all electrons are paired, the MO diagram indicates paramagnetism, with two unpaired electrons. The MO diagram explains the magnetic behaviour of dioxygen.



References

1. NIST, Calculated Geometries available for H_2^+ (Hydrogen cation) 2Σg+ D∞h, available at https://cccbdb.nist.gov/diatomicexpbondx.asp
2. Merritt, J. M.; Bondybey, V. E.; Heaven, M. C., Beryllium Dimer-Caught in the Act of Bonding. *Science* **2009,** *324* (5934), 1548-1551.

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- **13.6: Assembling the Complete Diagram and Electron Population** by Chris Schaller is licensed CC BY-NC 3.0. Original source: https://employees.csbsju.edu/cschaller/structure.htm.

3.4.8: Molecular Orbitals of Heteronuclear Diatomic Molecules

Diatomic molecules with two non-identical atoms are called **heteronuclear** diatomic molecules. When atoms are not identical, the molecule forms by combining atomic orbitals of unequal energies. *The result is a bond in which atomic orbitals contribute unevenly to each molecular orbital*. The application of molecular orbital theory to heteronuclear diatomic molecules is similar to the case of homonuclear diatomics, except that the atomic orbitals from each atom have different energies and contribute unequally to molecular orbitals. As a result both the symmetry of the atomic orbitals and their energies must be considered to determine if they will combine into molecular orbitals.

Energies of Atomic Orbitals

In the case where atomic orbitals of like symmetry have different energies, they combine less favorably than orbitals that are closer to one another in energy. As a general rule, orbitals that have energy differences of greater than 10-14 eV do not combine favorably. In the molecular orbital diagram, the closer a molecular orbital is to an atomic orbital, the more that atomic orbital contributes to the molecular orbital. This last point is helpful for back-of-the napkin estimations of what the molecular orbitals "look" like. Although an estimation of the differences in energy is usually sufficient, the energy difference between atomic orbitals can be calculated from orbital ionization energies

Orbital Ionization Energies

There are two approaches you can use to "know" or estimate the atomic orbital energy levels.

1. Use a table of atomic orbital ionization energies, like those found in Table 3.4.8.1.
2. When you do not have access to a table of values like the one below, use periodic trends in electronegativity and/or ionization energies as your guide to approximate relative values for different atoms.

Table 3.4.8.1: These are one-electron ionization energies of the valence orbitals calculated by average energies of both the ground-state and ionized-state configurations. (From Harry Gray, “Electrons and Chemical Bonding,” Benjamin, 1964, Appendix)

Atom	1s	2s	2p	3s	3p	4s	4p	Atom	3d	4s	4p
H	−13.64							Sc	−4.71	−5.70	−3.22
He	−24.55							Ti	−5.58	−6.08	−3.35
Li		−5.46						V	−6.32	−6.32	−3.47
Be		−9.30						Cr	−7.19	−6.57	−3.47
B		−14.01	−8.31					Mn	−7.93	−6.82	−3.60
C		−19.47	−10.66					Fe	−8.68	−7.07	−3.72
N		−25.54	−13.14					Ni	−10.04	−7.56	−3.84
O		−32.36	−15.87					Cu	−10.66	−7.69	−3.97
F		−46.37	−18.72								
Ne		−48.48	−21.57								
Na				−5.21							
Mg				−7.69							
Al				−11.28	−5.95						
Si				−15.00	−7.81						
P				−18.72	−10.17						
S				−20.71	−11.65						
Cl				−25.29	−13.76						
Ar				−29.26	−15.87						
K						−4.34					
Ca						−6.08					
Zn						−9.42					
Ga						−12.65	−5.95				
Ge						−15.62	−7.56				
As						−17.61	−9.05				
Se						−20.83	−10.79				
Br						−24.05	−12.52				
Kr						−27.52	−14.26				

Molecular Orbital Diagrams for Heteronuclear Diatomic Molecules

The molecular orbital diagram of a heteronuclear diatomic molecule is approached in a way similar to that of a homonuclear diatomic molecule. The heteronuclear diatomic molecular orbital diagrams look similar to those of homonuclear diatomics, but with the difference that the more electronegative atom will have orbitals at a lower energy level. The more electronegative atom will be placed on the right side of the diagram with its atomic orbitals shown lower in energy than those of the less electronegative atom on the left. As with homonuclear diatomics, orbital mixing can affect the arrangement of the molecular orbitals. Molecular orbital diagrams describing the bonding of two elements that are both oxygen, fluorine, or a later element do not show sp mixing, and will have an arrangement like that for O_2 or F_2. Diagrams describing bonding of an atom that shows sp mixing (such as CO, NO, NO^+) will have the ordering of energy levels shown by N_2. A good animation of the molecular orbitals in the CO molecule can be found on the University of Liverpool **Structure and Bonding** website. Two examples of heteronuclear diatomic molecules will be explored below as illustrative examples.

Carbon monoxide MO diagram

Carbon monoxide is an example of a heteronuclear diatomic molecule where both atoms are second-row elements. The valence molecular orbitals in both atoms are the $2s$ and $2p$ orbitals. The molecular orbital diagram for carbon monoxide (Figure 3.4.8.1) is constructed in a way similar to how you would construct dicarbon or dioxygen, except that the oxygen orbitals have a lower potential energy than analogous carbon orbitals. The labeling of molecular orbitals in this diagram follows a convention by which orbitals are given serial labels according to type of orbital (σ, π, etc.). The lowest energy orbitals of any type are assigned a value of 1 and higher energy orbitals of the same type are assigned by increasing intervals (..2, 3, 4...).

A consequence of unequal atomic orbital energy levels is that orbital mixing is significant. Notice the order of the molecular orbitals labeled 1π and 3σ in Figure 3.4.8.1. This is a similar order of π and σ orbitals to the one we saw in the case of the σ_g and π_u orbitals of N_2 and lighter diatomics of the second period. Because the oxygen $2p_z$ orbital is close in energy to both the carbon $2p_z$

and carbon $2s$, these three orbitals will have significant interaction (mixing). The result is an increase in the energy of the 3σ orbital and a decrease in energy of the $2\sigma^*$ orbital, resulting in the diagram shown in Figure 3.4.8.1.

In the case of carbon monoxide (Figure 3.4.8.1), atomic orbitals contribute unequally to each molecular orbital. For example, because the $2s$ orbital of oxygen is very close in energy to the 2σ moelcular orbital, it contributes to that molecular orbital more than the $2s$ orbital from carbon. Notice the shape of this 2σ orbital and how it is unevenly distributed over the two atoms; it is more heavily distributed on the oxygen because it is most like the oxygen $2s$. This is in line with the assumption that electron density is distributed more on oxygen because it is more electronegative than carbon. Likewise, the 1π orbitals are unevenly distributed, with more distribution close to the oxygen.

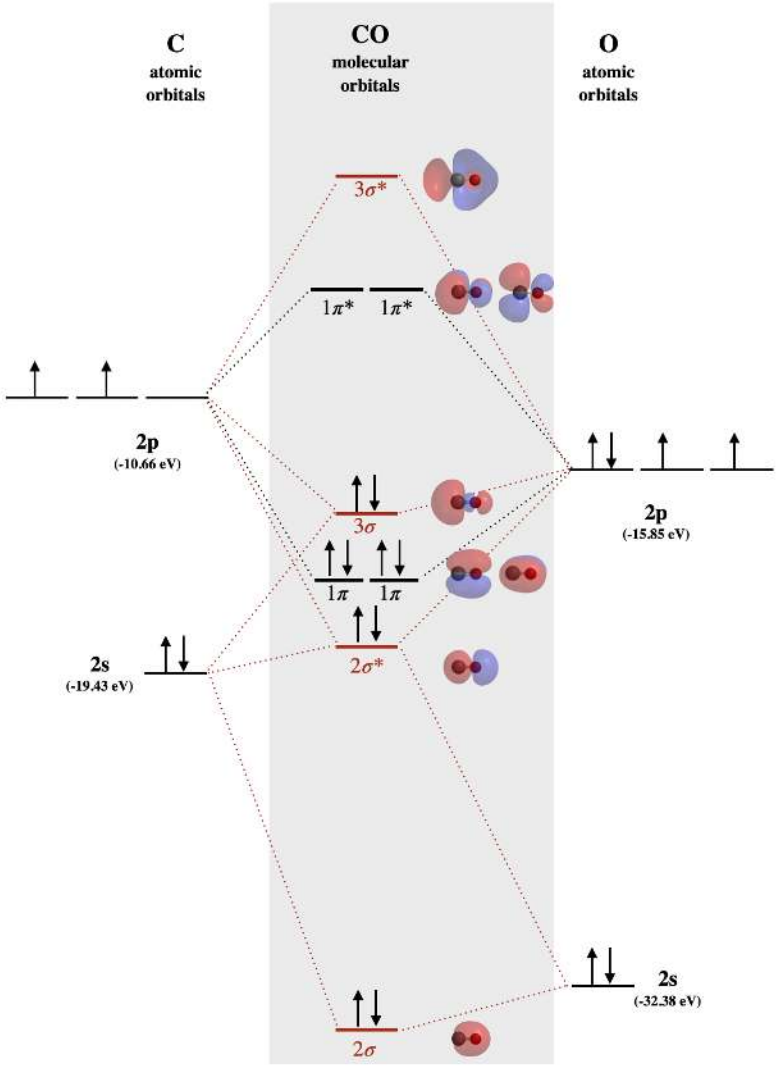


Figure 3.4.8.1: Molecular orbital diagram of carbon monoxide. The labeling of molecular orbitals in this diagram follows a convention by which orbitals are given serial names according to the type of orbital (σ, π, etc.). The lowest energy orbitals of any type are assigned a value of 1 and higher energy orbitals of the same type are assigned by increasing intervals (..2, 3, 4...). The orbital labeling system described previously is inappropriate for heteronuclear diatomic molecules that cannot be assigned g and u subscripts. Molecular orbital surfaces were calculated using Spartan software. (Kathryn Haas, CC-BY-NC-SA)

Hydrogen fluoride MO diagram

Hydrogen fluoride is an example of a heteronuclear diatomic molecule in which the two atoms are from different periods. In this case, the valence orbital of H is $1s$ while those of F are $2s$ and $2p$. The molecular orbital diagram for HF is shown in Figure 3.4.8.2.

Three of these orbitals have compatible symmetry for mixing; these are the hydrogen $1s$, fluorine $2s$, and fluorine $2p$. However, the extent to which they will interact depends on their relative energies. Fluorine is more electronegative than H, and the fluorine atom has a higher first ionization energy than does hydrogen. From these trends, we can expect that the fluorine valence orbitals are

lower in energy than that of hydrogen. From Table **3.4.8.1** we find that the 1s orbital of H (-13.6 eV) is higher in energy than both fluorine orbitals (-18.7 and -40.2 eV, respectively for $2p$ and $2s$). The energies of hydrogen $1s$ and fluorine $2p$ are a good match for combination; however, the fluorine $2s$ orbital is much too different to create a productive interaction. Therefore, we expect that the fluorine $2s$ will create a non-bonding molecular orbital, while the $1s$ and $2p_z$ orbitals combine to make σ bonding and σ^* antibonding molecular orbitals. The remaining $2p_x$ and $2p_y$ orbitals do not have compatible symmetry for bonding with hydrogen, and they will form non-bonding π molecular orbitals. The non-bonding orbitals will have similar energy and character as their component atomic orbitals.

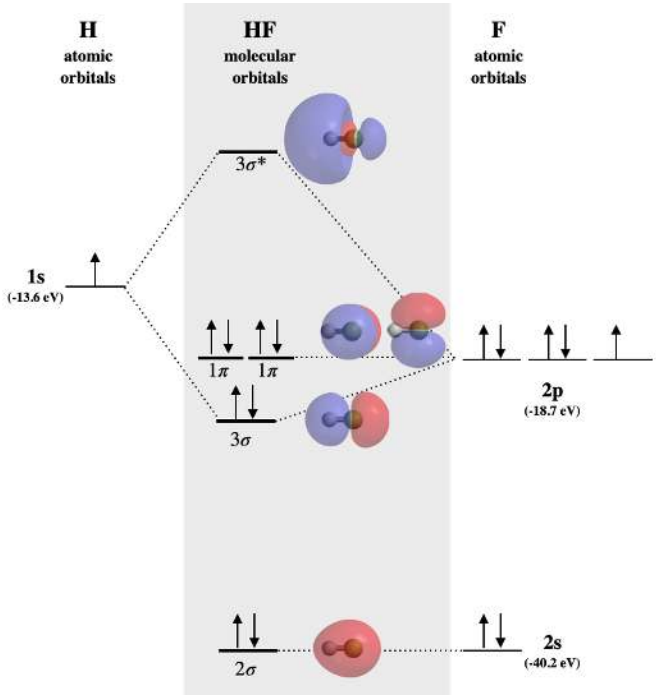


Figure **3.4.8.2**: Molecular Orbital diagram of hydrogen fluoride. Molecular orbitals calculated using Spartan software. (Kathryn Haas, CC-BY-NC-SA)

Chemical reactions take place at the HOMO and LUMO orbitals

Knowledge of molecular orbital diagrams, and the shapes of molecular orbitals, can be used to accurately explain and predict chemical reactivity. Chemical reactions take place using the highest occupied molecular orbitals (HOMO) of a nucleophile or Lewis base, and the lowest unoccupied molecular orbital (LUMO) of an electrophile or Lewis acid.

> *Lewis bases react using electrons in the HOMO, while Lewis acids react using the empty LUMO.*

Example: Reactivity of CO with metal ions

CO is an excellent ligand for many metal ions. In fact, the strong affinity between CO and the heme iron (Fe) ions in hemoglobin can explain the mechanism of carbon monoxide poisoning. When CO binds in place of O_2 to hemoglobin, that hemoglobin can no longer carry O_2 to tissue cells. CO binding to hemoglobin is strong and practically irreversible. When CO binds to metal ions, it does so through the carbon atom. This is contrary to expectations based on the Lewis structure and the known bond polarity, where electron density is polarized toward oxygen. The distribution of the electron density of the HOMO of CO can explain this observation!

Problems

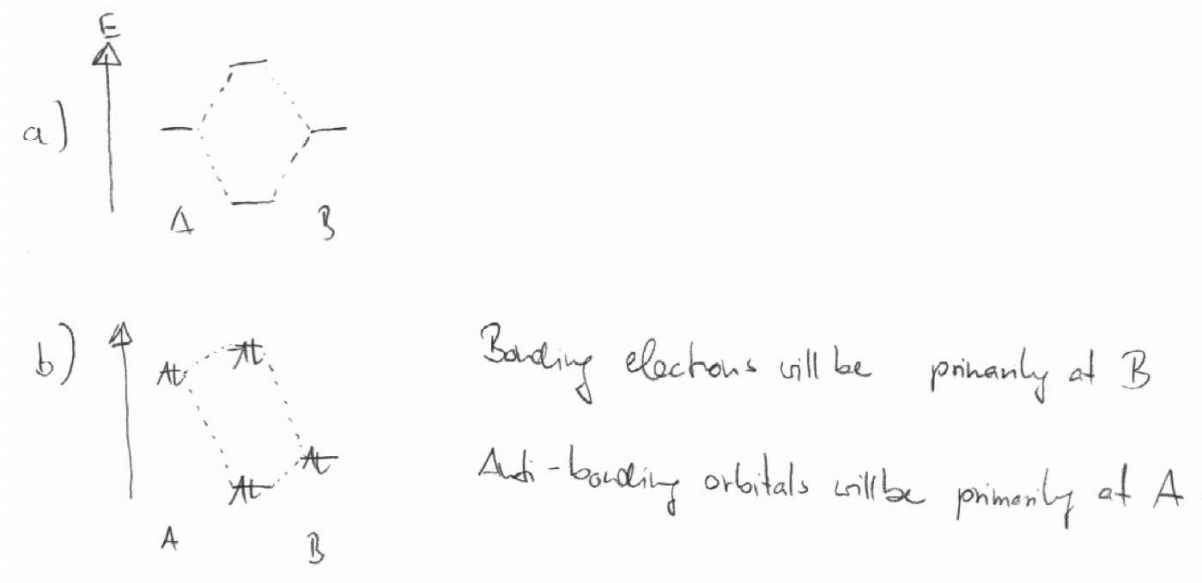
Exercise 3.4.8.1

Qualitatively construct the MO diagrams composed of

a) two 2s atom orbitals A and B of equal energy.

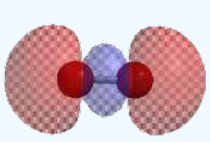
b) two 2s atom orbitals where the orbital energy of atom A is significantly higher than that of B. If both the bonding and the antibonding MO are filled with electrons, where will bonding and antibonding electrons primarily be located? Briefly explain your decision.

Answer

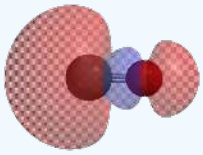


Exercise 3.4.8.2

Examine the shape of the 3σ orbital of carbon monoxide in Figure **3.4.8.1**. Describe what ways this shape is different from the shape of the σ_g orbitals from second period homonuclear diatomic molecules (see Fig. 5.2.1.1). Rationalize these differences. Both orbitals are re-created below for convenience.



σ_g of homonuclear diatomic



3σ of CO

Answer

The 3σ orbital is like the σ_g in that it has three lobes and two nodes distributed along the internuclear bond. They are different in their distribution. The two external lobes of σ_g are evenly distributed because they are an equal combination of two p_z orbitals (one from each atom). The 3σ orbital is more heavily distributed toward the carbon atom, the less electronegative atom, than toward the oxygen. The unequal distribution of 3σ is apparent in the unequal sizes of its exterior lobes and the uneven shape of the interior lobe. The heavier distribution within the exterior lobe on carbon is caused by the mixing of the carbon $2s$ orbital with carbon and oxygen $2p_z$ orbitals. The uneven shape of the interior lobe, where it leans toward oxygen, is best explained by the fact that the 3σ orbital is closer in energy to the oxygen $2p_z$ than the carbon $2p_z$.

? Exercise \(\PageIndex{3}\)

Refer to the MO diagram for CO. Identify the HOMO and explain why CO bonds to metal ions through the carbon atom rather than through the oxygen atom.

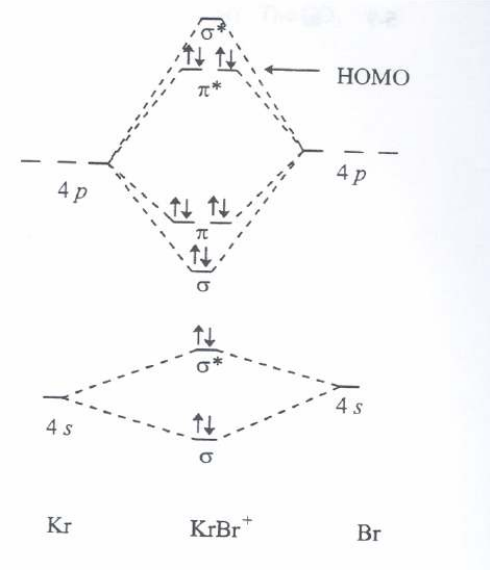
Answer

In the interaction between CO and a metal ion, CO would act as a Lewis base; thus it will react using electrons in its HOMO. The MO diagram for CO is shown in Figure **3.4.8.1**: the HOMO is the **3σ** orbital (also discussed in ? Exercise **3.4.8.1**). The electron density of that MO is centered around the carbon atom, thus the carbon atom will be a better Lewis base than the O atom.

Exercise 3.4.8.4

For the hypothetical $BrKr^+$ molecule: Toward which atom is the HOMO polarized? Explain briefly why.

Answer



Sources:

- Gray, Harry. *Electrons and Chemical Bonding*, Benjamin, 1964.
- Miessler, Gary L, and Donald A. Tarr. *Inorganic Chemistry*. Upper Saddle River, N.J: Pearson Education, 2014. Print.

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3.4.9: Ionic Compounds and Molecular Orbitals

Ionic interactions lie at one extreme on a spectrum of bonding. On the opposite end of the spectrum are the non-polar covalent bonds (e.g., homonuclear diatomics). In these molecules, molecular orbitals are formed by equal-energy atomic orbitals, resulting in electron density evenly distributed over the molecule. In the middle of the spectrum are the cases of polar covalent bonds (e.g., heteronuclear diatomics), in which atomic orbitals of unequal energies contribute unequally to molecular orbitals, resulting in uneven distribution of electron density across the molecule. In the case of polar bonds, the electron density is shifted toward the more electronegative atom since that atom contributes more to the lowest energy bonding molecular orbitals. Molecular orbital diagrams can be drawn for ionic compounds as if they are extremely polar bonds in which electrons are not only shifted toward, but are transferred completely to the more electronegative atom.

Example: NaCl

In **NaCl**, the sodium **3*s*** orbital (-5.2 eV) is significantly higher in energy than the chlorine valence orbitals. The chlorine **3*s*** and **3p_z** orbitals have compatible symmetry, yet only the **3p_z** orbital (-13.8 eV) is close enough in energy to interact with the Na **3*s***; still, the energy difference is large enough to make bonding weak. The Na **3*s*** orbital combines with Cl **3p_z** to form the molecular orbitals labeled **4σ** and **4σ*** in Figure **3.4.9.1**. The **4σ** orbital is weakly bonding, but is very close in energy to the Cl **3p_z** orbital, and is mostly Cl-like in character. Notice that all **σ** orbitals look very much like either **s** or **p** orbitals centered on the **Cl** atom, while the **4σ*** orbital is centered almost entirely on Na. The lack of molecular orbitals that are distributed over both atoms at once is consistent with a lack of significant covalent bond character in **NaCl**. The bonding here is characterized by transfer of one electron from **Na** to **Cl** and is almost entirely electrostatic. Bonding that is mostly electrostatic in character is non-directional, unlike true covalent bonding.

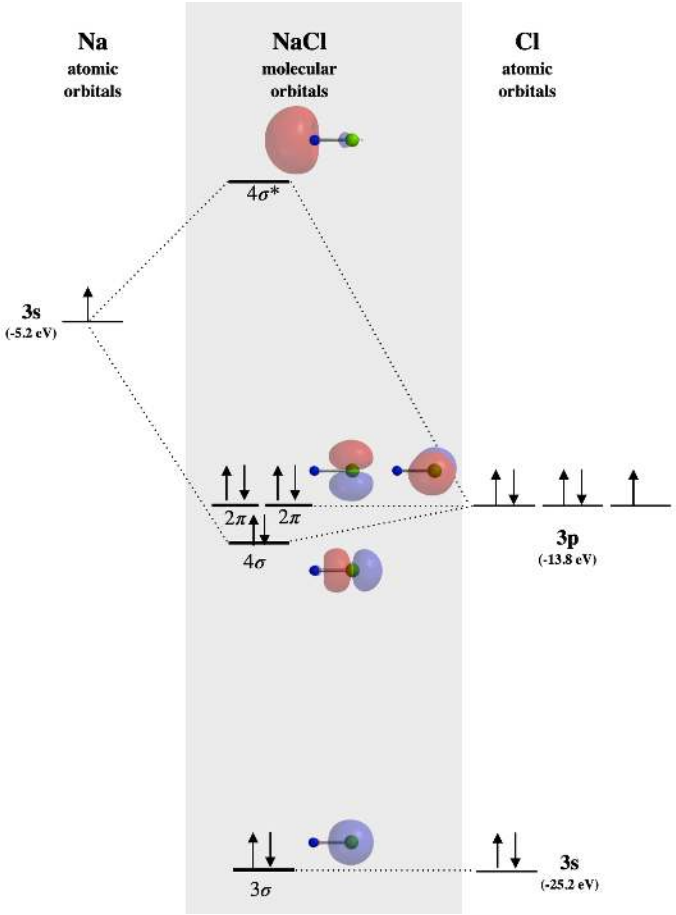


Figure **3.4.9.1**: The molecular orbital diagram for sodium chloride. Molecular orbital surfaces calculated using Spartan software indicate almost no covalent nature of bonding. (CC-BY-NC-SA, Kathryn Haas)

Exercise 3.4.9.1

Draw the molecular orbital diagram for **LiF**. Make sure to label all molecular orbitals appropriately, and specify whether they are mostly bonding, non-bonding, or antibonding. Identify the HOMO and LUMO. Sketch the approximate shapes of all orbitals.

Answer

We expect **LiF** to be an ionic compound because the energy difference in valence orbitals is at least 10-14 eV. (See Table 5.3.1) There are a variety of ways used to label molecular orbitals. In the figure below, we are using the convention of labeling each type of orbital with numbers starting from the lowest-energy orbitals. The 1σ orbital would be mostly F $1s$ in character and is not shown. The 2σ orbital is mostly non-bonding in nature, although it has a very small contribution from $2s$ of Li due to compatible symmetry. The 3σ orbital is slightly bonding but it is mostly F$2p$ in character. The two 1π orbitals are completely non-bonding. The $3\sigma^*$ orbital is antibonding.

- HOMO is 1π
- LUMO is $3\sigma^*$

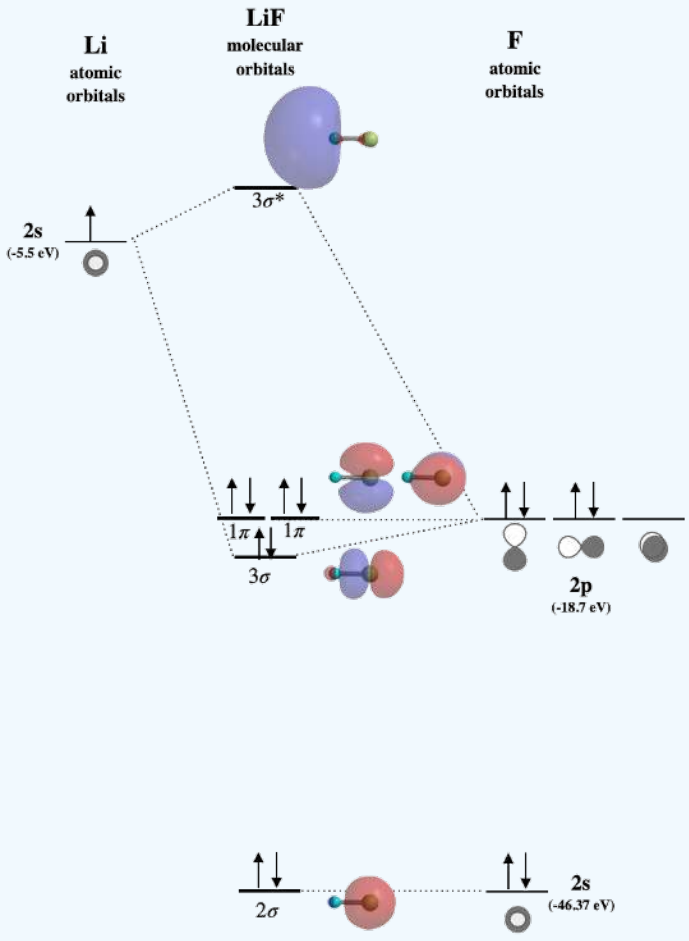


Figure for Exercise 3.4.9.1: Molecular orbital diagram for the ionic compund, LiF. (CC-BY-NC-SA, Kathryn Haas)

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CHAPTER OVERVIEW

Unit 4: Reactivity- Redox Chemistry

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4.1: Redox Reactions

One of the simplest chemical reactions involves the transfer of one or more electrons between two atoms. In the simple reaction:

$$2\,Na + Cl_2 \longrightarrow 2\,NaCl \tag{4.1.1}$$

we assume that sodium transfers an electron to chlorine creating the sodium ion and the chloride ion. We can write the two steps of this reaction as:

$$Na \longrightarrow Na^+ + e^- \tag{4.1.2}$$

and

$$Cl_2 + 2\,e^- \longrightarrow 2\,Cl^- \tag{4.1.3}$$

The first of these steps involves the loss of an electron and is called an oxidation reaction, while the second step involves the gain of an electron and is called a reduction reaction. The simple nemonic "LEO roars GER" or Loss of Electrons - Oxidation; Gain of Electrons - Reduction has been used by several generations of students to remember these definitions.

Oxidation and reduction reactions (usually called redox reactions) are important in biochemistry and important families of enzymes are called reductases or oxidases based on their reduction or oxidation catalysis. We recognize ethanol as common drinking alcohol, but most people don't realize that ethanol is generated by fermentation reactions that naturally take place in the intestines. The body always has a small amount of ethanol being transported across the intestine walls. As a result, the body has an enzyme to metabolize ethanol called ethanol oxidase. (The body didn't evolve to make ethanol oxidase to compensate for the consumption of fermented beverages like beer and wine since they are relatively recent creations on an evolutionary time scale. Ethanol oxidase is present in the body because it had to be there to compensate for the background ethanol.)

Redox chemistry also forms the basis of corrosion chemistry and battery chemistry (electrochemistry). Simple electrochemical reactions are redox reactions. If we take a piece of zinc metal and put it into a beaker of HCl, we will quickly notice the formation of bubbles on the surface of the zinc. Were we to leave the zinc in the acid for several minutes, we'd easily observe that the zinc is being dissolved while a gas is being liberated. This process is illustrated below: The reaction taking place here is obviously:

$$Zn + 2\,H^+ \longrightarrow Zn^{2+} + H_2 \tag{4.1.4}$$

In this reaction, the hydrogen ions are being reduced while the zinc is being oxidized. A similar reaction may be observed if we place a zinc bar into a solution containing copper sulfate. Here the reaction is:

$$Zn + Cu^{2+} \longrightarrow Cu + Zn^{2+} \tag{4.1.5}$$

Again the zinc is being oxidized while the copper is being reduced. Unlike the case of zinc in acid, the reaction will only continue until the copper has formed a film on the surface of the zinc, at which point the reaction stops since zinc ions are no longer able to escape to the solution.

Rules for assigning oxidation numbers:

1. The oxidation number of a free element = 0.
2. The oxidation number of a monatomic ion = charge on the ion.
3. The oxidation number of hydrogen = + 1 and rarely - 1.
4. The oxidation number of oxygen = - 2 and in peroxides - 1.
5. The sum of the oxidation numbers in a polyatomic ion = charge on the ion. Elements in group 1, 2, and aluminum are always as indicated on the periodic table.

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4.2: Definitions of Oxidation and Reduction

Oxidation and reduction in terms of electron transfer

The terms **oxidation** and **reduction** can be defined in terms of the addition or loss of electrons.

Oxidation and Reduction with respect to Electron Transfer

- Oxidation is **loss** of electrons
- Reduction is **gain** of electrons

In addition to "LEO roars GER" (loss of electrons - oxidation, gain of electron - reduction), another convenient acronym is :

OIL RIG

oxidation is loss reduction is gain

$$Na \longrightarrow Na^+ + e^- \tag{4.2.1}$$

- sodium is oxidized to the +1 oxidation state.

$$Cl_2 + 2\,e^- \longrightarrow 2\,Cl^- \tag{4.2.2}$$

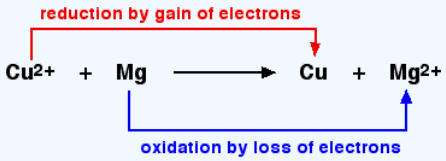
- chlorine is reduced to the -1 oxidation state.

Example 1

The equation below shows an obvious example of oxygen transfer in a simple redox reaction:

$$CuO + Mg \rightarrow Cu + MgO$$

Copper(II) oxide and magnesium oxide are both ionic compounds. If the above is written as an ionic equation, it becomes apparent that the oxide ions are spectator ions. Omitting them gives:



In the above reaction, magnesium reduces the copper(II) ion by transferring electrons to the ion and neutralizing its charge. Therefore, magnesium is a reducing agent. Another way of putting this is that the copper(II) ion is removing electrons from the magnesium to create a magnesium ion. The copper(II) ion is acting as an oxidizing agent.

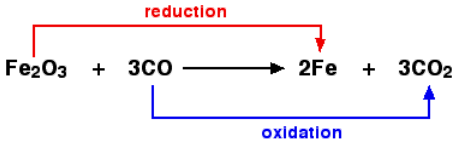
Oxidation and reduction in terms of oxygen transfer

The terms oxidation and reduction can be defined in terms of the adding or removing oxygen to a compound. While this is not the most robust definition, as discussed below, it is the easiest to remember.

Oxidation and Reduction with respect to Oxygen Transfer

- Oxidation is the **gain** of oxygen.
- Reduction is the **loss** of oxygen.

For example, in the extraction of iron from its ore:



An oxidizing agent is substance which oxidizes something else. In the above example, the iron(III) oxide is the oxidizing agent. A reducing agent reduces something else. In the equation, the carbon monoxide is the reducing agent.

- Oxidizing agents **give** oxygen to another substance.
- Reducing agents **remove** oxygen from another substance.

Oxidation and reduction in terms of hydrogen transfer

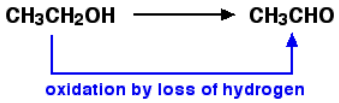
These are definitions are less commonly used, and you are most likely to encounter them in organic chemistry.

Oxidation and Reduction with respect to Hydrogen Transfer

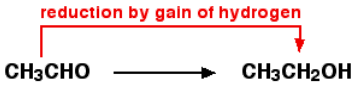
- Oxidation is the **loss** of hydrogen.
- Reduction is the **gain** of hydrogen.

Notice that these are exactly the opposite of the oxygen definitions (#1).

For example, ethanol can be oxidized to ethanal:



An oxidizing agent is required to remove the hydrogen from the ethanol. A commonly used oxidizing agent is potassium dichromate(VI) solution acidified with dilute sulfuric acid. Ethanal can also be reduced back to ethanol by adding hydrogen. A possible reducing agent is sodium tetrahydridoborate, $NaBH_4$. Again the equation is too complicated to consider at this point.



More precise definitions of oxidizing and reducing agents are

- Oxidizing agents **add** oxygen to another substance or **remove** hydrogen from it.
- Reducing agents **remove** oxygen from another substance or **add** hydrogen to it.

Summary

Confusion can result from trying to learn both the definitions of oxidation and reduction in terms of electron transfer and the definitions of oxidizing and reducing agents in the same terms. The following thought pattern can be helpful:

- An oxidizing agent oxidizes something else.
- Oxidation is loss of electrons (OIL RIG).
- Therefore, an oxidizing agent takes electrons from that other substance.
- Therefore, an oxidizing agent must gain electrons.

Here is another mental exercise:

- An oxidizing agent oxidizes something else.
- Therefore, the oxidizing agent must be reduced.
- Reduction is gain of electrons (OIL RIG).
- Therefore, an oxidizing agent must gain electrons.

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4.3: Oxidation Numbers and Redox Reactions

Redox reactions may involve proton transfers, electron transfers, and other bond-breaking and bond-making processes. As a result, the equations involved are can be more difficult to interpret and balance than those describing acid-base reactions. To recognize redox reactions, we must be able to identify when a species is oxidized or reduced; to do this we assign assign **oxidation numbers** to each atom in a reaction. Then, we compare the oxidation states of eac atom on the reactants side and to the atoms on the products side. When changes occur, we know a readox reaction has taken place.

$$\overset{0}{\mathrm{Cu}} + 2\overset{+5\ -2}{\mathrm{NO_3^-}} + 4\overset{+1\ -2}{\mathrm{H_3O^+}} \rightarrow \overset{+1}{\mathrm{Cu^{2+}}} + 2\overset{+5\ -2}{\mathrm{NO_2}} + 6\ \overset{+1\ -2}{\mathrm{H_2O}}$$

In the reaction above, the nitrogen in the NO_3^- ion is assigned an oxidation number of +5, and each oxygen is assigned an oxidation number of –2. This assignment corresponds to the nitrogen having lost five valence electrons to the more electronegative oxygen atoms. The nitrogen in the NO_2 ion has an oxidation number of + 4, which corresponds to the loss of four valence electrons to the more electronegative oxygen atoms. The nitrogen atom may be thought of as having one valence electron for itself, that is, one more electron than it had in NO_3^-. Through this reaction, nitrogen gains one electron in going from NO_3^- to NO_2, and we say nitrogen is reduced by the reaction.

In the same reaction, the oxidation number of copper increased from 0 to +2; we say that copper is oxidized by the reaction and lost two electrons. The nitrogen was reduced by electrons donated by copper, and so copper was the reducing agent. Copper was oxidized because its electrons were accepted by an oxidizing agent, nitrogen (or nitrate ion).

A word of caution: Although they are useful and necessary for recognizing redox reactions, oxidation numbers are a highly artificial device. The nitrogen atom in NO_3^- does not really have a +5 charge which can be reduced to +4 in NO_2. Instead, there are covalent bonds and electron-pair sharing between nitrogen and oxygen in both species, and nitrogen has certainly not lost its valence electrons entirely to oxygen. Even though this may (and indeed should) make you suspicious of the validity of oxidation numbers, they are undoubtedly a useful tool for spotting electron-transfer processes. So long as they are used for that purpose only, and not taken to mean that atoms in covalent species actually have the large charges oxidation numbers often imply, their use is quite valid.

The general rules for oxidation numbers are seen below, taken from the following page in the Analytical Chemistry Core Textbook: Oxidation States

Rules for Assigning Oxidation Numbers

- The oxidation state of an uncombined element is zero. This applies regardless of the structure of the element: Xe, Cl_2, S_8, and large structures of carbon or silicon each have an oxidation state of zero. (Since atoms of the same element always form pure covalent bonds, they share electrons equally, neither losing nor gaining, e.g., Cl_2.)
- The sum of the oxidation states of all the atoms or ions in a neutral compound is zero. (When an electron is lost by one atom (+1 contribution to oxidation number), the same electron must be gained by another atom (–1 contribution to oxidation number).)
- The sum of the oxidation states of all the atoms in an ion is equal to the charge on the ion.
- The more electronegative element in a substance is assigned a negative oxidation state. The less electronegative element is assigned a positive oxidation state. Remember that electronegativity is greatest at the top-right of the periodic table and decreases toward the bottom-left.

- Some elements almost always have the same oxidation states in their compounds:

Element	Usual oxidation state	Exceptions
Group 1 metals	Always +1	
Group 2 metals	Always +2	
Oxygen	Usually -2	Peroxides and F_2O (see below)
Hydrogen	Usually +1	Metal hydrides (-1) (see below)
Fluorine	Always -1	
Chlorine	usually -1	Compounds with O or F (see below)

Exceptions:

Hydrogen in the metal hydrides: Metal hydrides include compounds like sodium hydride, NaH. Here the hydrogen exists as a hydride ion, H^-. The oxidation state of a simple ion like hydride is equal to the charge on the ion—in this case, -1.

Alternatively, the sum of the oxidation states in a neutral compound is zero. Because Group 1 metals always have an oxidation state of +1 in their compounds, it follows that the hydrogen must have an oxidation state of -1 (+1 -1 = 0).

Oxygen in peroxides: Peroxides include hydrogen peroxide, H_2O_2. This is an electrically neutral compound, so the sum of the oxidation states of the hydrogen and oxygen must be zero.

Because each hydrogen has an oxidation state of +1, each oxygen must have an oxidation state of -1 to balance it.

Oxygen in F_2O: The deviation here stems from the fact that oxygen is less electronegative than fluorine; the fluorine takes priority with an oxidation state of -1. Because the compound is neutral, the oxygen has an oxidation state of +2.

Chlorine in compounds with fluorine or oxygen: Because chlorine adopts such a wide variety of oxidation states in these compounds, it is safer to simply remember that its oxidation state is *not* -1, and work the correct state out using fluorine or oxygen as a reference.

✔ Example 4.3.1: Chromium

What is the oxidation state of chromium in Cr^{2+}?

Solution

For a simple ion such as this, the oxidation state equals the charge on the ion: +2 (by convention, the + sign is always included to avoid confusion)

What is the oxidation state of chromium in $CrCl_3$?

This is a neutral compound, so the sum of the oxidation states is zero. Chlorine has an oxidation state of -1 (no fluorine or oxygen atoms are present). Let **n** equal the oxidation state of chromium:

$$n + 3(-1) = 0$$

$$n = +3$$

The oxidation state of chromium is +3.

✔ Example 4.3.2: Chromium

What is the oxidation state of chromium in $Cr(H_2O)_6^{3+}$?

Solution

This is an ion and so the sum of the oxidation states is equal to the charge on the ion. There is a short-cut for working out oxidation states in complex ions like this where the metal atom is surrounded by electrically neutral molecules like water or ammonia.

The sum of the oxidation states in the attached neutral molecule must be zero. That means that you can ignore them when you do the sum. This would be essentially the same as an unattached chromium ion, Cr^{3+}. The oxidation state is +3.

What is the oxidation state of chromium in the dichromate ion, $Cr_2O_7^{2-}$?

The oxidation state of the oxygen is -2, and the sum of the oxidation states is equal to the charge on the ion. Don't forget that there are 2 chromium atoms present.

$$2n + 7(-2) = -2$$

$$n = +6$$

Example 4.3.3: Copper

What is the oxidation state of copper in $CuSO_4$?

Solution

Unfortunately, it isn't always possible to work out oxidation states by a simple use of the rules above. The problem in this case is that the compound contains two elements (the copper and the sulfur) with variable oxidation states.

In cases like these, some chemical intuition is useful. Here are two ways of approaching this problem:

- Recognize $CuSO_4$ as an ionic compound containing a copper ion and a sulfate ion, SO_4^{2-}. To form an electrically neutral compound, the copper must be present as a Cu^{2+} ion. The oxidation state is therefore +2.
- Recognize the formula as being copper(II) sulfate (the (II) designation indicates that copper is in a +2 oxidation state, as discussed below).

Problems

Exercise 4.3.1

Assign oxidation states to each atom in the reaction. Determine which species are the oxidizing and reducing agents.

$$2\,MnO_4^- + 5\,SO_2 + 6\,H_2O \longrightarrow 5\,SO_4^{2-} + 2\,Mn^{2+} + 4\,H_3O^+$$

Answer

The only atoms which change are Mn, from +7 to +2, a reduction, and S, from +4 to +6, an oxidation. The reaction is a redox process. SO_2 has been oxidized by MnO_4^-, and so $MnO_4^-$is the oxidizing agent. MnO_4^- has been reduced by SO_2, and so SO_2 is the reducing agent.

$$\overset{+7\ -2}{2MnO_4^-} + \overset{+4\ -2}{5SO_2} + \overset{+1\ -2}{6H_2O} \rightarrow \overset{+6\ -2}{5SO_4^{2-}} + \overset{+2}{2Mn^{2+}} + \overset{+1\ -2}{4H_3O^+}$$

Exercise 4.3.2

Assign oxidation states to each atom in the reaction. Determine which species are the oxidizing and reducing agents.

$$NH_4^+ + PO_4^{3-} \longrightarrow NH_3 + PO_4^{2-}$$

Answer

Oxidation numbers show that no redox has occurred. This is an acid-base reaction because a proton, but no electrons, has been transferred.

$$\overset{-3\,+1}{\mathrm{NH_4^+}} + \overset{+5\,-2}{\mathrm{PO_4^{3-}}} \rightarrow \overset{-3\,+1}{\mathrm{NH_3}} + \overset{+1\,+5\,-2}{\mathrm{HPO_4^{2-}}}$$

Exercise 4.3.3

Assign oxidation states to each atom in the reaction. Determine which species are the oxidizing and reducing agents.

$\mathbf{HClO + H_2S \longrightarrow H_3O^+ + Cl^- + S}$

Answer

H_2S has been oxidized, losing two electrons to form elemental S. Since H_2S donates electrons, it is the reducing agent. HClO accepts these electrons and is reduced to Cl^-. Since it accepts electrons, HClO is the oxidizing agent.

$$\overset{+1\,+1\,-2}{\mathrm{HClO}} + \overset{+1\,-2}{\mathrm{H_2S}} \rightarrow \overset{+1\,-2}{\mathrm{H_3O^+}} + \overset{-1}{\mathrm{Cl^-}} + \overset{0}{\mathrm{S}}$$

Exercise 4.3.4

Determine the Oxidation States of each element in the following reactions:

a. $\mathbf{Fe\,(s) + O_2\,(g) \longrightarrow Fe_2O_3\,(g)}$
b. $\mathbf{Fe^{2+}\,(aq)}$
c. $\mathbf{Ag\,(s) + H_2S \longrightarrow Ag_2S\,(g) + H_2\,(g)}$

Answer

A. **Fe** and $\mathbf{O_2}$ are free elements; therefore, they each have an oxidation state of 0 according to Rule #1. The product has a total oxidation state equal to 0, and following Rule #6, **O** has an oxidation state of -2, which means **Fe** has an oxidation state of +3. \
B. The oxidation state of **Fe** ions just corresponds to its charge since it is a single element species; therefore, the oxidation state is +2.
C. **Ag** has an oxidation state of 0, **H** has an oxidation state of +1 according to Rule #5, $\mathbf{H_2}$ has an oxidation state of 0, **S** has an oxidation state of -2 according to Rule #7, and hence **Ag** in $\mathbf{Ag_2S}$ has an oxidation state of +1.

Exercise 4.3.5

Determine the oxidation states of the phosphorus atom bold element in each of the following species:

a. $\mathbf{Na_3PO_3}$
b. $\mathbf{H_2PO_4^-}$

Answer

A. The oxidation numbers of **Na** and **O** are +1 and -2. Because sodium phosphite is neutral species, the sum of the oxidation numbers must be zero. Letting *x* be the oxidation number of phosphorus, 0= 3(+1) + *x* + 3(-2). *x*=oxidation number of P= +3.
B. Hydrogen and oxygen have oxidation numbers of +1 and -2. The ion has a charge of -1, so the sum of the oxidation numbers must be -1. Letting *y* be the oxidation number of phosphorus, -1= *y* + 2(+1) +4(-2), *y*= oxidation number of P= +5.

Exercise 4.3.6

Determine which element is oxidized and which element is reduced in the following reactions (be sure to include the oxidation state of each):

a. $\mathbf{Zn + 2\,H^+ \longrightarrow Zn^{2+} + H_2}$
b. $\mathbf{2\,Al + 3\,Cu^{2+} \longrightarrow 2\,Al^{3+} + 3\,Cu}$

c. $CO_3^{2-} + 2H^+ \longrightarrow CO_2 + H_2O$

Answer

A. Zn is oxidized (Oxidation number: 0 → +2); H^+ is reduced (Oxidation number: +1 → 0)

B. Al is oxidized (Oxidation number: 0 → +3); Cu^{2+} is reduced (+2 → 0)

C. This is not a redox reaction because each element has the same oxidation number in both reactants and products: O= -2, H= +1, C= +4.

? Exercise 4.3.7

Determine what is the oxidizing and reducing agents in the following reaction.

$$Zn + 2H^+ \longrightarrow Zn^{2+} + H_2$$

Answer

The oxidation state of **H** changes from +1 to 0, and the oxidation state of **Zn** changes from 0 to +2. Hence, **Zn** is oxidized and acts as the *reducing agent*. H^+ ion is reduced and acts as the *oxidizing agent*.

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4.4: Oxidation Numbers and Formal Charge

An Alternative Method to Assign Oxidation Numbers

In addition to using the rules set out in 4.3 Oxidation Numbers and Redox Reactions, we can obtain oxidation numbers using electronegativity. Starting with a complete Lewis structure, electrons from each covalent bond are arbitrarily assigned to the more electronegative atom in the bond. If two like atoms are joined, each atom is assigned half the bonding electrons.(Note: This is in contrast to the Formal Charge which divides each bonding pair equally without concern for which atom may be more electronegative.) When all bonding electrons in a structure have been assigned, the charge remaining on each atom is said to be its oxidation number.

The Oxidation Number is defined by the relationship:

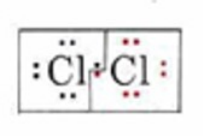
Oxidation Number = [*number of valence electrons in an isolated atom*] - [number of assigned electrons]

Example 4.4.1: Oxidation Number

Determine the oxidation number of each atom in the formulas Cl_2.

Solution:

Begin by drawing a Lewis diagram:



In the Lewis diagram, electrons have been color coded to indicate the atom from which they came originally. The boxes enclose electrons assigned to a given atom by the rules for determining oxidation number.

Since the bond in Cl_2 is purely covalent and the electrons are shared equally, one electron from the bond is assigned to each Cl, giving the same number of valence electrons (7) as a neutral Cl atom. Thus neither atom has lost any electrons, and the oxidation number is 0. This is indicated by writing a 0 above the symbol for chlorine in the formula

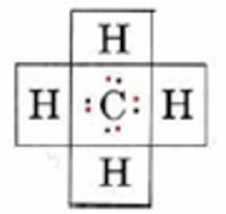
$$\overset{0}{Cl}_2$$

Example 4.4.2

Determine the oxidation number of each atom in the formula CH_4.

Solution:

Begin by drawing a Lewis diagram:



In the Lewis diagram, electrons have been color coded to indicate the atom from which they came originally. The boxes enclose electrons assigned to a given atom by the rules for determining oxidation number.

Since C is more electronegative than H, the pair of electrons in each C—H bond is assigned to C. Therefore each H has *lost* the one valence electron it originally had, giving an oxidation number of +1. The C atom has *gained* four electrons, giving it a negative charge and hence an oxidation number of – 4:

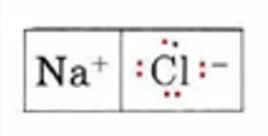
$$\overset{-4}{C}\overset{+1}{H}_4$$

Example 4.4.3

Determine the oxidation number of each atom in the formula NaCl.

Solution:

Begin by drawing a Lewis diagram:



In the Lewis diagram, electrons have been color coded to indicate the atom from which they came originally. The boxes enclose electrons assigned to a given atom by the rules for determining oxidation number.

In NaCl each Na atom has lost an electron to form an Na^+ ion, and each Cl atom has gained an electron to form Cl^-. The oxidation numbers therefore correspond to the ionic charges:

$$\overset{+1}{Na}\ \overset{-1}{Cl}$$

Example 4.4.4

Determine the oxidation number of each atom in the formula OF_2.

Solution:

Begin by drawing a Lewis diagram:



In the Lewis diagram, electrons have been color coded to indicate the atom from which they came originally. The boxes enclose electrons assigned to a given atom by the rules for determining oxidation number.

Since F is more electronegative than O, the bonding pairs are assigned to F in oxygen difluoride (OF_2). The O is left with four valence electrons, and each F has eight. The oxidation numbers are

$$\overset{+2}{O}\ \overset{-1}{F_2}$$

Example 4.4.5

Determine the oxidation number of each atom in the formula H_2O_2.

Solution:

Begin by drawing a Lewis diagram:



In the Lewis diagram, electrons have been color coded to indicate the atom from which they came originally. The boxes enclose electrons assigned to a given atom by the rules for determining oxidation number.

In Hydrogen peroxide (H_2O_2) the O—H bond pairs are assigned to the more electronegative O's, but the O—O bond is purely covalent, and the electron pair is divided equally. This gives each O seven electrons, a gain of 1 over the neutral atom. The oxidation numbers are

$$\overset{+1}{H_2}\ \overset{-1}{O_2}$$

Formal Charge

The method of assigning oxidation numbers that is given above bares some similarity to the process of assigning formal charges on a Lewis structure. Oxidation states and formal charge are both somewhat artificial devices that exists in the minds of chemists (not within the molecules, themselves) to help keep track of electrons in their bonding configurations. However, their assumptions are different and should not be confused. When assigning *formal charges*, **all of the bonding electrons are divided equally between atoms in the bond**; we assume the bonds are 100% *covalent* in nature. When assigning *oxidation numbers*, **all of the bonding electrons are assigned to the more electronegative atom in the bond**; we assume that the bonds are 100% *ionic* in nature. In both cases, the formal charges and oxidaton nubmers of all atoms in a molecule or ion must sum to the charge on the molecule/ion.

The Formal Charge is defined by the relationship:

Formal Charge = [*number of valence electrons in an isolated atom*] - [(*number of lone pair electrons*) + ½ (*number of bonding electrons*)]

With the definitions above, we can calculate the Formal Charge on the thiocyanate Ion, SCN^-:

Table **4.4.1**

	**S**	**C**	**N**
Valence electrons	6	4	5
Lone pair electrons	6	0	2
Shared electrons (bonds)	2 (1)	8 (4)	6 (3)
Formal Charge =	6 - (6 + ½·2)	4 - (0 + ½·8)	5 - (2 + ½·6)
Formal Charge	-1	0	0

Problems

? Exercise 4.4.1

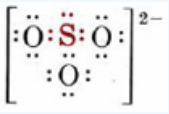
Determine the oxidation number of each atom in the formula SO_3^{2-}.

Answer

In SO_3^{2-} the S—O bond pairs are assigned to the more electronegative O's. This gives each O eight electrons, a gain of 2 over the neutral atom. The S is left with two valence electrons The oxidation numbers are

$$\overset{+4}{S}\ \overset{-2}{O_3}$$

$$(+4) + (-2 \times 3) = -2 \qquad (4.4.1)$$



Exercise 4.4.2

Determine the oxidation number of each element in the formula NaClO.

Answer

In NaClO, the O is the most electronegative atom, followed by Cl. The O is assigned eight electrons (a gain of two), chlorine is assigned six electrons (a loss of one), and sodium has lost two electrons.

$$\overset{+1}{\mathrm{Na}}\ \overset{+1}{\mathrm{Cl}}\ \overset{-2}{\mathrm{O}}$$

$$(+1)+(-1)+(-2)=0 \tag{4.4.2}$$



Exercise 4.4.3

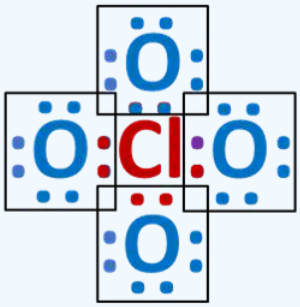
Determine the oxidation number of each element in the formula ClO_4^-.

Answer

In ClO_4^- O is the more electronegative atom so each O is assigned eight electrons (a gain of two electrons). The Cl is assigned no electrons (a loss of seven electrons).

$$\overset{+7}{\mathrm{Cl}}\ \overset{-2}{\mathrm{O}}_4$$

$$(+7)+(-2\times 4)=-1 \tag{4.4.3}$$



Exercise 4.4.4

Determine the oxidation number of each element in the formula MgH_2.

Answer

In MgH_2, H is the more electronegative atom so each is assigned two electrons (a gain of one electron) and Mg is assigned no electrons (a loss of two electrons)

$$\overset{+2}{\mathrm{Mg}}\ \overset{-1}{\mathrm{H}}_2$$

$$(+2)+(-1\times 2)=0 \tag{4.4.4}$$



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4.5: Balancing Redox Reactions

Oxidation-Reduction Reactions, or redox reactions, are reactions in which one reactant is oxidized and one reactant is reduced simultaneously. This module demonstrates how to balance various redox equations.

Identifying Redox Reactions

The first step in balancing any redox reaction is determining whether or not it is even an oxidation-reduction reaction. This requires that one and typically more species changing oxidation states during the reaction. To maintain charge neutrality in the sample, the redox reaction will entail both a reduction component and an oxidation components. These are often separated into independent two hypothetical **half-reactions** to aid in understanding the reaction. This requires identifying which element is oxidized and which element is reduced. For example, consider this reaction:

$$\mathrm{Cu\,(s) + 2\,Ag^{+}\,(aq)\ \rightarrow Cu^{2+}\,(aq) + 2\,Ag\,(s)}$$

The first step in determining whether the reaction is a redox reaction is to split the equation into two hypothetical *half-reactions*. Let's start with the half-reaction involving the copper atoms:

$$\mathrm{Cu\,(s)\ \rightarrow Cu^{2+}\,(aq)}$$

The oxidation state of copper on the left side is 0 because it is an element on its own. The oxidation state of copper on the right hand side of the equation is +2. The copper in this half-reaction is oxidized as the oxidation states increases from 0 in Cu to +2 in $\mathrm{Cu^{2+}}$. Now consider the silver atoms

$$\mathrm{2\,Ag^{+}\,(aq)\ \rightarrow 2\,Ag\,(s)}$$

In this half-reaction, the oxidation state of silver on the left side is a +1. The oxidation state of silver on the right is 0 because it is an pure element. Because the oxidation state of silver decreases from +1 to 0, this is the reduction half-reaction.

Consequently, this reaction is a redox reaction as both reduction and oxidation half-reactions occur (via the transfer of electrons, that are not explicitly shown in equations 2). Once confirmed, it often necessary to balance the reaction (the reaction in equation 1 is balanced already though), which can be accomplished in two ways because the reaction could take place in neutral, acidic or basic conditions.

Balancing Redox Reactions

Balancing redox reactions is slightly more complex than balancing standard reactions, but still follows a relatively simple set of rules. One major difference is the necessity to know the half-reactions of the involved reactants; a half-reaction table is very useful for this. Half-reactions are often useful in that two half reactions can be added to get a total net equation. Although the half-reactions must be known to complete a redox reaction, it is often possible to figure them out without having to use a half-reaction table. This is demonstrated in the acidic and basic solution examples. Besides the general rules for neutral conditions, additional rules must be applied for aqueous reactions in acidic or basic conditions.

One method used to balance redox reactions is called the **Half-Equation Method**. In this method, the equation is separated into two half-equations; one for oxidation and one for reduction.

Half-Equation Method to Balance redox Reactions in **Acidic** Aqueous Solutions

Each reaction is balanced by adjusting coefficients and adding $\mathrm{H_2O}$, $\mathrm{H^{+}}$, and $\mathrm{e^{-}}$ in this order:

1. Balance elements in the equation other than O and H.
2. Balance the oxygen atoms by adding the appropriate number of water ($\mathrm{H_2O}$) molecules to the opposite side of the equation.
3. Balance the hydrogen atoms (including those added in step 2 to balance the oxygen atom) by adding $\mathrm{H^{+}}$ ions to the opposite side of the equation.
4. Add up the charges on each side. Make them equal by adding enough electrons ($\mathrm{e^{-}}$) to the more positive side. (Rule of thumb: $\mathrm{e^{-}}$ and $\mathrm{H^{+}}$ are almost always on the same side.)

5. The e^- on each side must be made equal; if they are not equal, they must be multiplied by appropriate integers (the lowest common multiple) to be made the same.
6. The half-equations are added together, canceling out the electrons to form one balanced equation. Common terms should also be canceled out.

The equation can now be checked to make sure that it is balanced.

Half-Equation Method to Balance redox Reactions in **Basic** Aqueous Solutions

Option 1

If the reaction is being balanced in a basic solution, the above steps are modified with the the addition of one step:

7. Add sufficient OH^- ions to fully react with all H^+ ions in the equation. Add this quantity of OH^- ions to both sides of the equation. H^+ ions and OH^- ions combine to produce H_2O. Cancel out the common terms.

Option 2

If the reaction is being balanced in a basic solution, the above steps are modified. Each reaction is balanced by adjusting coefficients and adding OH^-, H_2O, and e^- in this order:

1. Balance elements in the equation other than O and H.
2. Balance the oxygen atoms by adding the appropriate number of hydroxide OH^- ions to the opposite side of the equation.
3. Balance the hydrogen atoms (including those added in step 2 to balance the oxygen atom) by adding H_2O to the opposite side of the equation.
4. Add up the charges on each side. Make them equal by adding enough electrons (e^-) to the more positive side. (Rule of thumb: e^- and H^+ are almost always on the same side.)
5. The e^- on each side must be made equal; if they are not equal, they must be multiplied by appropriate integers (the lowest common multiple) to be made the same.
6. The half-equations are added together, canceling out the electrons to form one balanced equation. Common terms should also be canceled out.

The equation can now be checked to make sure that it is balanced.

Neutral Conditions

The first step to balance any redox reaction is to separate the reaction into half-reactions. The substance being reduced will have electrons as reactants, and the oxidized substance will have electrons as products. (Usually all reactions are written as reduction reactions in half-reaction tables. To switch to oxidation, the whole equation is reversed and the voltage is multiplied by -1.) Sometimes it is necessary to determine which half-reaction will be oxidized and which will be reduced. In this case, whichever half-reaction has a higher reduction potential will by reduced and the other oxidized.

Example 4.5.1: Balancing in a Neutral Solution

Balance the following reaction

$$Cu^+(aq) + Fe(s) \rightarrow Fe^{3+}(aq) + Cu(s)$$

Solution

Step 1: Separate the half-reactions. By searching for the reduction potential, one can find two separate reactions:

$$Cu^+(aq) + e^- \rightarrow Cu(s)$$

and

$$Fe^{3+}(aq) + 3e^- \rightarrow Fe(s)$$

The copper reaction has a higher potential and thus is being reduced. Iron is being oxidized so the half-reaction should be flipped. This yields:

$$Cu^{+}(aq) + e^{-} \rightarrow Cu(s)$$

and

$$Fe(s) \rightarrow Fe^{3+}(aq) + 3e^{-}$$

Step 2: Balance the electrons in the equations. In this case, the electrons are simply balanced by multiplying the entire $Cu^{+}(aq) + e^{-} \rightarrow Cu(s)$ half-reaction by 3 and leaving the other half reaction as it is. This gives:

$$3Cu^{+}(aq) + 3e^{-} \rightarrow 3Cu(s)$$

and

$$Fe(s) \rightarrow Fe^{3+}(aq) + 3e^{-}$$

Step 3: Adding the equations give:

$$3Cu^{+}(aq) + 3e^{-} + Fe(s) \rightarrow 3Cu(s) + Fe^{3+}(aq) + 3e^{-}$$

The electrons cancel out and the balanced equation is left.

$$3Cu^{+}(aq) + Fe(s) \rightarrow 3Cu(s) + Fe^{3+}(aq)$$

Acidic Conditions

Acidic conditions usually implies a solution with an excess of H^{+} concentration, hence making the solution acidic. The balancing starts by separating the reaction into half-reactions. However, instead of immediately balancing the electrons, balance all the elements in the half-reactions that are not hydrogen and oxygen. Then, add H_2O molecules to balance any oxygen atoms. Next, balance the hydrogen atoms by adding protons (H^{+}). Now, balance the *charge* by adding electrons and scale the electrons (multiply by the lowest common multiple) so that they will cancel out when added together. Finally, add the two half-reactions and cancel out common terms.

Example 4.5.2: Balancing in a Acid Solution

Balance the following redox reaction in acidic conditions.

$$Cr_2O_7^{2-}(aq) + HNO_2(aq) \rightarrow Cr^{3+}(aq) + NO_3^{-}(aq)$$

Solution

Step 1: Separate the half-reactions. The table provided does not have acidic or basic half-reactions, so just write out what is known.

$$Cr_2O_7^{2-}(aq) \rightarrow Cr^{3+}(aq)$$

$$HNO_2(aq) \rightarrow NO_3^{-}(aq)$$

Step 2: Balance elements other than O and H. In this example, only chromium needs to be balanced. This gives:

$$Cr_2O_7^{2-}(aq) \rightarrow 2Cr^{3+}(aq)$$

and

$$HNO_2(aq) \rightarrow NO_3^{-}(aq)$$

Step 3: Add H_2O to balance oxygen. The chromium reaction needs to be balanced by adding 7 H_2O molecules. The other reaction also needs to be balanced by adding one water molecule. This yields:

$$Cr_2O_7^{2-}(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$$

and

$$HNO_2(aq) + H_2O(l) \rightarrow NO_3^{-}(aq)$$

Step 4: Balance hydrogen by adding protons (H^+). 14 protons need to be added to the left side of the chromium reaction to balance the 14 (2 per water molecule * 7 water molecules) hydrogens. 3 protons need to be added to the right side of the other reaction.

$$14\,H^+(aq) + Cr_2O_7{}^{2-}(aq) \rightarrow 2\,Cr^{3+}(aq) + 7\,H_2O(l)$$

and

$$HNO_2(aq) + H_2O(l) \rightarrow 3\,H^+(aq) + NO_3{}^-(aq)$$

Step 5: Balance the charge of each equation with electrons. The chromium reaction has (14+) + (2-) = 12+ on the left side and (2 * 3+) = 6+ on the right side. To balance, add 6 electrons (each with a charge of -1) to the left side:

$$6\,e^- + 14\,H^+(aq) + Cr_2O_7{}^{2-}(aq) \rightarrow 2\,Cr^{3+}(aq) + 7\,H_2O(l)$$

For the other reaction, there is no charge on the left and a (3+) + (-1) = 2+ charge on the right. So add 2 electrons to the right side:

$$HNO_2(aq) + H_2O(l) \rightarrow 3\,H^+(aq) + NO_3{}^-(aq) + 2\,e^-$$

Step 6: Scale the reactions so that the electrons are equal. The chromium reaction has $6e^-$ and the other reaction has $2e^-$, so it should be multiplied by 3. This gives:

$$6\,e^- + 14\,H^+(aq) + Cr_2O_7{}^{2-}(aq) \rightarrow 2\,Cr^{3+}(aq) + 7\,H_2O(l)\cdot$$

and

$$3\times\left[HNO_2(aq) + H_2O(l) \rightarrow 3\,H^+(aq) + NO_3{}^-(aq) + 2\,e^-\right]$$
$$3\,HNO_2(aq) + 3\,H_2O(l) \rightarrow 9\,H^+(aq) + 3\,NO_3{}^-(aq) + 6\,e^-$$

Step 7: Add the reactions and cancel out common terms.

$$\begin{aligned} &3\,HNO_2(aq) + 3\,H_2O(l) \rightarrow 9\,H^+(aq) + 3\,NO_3{}^-(aq) + 6\,e^- \\ &6\,e^- + 14\,H^+(aq) + Cr_2O_7{}^{2-}(aq) \rightarrow 2\,Cr^{3+}(aq) + 7\,H_2O(l) \\ \hline &3\,HNO_2(aq) + \cancel{3\,H_2O(l)} + \cancel{6e^-} \\ &\quad + 14\,H^+(aq) + Cr_2O_7{}^{2-}(aq) \rightarrow 9\,H^+(aq) + 3\,NO_3{}^-(aq) + \cancel{6e^-} \\ &\qquad\qquad + 2\,Cr^{3+}(aq) + \cancel{7}^{4}H_2O(l) \end{aligned}$$

The electrons cancel out as well as 3 water molecules and 9 protons. This leaves the balanced net reaction of:

$$3\,HNO_2(aq) + 5\,H^+(aq) + Cr_2O_7{}^{2-}(aq) \rightarrow 3\,NO_3{}^-(aq) + 2\,Cr^{3+}(aq) + 4\,H_2O(l)$$

Example 4.5.3

Balance the following redox reaction in acidic conditions.

$$\overset{+5\,-2}{IO_3^-} + \overset{+4\,-2}{SO_2} + \overset{+1\,-2}{H_2O} \rightarrow \overset{0}{I_2} + \overset{+6\,-2}{SO_4^{2-}} + \overset{+1\,-2}{H_3O^+} \quad (1)$$

Solution

Step 1: Separate the half-reactions. The table provided does not have acidic or basic half-reactions, so just write out what is known.

$$SO_2 \longrightarrow SO_4{}^{2-}$$

$$IO^{3-} \longrightarrow I_2$$

Step 2: Balance elements other than O and H.

$$SO_2 \longrightarrow SO_4{}^{2-}$$

$$2\,IO_3{}^- \longrightarrow I_2$$

Step 3: Add H_2O to balance oxygen.

$$SO_2 + 2H_2O \longrightarrow SO_4^{2-}$$

$$2IO_3^- \longrightarrow I_2 + 6H_2O$$

Step 4: Balance hydrogen by adding protons (H^+).

$$SO_2 + 2H_2O \longrightarrow SO_4^{2-} + 2H^+$$

$$12H^+ + 2IO_3^- \longrightarrow I_2 + 6H_2O$$

Step 5: Balance the charge of each equation with electrons.

$$SO_2 + 2H_2O \longrightarrow SO_4^{2-} + 2H^+ + 2e^-$$

(The total charge on the left side was 0, but on the right it was – 2 + 4 = +2. Therefore $2e^-$ were needed on the right.)

$$10e^- + 12H^+ + 2IO_3^- \longrightarrow I_2 + 6H_2O$$

(The total charge on the left was 12 - 2 = +10, but on the right it was 0. Therefore $10e^-$ were needed on the left.)

Step 6: Scale the reactions so that the electrons are equal.

Since only 2 electrons are donated in the oxidation half-equation, while 10 are required by the reduction, the oxidation must occur 5 times for each reduction. That is, both sides of the oxidation half-equation must be multiplied by 5

$$5SO_2 + 10H_2O \longrightarrow 5SO_4^{2-} + 20H^+ + \cancel{10e^-}$$

$$\cancel{10e^-} + 12H^+ + 2IO_3^- \longrightarrow I_2 + 6H_2O$$

Step 7: Add the reactions and cancel out common terms.

$$5SO_2 + 4H_2O + 2IO_3^- \longrightarrow 5SO_4^{2-} + 8H^+ + I_2$$

Note that when the half-equations were summed, the number of electrons was the same on both sides, and so no free electrons (which could not exist in aqueous solution) appear in the final result. It also would be more accurate to write H_3O^+ instead of H^+ for the hydronium ion. This can be done by adding $8H_2O$ to both sides of the equation:

$$5SO_2 + 12H_2O + 2IO_3^- \longrightarrow 5SO_4^{2-} + 8H_3O^+ + I_2$$

(On the right, the $8H_2O$ molecules are protonated to $8H_3O^+$. It is also a good idea at this point to check that all atoms, as well as the electrical charges, balance.

Basic Conditions

Bases dissolve into OH^- ions in solution; hence, balancing redox reactions in basic conditions requires OH^-. Follow the same steps as for acidic conditions. The only difference is adding hydroxide ions to each side of the net reaction to balance any H^+. OH^- and H^+ ions on the same side of a reaction should be added together to form water. Again, any common terms can be canceled out.

Example 4.5.4: Balancing in Basic Solution

Balance the following redox reaction in basic conditions.

$$Ag(s) + Zn^{2+}(aq) \rightarrow Ag_2O(aq) + Zn(s)$$

Solution

Go through all the same steps as if it was in acidic conditions.

Step 1: Separate the half-reactions.

$$Ag(s) \rightarrow Ag_2O(aq)$$

$$Zn^{2+}(aq) \rightarrow Zn(s)$$

Step 2: Balance elements other than O and H.

$$2\,Ag\,(s)\ \rightarrow Ag_2O\,(aq)$$

$$Zn^{2+}\,(aq)\ \rightarrow Zn\,(s)$$

Step 3: Add H_2O to balance oxygen.

$$H_2O\,(l) + 2\,Ag\,(s)\ \rightarrow Ag_2O\,(aq)$$

$$Zn^{2+}\,(aq)\ \rightarrow Zn\,(s)$$

Step 4: Balance hydrogen with protons.

$$H_2O\,(l) + 2\,Ag\,(s)\ \rightarrow Ag_2O\,(aq) + 2\,H^+\,(aq)$$

$$Zn^{2+}\,(aq)\ \rightarrow Zn\,(s)$$

Step 5: Balance the charge with e^-.

$$H_2O\,(l) + 2\,Ag\,(s)\ \rightarrow Ag_2O\,(aq) + 2\,H^+\,(aq) + 2\,e^-$$

$$Zn^{2+}\,(aq) + 2\,e^-\ \rightarrow Zn\,(s)$$

Step 6: Scale the reactions so that they have an equal amount of electrons. In this case, it is already done.

Step 7: Add the reactions and cancel the electrons.

$$H_2O\,(l) + 2\,Ag\,(s) + Zn^{2+}\,(aq)\ \rightarrow Zn\,(s) + Ag_2O\,(aq) + 2\,H^+(aq)\,.$$

Step 8: Add OH^- to balance H^+. There are 2 net protons in this equation, so add 2 OH^- ions to each side.

$$H_2O\,(l) + 2\,Ag\,(s) + Zn^{2+}\,(aq) + 2\,OH^-\,(aq)\ \rightarrow Zn\,(s) + Ag_2O\,(aq) + 2\,H^+\,(aq) + 2\,OH^-(aq)\,.$$

Step 9: Combine OH^- ions and H^+ ions that are present on the same side to form water.

$$\cancel{H2O(l)} + 2\,Ag\,(s) + Zn^{2+}\,(aq) + 2\,OH^-\,(aq) \longrightarrow Zn\,(s) + Ag_2O\,(aq) + \cancel{2}\,H_2O\,(l)$$

Step 10: Cancel common terms.

$$2\,Ag\,(s) + Zn^{2+}\,(aq) + 2\,OH^-\,(aq)\ \rightarrow Zn\,(s) + Ag_2O\,(aq) + H_2O\,(l)$$

Example 4.5.5

Balance the following redox reaction in basic conditions.

$$\overset{+7\ -2}{2MnO_4^-} + \overset{-2\ +1\ -2\ +1}{CH_3OH} + \rightarrow \overset{+4\ -2}{MnO_2} + \overset{+1\ -2}{H_2O} + \overset{+1\ +2\ -2\ -2}{HCOO^-} \quad \overset{+2}{2Mn^{2+}} + \overset{-2\ +1}{OH^-} \quad (2)$$

Solution

Step 1: Separate the half-reactions.

$$CH_3OH \longrightarrow HCOO^-$$

$$MnO_4^- \longrightarrow MnO_2$$

Step 2: Balance elements other than O and H.

(No change)

$$CH_3OH \longrightarrow HCOO^-$$

$$MnO_4^- \longrightarrow MnO_2$$

Step 3: Add OH^- to balance oxygen.

$$CH_3OH + OH^- \longrightarrow HCOO^-$$

$$MnO_4^- \longrightarrow MnO_2 + 2\,OH^-$$

Step 4: Balance hydrogen with H_2O.

$$CH_3OH + 5\,OH^- \longrightarrow HCOO^- + 4\,H_2O$$

(Four hydrogens were needed on the right, and so 4 water molecules were added on the right and 4 hydroxide ions on the left.)

$$MnO_4^- + 2\,H_2O \longrightarrow MnO_2 + 4\,OH^-$$

(Two hydrogens were needed on the left, and so 2 water molecules were added on the left and 2 hydroxide ions were added on the right. Note that the added hydroxide ions are to maintain the balance of oxygen atoms.)

Step 5: Balance the charge with e^-.

$$CH_3OH + 5\,OH^- \longrightarrow HCOO^- + 4\,H_2O + 4\,e^-$$

(The total charge on the left was -5, but on the right it was -1, and so $4e^-$ were added on the right.)

$$MnO_4^- + 2\,H_2O + 3\,e^- \longrightarrow MnO_2 + 4\,OH^-$$

(The total charge on the left was -1, but on the right it was -4, and so $3e^-$ were added on the left.)

Step 6: Scale the reactions so that they have an equal amount of electrons.

Multiplying the oxidation half-equation by 3 and the reduction half-equation by 4 adjusts each so it involves $12e^-$.

$$3\,CH_3OH + 15\,OH^- \longrightarrow 3\,HCOO^- + 12\,H_2O + 12\,e^-$$

$$4\,MnO_4^- + 8\,H_2O + 12\,e^- \longrightarrow 4\,MnO_2 + 16\,OH^-$$

Step 7: Add the reactions and cancel the electrons.

$$3\,CH_3OH + 4\,MnO_4^- \longrightarrow 3\,HCOO^- + 4\,MnO_2 + OH^-$$

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4.6: Balancing Redox Reactions - Exercises

Oxidation-Reduction or "redox" reactions occur when elements in a chemical reaction gain or lose electrons, causing an increase or decrease in oxidation numbers. The Half Equation Method is used to balance these reactions.

In a redox reaction, one or more element becomes oxidized, and one or more element becomes reduced. Oxidation is the loss of electrons whereas reduction is the gain of electrons. An easy way to remember this is to think of the charges: an element's charge is reduced if it gains electrons (an acronym to remember the difference is LEO = Lose Electron Oxidation & GER = Gain Electron Reduction). Redox reactions usually occur in one of two environments: acidic or basic. In order to balance redox equations, understanding oxidation states is necessary.

Some points to remember when balancing redox reactions:

- The equation is separated into two half-equations, one for oxidation, and one for reduction.
- The equation is balanced by adjusting coefficients and adding H_2O, H^+, and e^- in this order:
  1. Balance the atoms in the equation, apart from O and H.
  2. To balance the Oxygen atoms, add the appropriate number of water (H_2O) molecules to the other side.
  3. To balance the Hydrogen atoms (including those added in step 2), add H^+ ions.
  4. Add up the charges on each side. They must be made equal by adding enough electrons (e^-) to the more positive side.
- The e^- on each side must be made equal; if they are not equal, they must be multiplied by appropriate integers to be made the same.
- The half-equations are added together, cancelling out the electrons to form one balanced equation. Cancel out as much as possible.
- (If the equation is being balanced in a basic solution, the appropriate number of OH^- must be added to turn the remaining H^+ into water molecules)
- The equation can now be checked to make sure it is balanced.

Problems

Exercise 4.6.1

Balance this reaction

$$\mathrm{MnO_4^- + I^- \longrightarrow I_2 + Mn^{2+}}$$

Answer

Steps to balance:

Step 1: Separate the half-reactions that undergo oxidation and reduction.

Oxidation:

$$\mathrm{I^- \longrightarrow I_2}$$

This is the oxidation half because the oxidation state changes from -1 on the left side to 0 on the right side. This indicates a gain in electrons.

Reduction:

$$\mathrm{MnO_4^- \longrightarrow Mn^{2+}}$$

This is the reduction half because the oxidation state changes from +7 on the left side to +2 on the right side. This indicates a reduction in electrons.

Step 2: In order to balance this half reaction we must start by balancing all atoms other than any Hydrogen or Oxygen atoms.

Oxidation:

$$2\,I^- \longrightarrow I_2$$

In order to balance the oxidation half of the reaction you must first add a 2 in front of the **I** on the left hand side so there is an equal number of atoms on both sides.

Reduction:

$$MnO_4^- \longrightarrow Mn^{2+}$$

For the reduction half of the reaction, you can notice that all atoms other than Hydrogen and Oxygen are already balanced because there is one manganese atom on both sides of the half reaction.

Step 3: Balance Oxygen atoms by adding H_2O to the side of the equation that needs Oxygen. Once you have completed this step add H^+ to the side of the equation that lacks **H** atoms necessary to be balanced.

Oxidation:

$$2\,I^- \longrightarrow I_2$$

Because there are no Oxygen or Hydrogen atoms in this half of the reaction, it is not required to perform any kind of balancing.

Reduction:

$$MnO_4^- \longrightarrow Mn^{2+} + 4\,H_2O$$

The first step in balancing this reaction using step 3 is to add4 H_2O atoms in order to balance the Oxygen atoms with the 4 on the other side of MnO4-

Reduction:

$$MnO_4^- + 8\,H^+ \longrightarrow Mn^{2+} + 4\,H_2O$$

Now that the Oxygen atoms have been balanced you can see that there are 8 **H** atoms on the right hand side of the equation and none on the left. Therefore, you must add 8 H^+ atoms to the left hand side of the equation to make it balanced.

Step 4: Now that the two half reactions have been balanced correctly one must balance the charges in each half reaction so that both the reduction and oxidation halves of the reaction consume the same number of electrons.

Oxidation:

$$2\,I^- \longrightarrow I_2 + 2\,e^-$$

Because of the fact that there are two **I**s on the left hand side of the equation which a charge of -1 we can state that the left hand side has an overall charge of -2. The I on the left side of the equation has an overall charge of 0. Therefore to balance the charges of this reaction we must add 2 electrons to the right side of the equation so that both sides of the equation have equal charges of -2.

Reduction:

$$5\,e^- + 8\,H^+ + MnO_4^- \longrightarrow Mn^{2+} + 4\,H_2O$$

Looking at the left hand side of the equation you can notice that there are 8 Hydrogen atoms with a +1 charge. There is also a MnO_4^- ion that has a charge of -1. When we add these two charges up we can calculate that the left hand side of the equation has an overall charge of +7. The right hand side has an **Mn** atom with a charge of +2 and then 4 water molecules that have charges of 0. Therefore, the overall charge of the right side is +2. We must add 5 electrons to the left side of the equation to make sure that both sides of the equation have equal charges of +2.

Step 5: Multiply both sides of both reactions by the least common multiple that will allow the half-reactions to have the same number of electrons and cancel each other out.

Oxidation: $10I^- \rightarrow 5I_2 + 10e^-$

We multiply this half reaction by 5 to come up with the following result above.

Reduction: $10e^- + 16H^+ + 2MnO_4^- \rightarrow 2Mn^{2+} + 8H_2O$

We multiply the reduction half of the reaction by 2 and arrive at the answer above.

By multiplying the oxidation half by 5 and the reduction half by 2 we are able to observe that both half-reactions have 10 electrons and are therefore are able to cancel each other out.

Step 6: Add the two half reactions in order to obtain the overall equation by canceling out the electrons and any $\mathbf{H_2O}$ and $\mathbf{H^+}$ ions that exist on both sides of the equation.

Overall:

$$\mathbf{10\,I^- + 16\,H^+ + 2\,MnO_4^- \longrightarrow 5\,I_2 + 2\,Mn^{2+} + 8\,H_2O}$$

In this problem, there is not anything that exists on both halves of the equation that can be cancelled out other than the electrons. Finally, double check your work to make sure that the mass and charge are both balanced. To double check this equation you can notice that everything is balanced because both sides of the equation have an overall charge of +4.

? Exercise 4.6.1

Balance this reaction in basic conditions.

$$\mathbf{MnO_4^- + I^- \longrightarrow I_2 + Mn^{2+}}$$

Answer

The balancing procedure in basic solution differs slightly because $\mathbf{OH^-}$ ions must be used instead of $\mathbf{H^+}$ ions when balancing hydrogen atoms. To give the previous reaction under basic conditions, sixteen $\mathbf{OH^-}$ ions can be added to both sides. on the left the $\mathbf{OH^-}$ and the $\mathbf{H^+}$ ions will react to form water, which will cancel out with some of the $\mathbf{H_2O}$ on the right.

$$\mathbf{10\,I^-(aq) + 2\,MnO_4^-(aq) + 16\,H^+(aq) + 16\,OH^-(aq) \longrightarrow 5\,I_2(s) + 2\,Mn^{2+}(aq) + 8\,H_2O(l) + 16\,OH^-(aq)}$$

On the left side the OH- and the $\mathbf{H^+}$ ions will react to form water, which will cancel out with some of the $\mathbf{H_2O}$ on the right:

$$\mathbf{10\,I^-(aq) + 2\,MnO_4^-(aq) + 16\,H_2O(l) \longrightarrow 5\,I_2(s) + 2\,Mn^{2+}(aq) + 8\,H_2O(l) + 16\,OH^-(aq)}$$

Eight water molecules can be canceled, leaving eight on the reactant side:

$$\mathbf{10\,I^-(aq) + 2\,MnO_4^-(aq) + 8\,H_2O(l) \longrightarrow 5\,I_2(s) + 2\,Mn^{2+}(aq) + 16\,OH^-(aq)}$$

This is the balanced reaction in basic solution.

? Exercise 4.6.1

Balance the following in an acidic solution.

$$\mathbf{SO_3^{2-}(aq) + MnO_4^-(aq) \rightarrow SO_4^{2-}(aq) + Mn^{2+}(aq)}$$

Answer

To balance a redox reaction, first take an equation and separate into two half reaction equations specifically oxidation and reduction, and balance them.

Step 1: Split into two half reaction equations: Oxidation and Reduction

Oxidation:

$$\mathbf{SO_3^{2-}(aq) \longrightarrow SO_4^{2-}(aq)}$$

[oxidation because oxidation state of sulfur increase from +4 to +6] Reduction:

$$MnO_4^+(aq) \longrightarrow Mn^{2+}(aq)$$

[Reduction because oxidation state of **Mn** decreases from +7 to +2]

$$5\,SO_3^{2-}(aq) + \cancel{5\,H_2O(l)} + 2\,MnO_4^-(aq) + \cancel{16\,H^+} + \cancel{10\,e^-} \rightarrow 5\,SO_4^{2-}(aq) + \cancel{10\,H^+(aq)} + 2\,Mn^{2+}(aq) + \cancel{8\,H_2O(l)} + \cancel{10\,e^-}$$

To get

$$5\,SO_3^{2-}(aq) + 2\,MnO_4^-(aq) + 6\,H^+ \rightarrow 5\,SO_4^{2-}(aq) + 2\,Mn^{2+}(aq) + 3\,H_2O(l)$$

The **S** and **Mn** atoms are already balanced,

Balancing **O** atoms

$$\text{Oxidation}: \quad SO_3^{2-}(aq) + H_2O(l) \rightarrow SO_4^{2-}(aq)$$
$$\text{Reduction}: \quad MnO_4^-(aq) \rightarrow Mn^{2+}(aq) + 4\,H_2O(l)$$

Then balance out **H** atoms on each side

$$\text{Oxidation}: \quad SO_3^{2-}(aq) + H_2O(l) \rightarrow SO_4^{2-}(aq) + 2\,H^+(aq)$$
$$\text{Reduction}: \quad MnO_4^-(aq) + 8H^+ \rightarrow Mn^{2+}(aq) + 4\,H_2O(l)$$

Step 3: Balance the charges of the half reactions by adding electrons

$$\text{Oxidation}: \quad SO_3^{2-}(aq) + H_2O(l) \rightarrow SO_4^{2-}(aq) + 2\,H^+(aq) + 2\,e^-$$
$$\text{Reduction}: \quad MnO_4^-(aq) + 8H^+ + 5\,e^- \rightarrow Mn^{2+}(aq) + 4\,H_2O(l)$$

Step 4: Obtain the overall redox equation by combining the half reaction, but multiply entire equation by number of electrons in oxidation with reduction equation, and number of electrons in reduction with oxidation equation.

$$\text{Oxidation}: \quad 5 \times \left[SO_3^{2-}(aq) + H_2O(l) \rightarrow SO_4^{2-}(aq) + 2\,H^+(aq) + 2\,e^-\right]$$
$$\text{Reduction}: \quad 2 \times \left[MnO_4^-(aq) + 8H^+ + 5\,e^- \rightarrow Mn^{2+}(aq) + 4\,H_2O(l)\right]$$

Overall Reaction:

$$\text{Oxidation}: \quad 5\,SO_3^{2-}(aq) + 5\,H_2O(l) \rightarrow 5\,SO_4^{2-}(aq) + 10\,H^+(aq) + 10\,e^-$$
$$\text{Reduction}: \quad 2\,MnO_4^-(aq) + 16\,H^+ + 10\,e^- \rightarrow 2\,Mn^{2+}(aq) + 8\,H_2O(l)$$
$$\text{total}: \quad 5\,SO_3^{2-}(aq) + 5\,H_2O(l) + 2\,MnO_4^-(aq) + 16\,H^+ + 10\,e^- \rightarrow 5\,SO_4^{2-}(aq) + 10\,H^+(aq) + 2\,Mn^{2+}(aq) + 8\,H_2O(l) + 10\,e^-$$

Step 5: Simplify and cancel out similar terms on both sides

Step 2: Balance each of the half equations in this order:

Atoms other than **H** and **O** O atoms by adding H_2O molecules with proper coefficients H atoms by adding H^+ with proper coefficients

? Exercise 4.6.1

Balance this reaction in both acidic and basic aqueous solutions

$$MnO_4^-(aq) + SO_3^{2-}(aq) \longrightarrow MnO_2(s) + SO_4^{2-}(aq)$$

Answer

First, they are separated into the half-equations:

$$MnO_4^-(aq) \longrightarrow MnO_2(s)$$

This is the reduction half-reaction because oxygen is LOST)

and

$$SO_3^{2-}(aq) \longrightarrow SO_4^{2-}(aq)$$

(the oxidation, because oxygen is GAINED)

Now, to balance the oxygen atoms, we must add two water molecules to the right side of the first equation, and one water molecule to the left side of the second equation:

$$MnO_4^-(aq) \longrightarrow MnO_2(s) + 2H_2O(l)$$

$$H_2O(l) + SO_3^{2-}(aq) \longrightarrow SO_4^{2-}(aq)$$

To balance the hydrogen atoms (those the original equation as well as those added in the last step), we must add four H^+ ions to the left side of the first equation, and two H^+ ions to the right side of the second equation.

$$4H^+ + MnO_4^-(aq) \longrightarrow MnO_2(s) + 2H_2O(l)$$

$$H_2O(l) + SO_3^{2-}(aq) \longrightarrow SO_4^{2-}(aq) + 2H^+$$

Now we must balance the charges. In the first equation, the charge is +3 on the left and 0 on the right, so we must add three electrons to the left side to make the charges the same. In the second equation, the charge is -2 on the left and 0 on the right, so we must add two electrons to the right.

$$3e^- + 4H^+ + MnO_4^-(aq) \longrightarrow MnO_2(s) + 2H_2O(l)$$

$$H_2O(l) + SO_3^{2-}(aq) - \longrightarrow SO_4^{2-}(aq) + 2H^+ + 2e^-$$

Now we must make the electrons equal each other, so we multiply each equation by the appropriate number to get the common multiple (in this case, by 2 for the first equation, and by 3 for the second).

$$2(3e^- + 4H^+ + MnO_4^-(aq) \longrightarrow MnO_2(s) + 2H_2O(l))$$

$$3(H_2O(l) + SO_3^{2-}(aq) \longrightarrow SO_4^{2-}(aq) + 2H^+ + 2e^-)$$

With the result:

$$6e^- + 8H^+ + 2MnO_4^-(aq) \longrightarrow 2MnO_2(s) + 4H_2O(l)$$

$$3H_2O(l) + 3SO_3^{2-}(aq) \longrightarrow 3SO_4^{2-}(aq) + 6H^+ + 6e^-$$

Now we cancel and add the equations together. We can cancel the $6e^-$ because they are on both sides. We can get rid of the $6H^+$ on both sides as well, turning the $8H^+$ in the first equation to $\mathbf{2H^+}$. The same method gets rid of the $\mathbf{3H_2O(l)}$ on the bottom, leaving us with just one $\mathbf{H_2O(l)}$ on the top. In the end, the overall reaction should have no electrons remaining. Now we can write one balanced equation:

$$2MnO_4^-(aq) + 2H^+ + 3SO_3^{2-}(aq) \longrightarrow H_2O(l) + 2MnO_2(s) + 3SO_4^{2-}(aq)$$

The equation is now balanced in an acidic environment.

To balance in a basic environment add $\mathbf{OH^-}$ to each side to neutralize the $\mathbf{H^+}$ into water molecules:

$$2MnO_4^-(aq) + 2H_2O + 3SO_3^{2-}(aq) \longrightarrow H_2O(l) + 2MnO_2(s) + 3SO_4^{2-}(aq) + 2OH^-$$

and then cancel the water molecules

$$2MnO_4^-(aq) + H_2O + 3SO_3^{2-}(aq) \longrightarrow + 2MnO_2(s) + 3SO_4^{2-}(aq) + 2OH^-$$

The equation is now balanced in a basic environment.

Exercise 4.6.1

Balance this reaction in acidic solution

$$Fe(OH)_3 + OCl^- \rightarrow FeO_4^{2-} + Cl^-$$

Answer

Step 1:

Reduction:

$$OCl^- \longrightarrow Cl^-$$

Oxidation:

$$Fe(OH)_3 \longrightarrow FeO_4^{2-}$$

Simplify:

$$3\,OCl^- + 2\,Fe(OH)_3 \rightarrow 3\,Cl^- + H_2O + 2\,FeO_4^{2-} + 4\,H^+$$

Step 4:

Overall Equation:

$$3\times\left[2\,H^+ + OCl^- + 2\,e^- \longrightarrow Cl^- + H_2O\right]$$
$$6\,H^+ + 3\,OCl^- + 6\,e^- \longrightarrow 3\,Cl^- + 3\,H_2O$$

and

$$2\times\left[Fe(OH)_3 + H_2O \longrightarrow FeO_4^{2-} + 3\,e^- + 5\,H^+\right]$$
$$2\,Fe(OH)_3 + 2\,H_2O \longrightarrow 2\,FeO_4^{2-} + 6\,e^- + 10\,H^+$$

Adding these together results

$$6\,H^+ + 3\,OCl^- + 2\,e^- + 2\,Fe(OH)_3 + 2\,H_2O \longrightarrow 3\,Cl^- + 3\,H_2O + 2\,FeO_4^{2-} + 6\,e^- + 10\,H^+$$

Step 5:

Steps 2 and 3:

Reduction:

$$2\,H^+ + OCl^- + 2\,e^- \longrightarrow Cl^- + H_2O$$

Oxidation:

$$Fe(OH)_3 + H_2O \longrightarrow FeO_4^{2-} + 3\,e^- + 5\,H^+$$

Exercise 4.6.1

Balance this equation in acidic aqueous solution

$$VO_4^{3-} + Fe^{2+} \longrightarrow VO^{2+} + Fe^{3+}$$

Answer

Step 1:

Oxidation:

$$Fe^{2+} \longrightarrow Fe^{3+}$$

Reduction:

$$VO_4^{3-} \longrightarrow VO^{2+}$$

Simplify:

$$Fe^{2+} + 6\,H^+ + VO_4^{3-} \rightarrow Fe^{3+} + VO^{2+} + 3\,H_2O$$

Step 4:

Overall Reaction:

$$Fe^{2+} \longrightarrow Fe^{3+} + e^-$$

+

$$6\,H^+ + VO_4^{3-} + e^- \longrightarrow VO^{2+} + 3\,H_2O$$

$$Fe^{2+} + 6\,H^+ + VO_4^{3-} + \cancel{e^-} \rightarrow Fe^{3+} + \cancel{e^-} + VO^{2+} + 3\,H_2O$$

Step 5:

Step 2/3:

Oxidation:

$$Fe^{2+} \longrightarrow Fe^{3+} + e^-$$

Reduction:

$$6\,H^+ + VO_4^{3-} + e^- \longrightarrow VO^{2+} + 3\,H_2O$$

? Exercise 4.6.1

Balance the following equation in both acidic and basic environments:

$$Cr_2O_7^{2-}(aq) + C_2H_5OH(l) \longrightarrow Cr^{3+}(aq) + CO_2(g)$$

Answer

In acidic aqueous solution:

$$2\,Cr_2O_7^-(aq) + 16\,H^+(aq) + C_2H_5OH(l) \longrightarrow 4\,Cr^{3+}(aq) + 2\,CO_2(g) + 11\,H_2O(l)$$

In basic aqueous solution:

$$2\,Cr_2O_7^-(aq) + 5\,H_2O(l) + C_2H_5OH(l) \longrightarrow 4\,Cr^{3+}(aq) + 2\,CO_2(g) + 16\,OH^-(aq)$$

? Exercise 4.6.1

Balance the following equation in both acidic and basic environments:

$$Fe^{2+}(aq) + MnO_4^-(aq) \longrightarrow Fe^{3+}(aq) + Mn^{2+}(aq)$$

Answer

In acidic aqueous solution:

$$MnO_4^-(aq) + 5\,Fe^{2+}(aq) + 8\,H^+(aq) \longrightarrow Mn^{2+}(aq) + 5\,Fe^{3+}(aq) + 4\,H_2O(l)$$

In basic aqueous solution:

$$MnO_4^-(aq) + 5\,Fe^{2+}(aq) + 4\,H_2O(l) \longrightarrow Mn^{2+}(aq) + 5\,Fe^{3+}(aq) + 8\,OH^-(aq)$$

References

1. Petrucci, Ralph, William Harwood, Geoffrey Herring, and Jeffry Madura. General Chemistry: Principles & Modern Applications. 9th edition. Upper Saddle River, New Jersey: Pearson Prentince Hall, 2007.

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4.7: Electrochemical Cells

Consider what happens when a clean piece of copper metal is placed in a solution of silver nitrate (Figure **4.7.1**). As soon as the copper metal is added, silver metal begins to form and copper ions pass into the solution. The blue color of the solution on the far right indicates the presence of copper ions. The reaction may be split into its two half-reactions. Half-reactions separate the oxidation from the reduction, so each can be considered individually.

$$\text{oxidation: } \mathrm{Cu}(s) \longrightarrow \mathrm{Cu}^{2+}(aq) + 2\,\mathrm{e}^- \tag{4.7.1}$$

$$\text{reduction: } 2 \times (\mathrm{Ag}^+(aq) + \mathrm{e}^- \longrightarrow \mathrm{Ag}(s)) \quad \text{or} \quad 2\,\mathrm{Ag}^+(aq) + 2\,\mathrm{e}^- \longrightarrow 2\,\mathrm{Ag}(s) \tag{4.7.2}$$

$$\text{overall: } 2\,\mathrm{Ag}^+(aq) + \mathrm{Cu}(s) \longrightarrow 2\,\mathrm{Ag}(s) + \mathrm{Cu}^{2+}(aq) \tag{4.7.3}$$

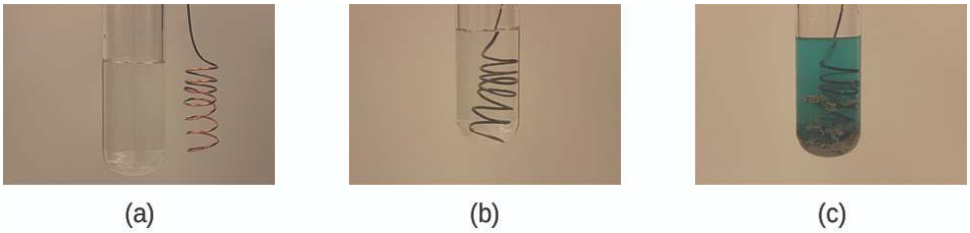


Figure **4.7.1**: When a clean piece of copper metal is placed into a clear solution of silver nitrate (a), an oxidation-reduction reaction occurs that results in the exchange of Cu^{2+} for Ag^+ ions in solution. As the reaction proceeds (b), the solution turns blue (c) because of the copper ions present, and silver metal is deposited on the copper strip as the silver ions are removed from solution. (credit: modification of work by Mark Ott)

Parts of an Electrochemical Cell

The redox reaction between Cu(s) and Ag^+ (aq) involves the movement of electrons. The two half-reactions can be physically separated to make an electrochemical cell as shown in Figure **4.7.2**. The beaker on the left side of the figure is called a half-cell, and contains a 1 *M* solution of copper(II) nitrate [$Cu(NO_3)_2$] with a piece of copper metal partially submerged in the solution. The copper metal is an electrode. The copper is undergoing oxidation; therefore, the copper electrode is the anode. The anode is connected to a voltmeter with a wire and the other terminal of the voltmeter is connected to a silver electrode by a wire. Electrons flow from the anode to the cathode. The silver is undergoing reduction; therefore, the silver electrode is the cathode. The half-cell on the right side of the figure consists of the silver electrode in a 1 *M* solution of silver nitrate ($AgNO_3$).

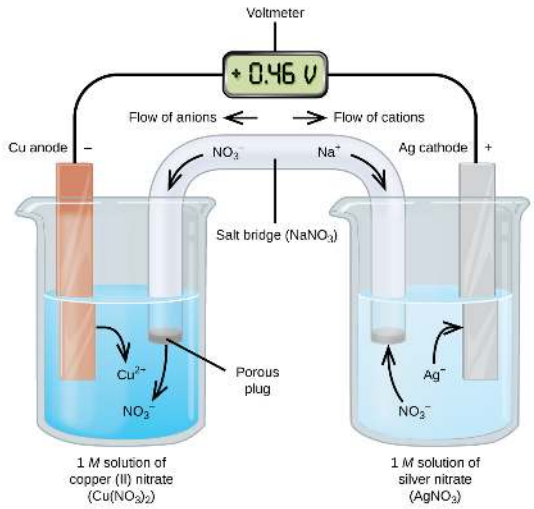


Figure **4.7.2**: In this standard galvanic cell, the half-cells are separated; electrons can flow through an external wire and become available to do electrical work.

The circuit is closed using a salt bridge, which transmits the current with moving ions. The salt bridge consists of a concentrated, nonreactive, electrolyte solution such as the sodium nitrate ($NaNO_3$) solution used in this example. As electrons flow from left to right through the electrode and wire, nitrate ions (anions) pass through the porous plug on the left into the copper(II) nitrate solution. This keeps the beaker on the left electrically neutral by neutralizing the charge on the copper(II) ions that are produced in

the solution as the copper metal is oxidized. At the same time, the nitrate ions are moving to the left, sodium ions (cations) move to the right, through the porous plug, and into the silver nitrate solution on the right. These added cations "replace" the silver ions that are removed from the solution as they were reduced to silver metal, keeping the beaker on the right electrically neutral. Without the salt bridge, the compartments would not remain electrically neutral and no significant current would flow. However, if the two compartments are in direct contact, a salt bridge is not necessary.

The voltmeter connected in the electrochemical circuit reads +0.46 V; this is called the ***cell potential***. The cell potential is created when the two dissimilar metals are connected, and is a measure of the energy per unit charge available from the oxidation-reduction reaction. The volt is the derived SI unit for electrical potential

$$\text{volt} = V = \frac{\text{J}}{\text{C}}$$

In this equation, A is the current in amperes and C the charge in coulombs. Note that volts must be multiplied by the charge in coulombs (C) to obtain the energy in joules (J).

Some oxidation-reduction reactions involve species that are poor conductors of electricity, and so an electrode is used that does not participate in the reactions. Frequently, the electrode is platinum, gold, or graphite, all of which are inert to many chemical reactions. One such system is shown in Figure **4.7.3**. Magnesium undergoes oxidation at the anode on the left in the figure and hydrogen ions undergo reduction at the cathode on the right. The reaction may be summarized as

$$\text{oxidation: } \text{Mg}(s) \longrightarrow \text{Mg}^{2+}(aq) + 2\,\text{e}^- \tag{4.7.4}$$
$$\text{reduction: } 2\,\text{H}^+(aq) + 2\,\text{e}^- \longrightarrow \text{H}_2(g) \tag{4.7.5}$$
$$\text{overall: } \text{Mg}(s) + 2\,\text{H}^+(aq) \longrightarrow \text{Mg}^{2+}(aq) + \text{H}_2(g) \tag{4.7.6}$$

The magnesium electrode is an active electrode because it participates in the oxidation-reduction reaction. Inert electrodes, like the platinum electrode in Figure **4.7.3**, do not participate in the oxidation-reduction reaction and are present so that current can flow through the cell. Platinum or gold generally make good inert electrodes because they are chemically unreactive.

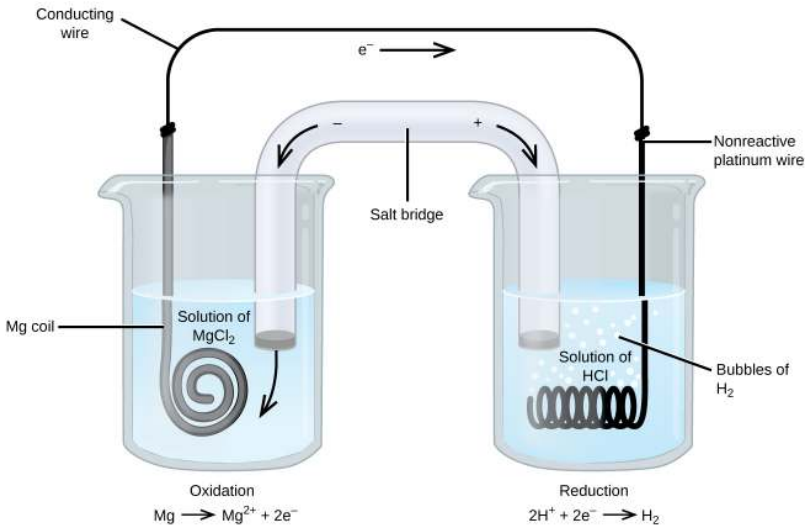


Figure **4.7.3**: The oxidation of magnesium to magnesium ion occurs in the beaker on the left side in this apparatus; the reduction of hydrogen ions to hydrogen occurs in the beaker on the right. A nonreactive, or inert, platinum wire allows electrons from the left beaker to move into the right beaker. The overall reaction is: $\text{Mg} + 2\,\text{H}^+ \longrightarrow \text{Mg}^{2+} + \text{H}_2$, *which is represented in cell notation as:* $\text{Mg}(s)\,|\,\text{Mg}^{2+}(aq)\,\|\,\text{H}^+(aq)\,|\,\text{H}_2(g)\,|\,\text{Pt}(s)$.

Two Types of Electrochemical Cells

Galvanic/Voltaic Cells

Galvanic cells, also known as voltaic cells, are electrochemical cells in which the oxidation-reduction reactions occur spontaneously and produce electrical energy. The examples shown in Figures **4.7.1** and **4.7.2** are galvanic cells. Galvanic cells have a positive cell potential. These cells are important because they are the basis for the batteries that fuel modern society.

Electrolytic Cells

It is possible to construct a cell that does work on a chemical system by driving an electric current through the system. These cells are called **electrolytic cells.** Electrolytic cells, like galvanic cells, are composed of two half-cells--one is a reduction half-cell, the other is an oxidation half-cell. The direction of electron flow in electrolytic cells, however, may be reversed from the direction of spontaneous electron flow in galvanic cells, but the definition of both cathode and anode remain the same, where reduction takes place at the cathode and oxidation occurs at the anode. Because the directions of both half-reactions have been reversed, the sign, but not the magnitude, of the cell potential has been reversed.

Electrolytic cells are very similar to voltaic (galvanic) cells in the sense that both require a salt bridge, both have a cathode and anode side, and both have a consistent flow of electrons from the anode to the cathode. However, there are also striking differences between the two cells. The main differences are outlined below:

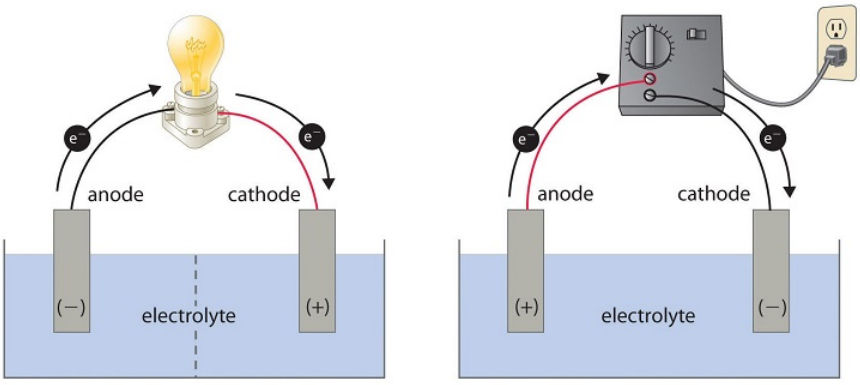


Figure 4.7.1: Electrochemical Cells. A galvanic cell (left) transforms the energy released by a spontaneous redox reaction into electrical energy that can be used to perform work. The oxidative and reductive half-reactions usually occur in separate compartments that are connected by an external electrical circuit; in addition, a second connection that allows ions to flow between the compartments (shown here as a vertical dashed line to represent a porous barrier) is necessary to maintain electrical neutrality. The potential difference between the electrodes (voltage) causes electrons to flow from the reductant to the oxidant through the external circuit, generating an electric current. In an electrolytic cell (right), an external source of electrical energy is used to generate a potential difference between the electrodes that forces electrons to flow, driving a nonspontaneous redox reaction; only a single compartment is employed in most applications. In both kinds of electrochemical cells, the anode is the electrode at which the oxidation half-reaction occurs, and the cathode is the electrode at which the reduction half-reaction occurs.

Table 4.7.1: Properties of Galvanic and Electrochemical Cells

Electrochemical cell (Galvanic Cell)	Electrolytic cell
A Galvanic cell converts chemical energy into electrical energy.	An electrolytic cell converts electrical energy into chemical energy.
Here, the redox reaction is spontaneous and is responsible for the production of electrical energy.	The redox reaction is not spontaneous and electrical energy has to be supplied to initiate the reaction.
The two half-cells are set up in different containers, being connected through the salt bridge or porous partition.	Both the electrodes are placed in a same container in the solution of molten electrolyte.
Here the anode is negative and cathode is the positive electrode. The reaction at the anode is oxidation and that at the cathode is reduction.	Here, the anode is positive and cathode is the negative electrode. The reaction at the anode is oxidation and that at the cathode is reduction.
The electrons are supplied by the species getting oxidized. They move from anode to the cathode in the external circuit.	The external battery supplies the electrons. They enter through the cathode and come out through the anode.

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4.8: Standard Reduction Potentials

In redox reactions the thermodynamic driving force can be measured as the **cell potential**. The cell potential results from the difference in the electrical potentials for each electrode. Standard cell potential determined using the *standard reduction cell potential* and the *standard oxidation cell potential*. The standard reduction potential is a measure of the likelihood that a species will be reduced. Likewise, the standard oxidation potential is a measure of the likelihood that a species will be oxidized. The equations that relate these three potentials are shown below:

$$E^o_{cell} = E^o_{reduction} \text{ of reaction at cathode} + E^o_{oxidation} \text{ of reaction at anode} \tag{4.8.1}$$

or alternatively

$$E^o_{cell} = E^o_{reduction} \text{ of reaction at cathode} - E^o_{reduction} \text{ of reaction at anode} \tag{4.8.2}$$

The standard oxidation potential and the standard reduction potential are opposite in sign to each other for the same chemical species.

- Relation Between Standard Reduction Potential (SRP) and the Standard Oxidation Potential (SOP)

$$E^o_0(SRP) = -E^o_0(SOP) \tag{4.8.3}$$

How the Standard Reduction Cell Potential is Experimentally Determined

It is impossible to determine the electrical potential of a single electrode; therefore, we use a reference electrode. This means, we assign an electrode an electrical potential value of zero and then compare the electrical potential of other electrodes to it. The standard hydrogen electrode (SHE) is commonly used for assessing the potential of half-cells. The SHE consists of 1 atm of hydrogen gas bubbled through a 1 M HCl solution at 298 K. Platinum, which is chemically inert, is used as the electrode. The reduction half-reaction chosen as the reference is

$$2\,H^+(aq,\,1\,M) + 2\,e^- \rightleftharpoons H_2(g,\,1\,\text{atm}) \quad E^\circ = 0\,V$$

$E°$ is the standard reduction potential. The superscript "°" on the E denotes standard conditions (1 bar or 1 atm for gases, 1 M for solutes). The voltage is defined as zero for all temperatures.

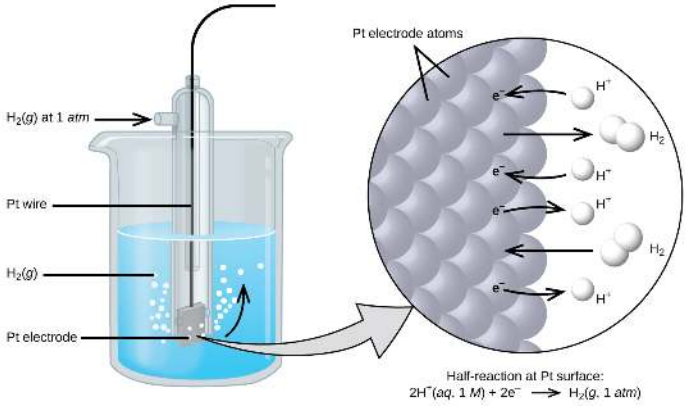


Figure 4.8.1: Hydrogen gas at 1 atm is bubbled through 1 M HCl solution. Platinum, which is inert to the action of the 1 M HCl, is used as the electrode. Electrons on the surface of the electrode combine with H^+ in solution to produce hydrogen gas.

A galvanic cell consisting of a SHE and Cu^{2+}/Cu half-cell can be used to determine the standard reduction potential for Cu^{2+} (Figure 4.8.2). Electrons flow from the anode to the cathode. The reactions, which are reversible, are

$$\begin{aligned}
&\text{Anode (oxidation): } H_2(g) \longrightarrow 2\,H^+(aq) + 2\,e^- \\
&\text{Cathode (reduction): } Cu^{2+}(aq) + 2\,e^- \longrightarrow Cu(s) \\
&\overline{\text{Overall: } Cu^{2+}(aq) + H_2(g) \longrightarrow 2\,H^+(aq) + Cu(s)}
\end{aligned}$$

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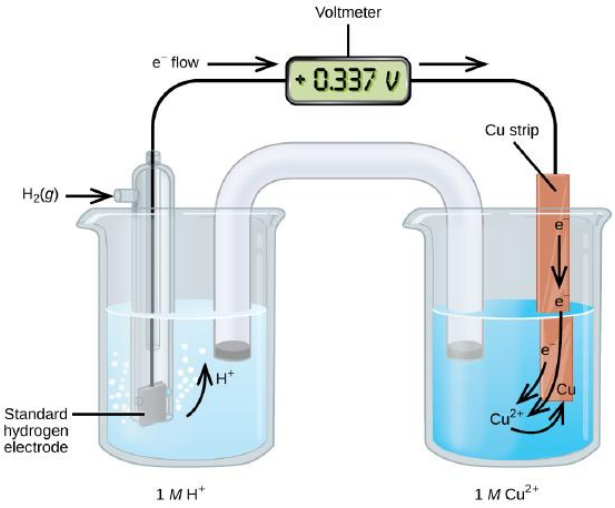


Figure **4.8.2**: A galvanic cell can be used to determine the standard reduction potential of Cu^{2+}.

The standard reduction potential can be determined by subtracting the standard reduction potential for the reaction occurring at the anode from the standard reduction potential for the reaction occurring at the cathode. The minus sign is necessary because oxidation is the reverse of reduction.

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$

$$+0.34\,\text{V} = E^\circ_{\text{Cu}^{2+}/\text{Cu}} - E^\circ_{\text{H}^+/\text{H}_2} = E^\circ_{\text{Cu}^{2+}/\text{Cu}} - 0 = E^\circ_{\text{Cu}^{2+}/\text{Cu}}$$

Using the SHE as a reference, other standard reduction potentials can be determined. Consider the cell shown in Figure **4.8.3**, where the electrons flow from left to right, and the reactions are

$$\begin{aligned}&\textbf{anode (oxidation):}\ \text{H}_2(g) \longrightarrow 2\,\text{H}^+(aq) + 2\,\text{e}^-\\ &\textbf{cathode (reduction):}\ 2\,\text{Ag}^+(aq) + 2\,\text{e}^- \longrightarrow 2\,\text{Ag}(s)\\ &\textbf{overall:}\ 2\,\text{Ag}^+(aq) + \text{H}_2(g) \longrightarrow 2\,\text{H}^+(aq) + 2\,\text{Ag}(s)\end{aligned}$$

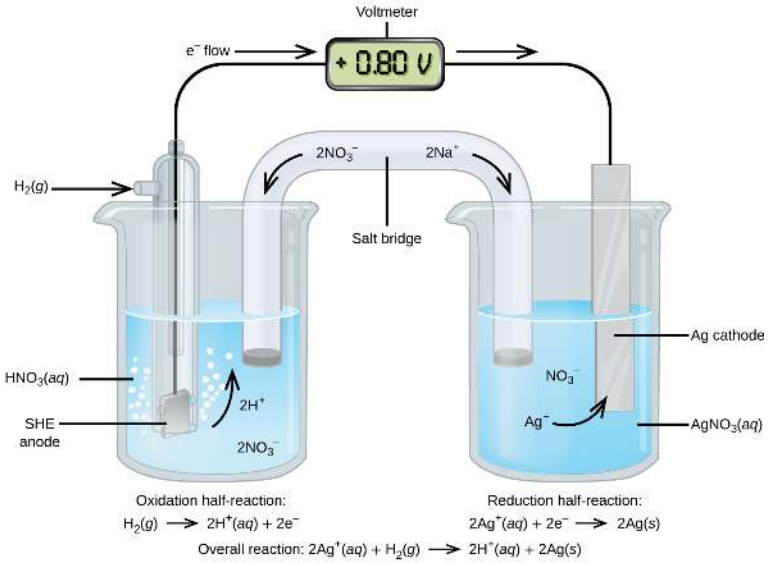


Figure **4.8.3**: A galvanic cell can be used to determine the standard reduction potential of Ag^+. The SHE on the left is the anode and assigned a standard reduction potential of zero.

The standard reduction potential can be determined by subtracting the standard reduction potential for the reaction occurring at the anode from the standard reduction potential for the reaction occurring at the cathode. The minus sign is needed because oxidation is the reverse of reduction.

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$

$$+0.80\ \text{V} = E^\circ_{\text{Ag}^+/\text{Ag}} - E^\circ_{\text{H}^+/\text{H}_2} = E^\circ_{\text{Ag}^+/\text{Ag}} - 0 = E^\circ_{\text{Ag}^+/\text{Ag}}$$

It is important to note that the potential is *not* doubled for the cathode reaction. The reason we don't need to multiply the Ag potential by 2 is that E^o is a measure of the free energy change **per electron**. Dividing the free energy change by the number of electrons makes E^o an **intensive property** (like pressure, temperature, etc.).

The SHE is rather dangerous and rarely used in the laboratory. Its main significance is that it established the zero for standard reduction potentials. Once determined, standard reduction potentials can be used to determine the standard cell potential, E°_{cell}, for any cell. For example, for the following cell:

$$\begin{aligned}&\text{anode (oxidation): } \text{Cu}(s) \longrightarrow \text{Cu}^{2+}(aq) + 2\,\text{e}^-\\ &\text{cathode (reduction): } 2\,\text{Ag}^+(aq) + 2\,\text{e}^- \longrightarrow 2\,\text{Ag}(s)\\ &\overline{\text{overall: } \text{Cu}(s) + 2\,\text{Ag}^+(aq) \longrightarrow \text{Cu}^{2+}(aq) + 2\,\text{Ag}(s)}\end{aligned}$$

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = E^\circ_{\text{Ag}^+/\text{Ag}} - E^\circ_{\text{Cu}^{2+}/\text{Cu}} = 0.80\ \text{V} - 0.34\ \text{V} = 0.46\ \text{V}$$

Again, note that when calculating E°_{cell}, standard reduction potentials always remain the same even when a half-reaction is multiplied by a factor.

The Activity Series

When solving for the standard cell potential, the species oxidized and the species reduced must be identified. This can be done using an activity series. The Table **4.8.1** shown below is an activity series; which is simply a table of standard reduction potentials in decreasing order. The species at the top have a greater likelihood of being reduced while the ones at the bottom have a greater likelihood of being oxidized. Therefore, when a species at the top is coupled with a species at the bottom, the one at the top will become reduced while the one at the bottom will become oxidized. A more complete list of standard reduction potentials is is provided in Tables P1 or P2.

Table **4.8.1**: Activity Series - Standard Reduction Potential for Selected Species

Reduction Half-Reaction	Standard Reduction Potential (V)
$F_2(g)+2e^- \rightarrow 2F^-(aq)$	+2.87
$S_2O_8^{2-}(aq)+2e^- \rightarrow 2SO_4^{2-}(aq)$	+2.01
$O_2(g)+4H^+(aq)+4e^- \rightarrow 2H_2O(l)$	+1.23
$Br_2(l)+2e^- \rightarrow 2Br^-(aq)$	+1.09
$Ag^+(aq)+e^- \rightarrow Ag(s)$	+0.80
$Fe^{3+}(aq)+e^- \rightarrow Fe^{2+}(aq)$	+0.77
$I_2(l) + 2e^- \rightarrow 2I^-(aq)$	+0.54
$Cu^{2+}(aq)+2e^- \rightarrow Cu(s)$	+0.34
$Sn^{4+}(aq)+2e^- \rightarrow Sn^{2+}(aq)$	+0.15
$S(s)+2H^+(aq)+2e^- \rightarrow H_2S(g)$	+0.14
$2H^+(aq)+2e^- \rightarrow H_2(g)$	**0.00**
$Sn^{2+}(aq)+2e^- \rightarrow Sn(g)$	-0.14
$V^{3+}(aq)+e^- \rightarrow V^{2+}(aq)$	-0.26
$Fe^{2+}(aq)+2e^- \rightarrow Fe(s)$	-0.44
$Cr^{3+}(aq)+3e^- \rightarrow Cr(s)$	-0.74
$Zn^{2+}(aq)+2e^- \rightarrow Zn(s)$	-0.76
$Mn^{2+}(aq)+2e^- \rightarrow Mn(s)$	-1.18
$Na^+(aq)+e^- \rightarrow Na(s)$	-2.71
$Li^+(aq)+e^- \rightarrow Li(s)$	-3.04

Problems

Exercise 4.8.1: Cell Potentials from Standard Reduction Potentials

What is the standard cell potential for a galvanic cell that consists of Au^{3+}/Au and Ni^{2+}/Ni half-cells? Identify the oxidizing and reducing agents.

Answer

Using Table **4.8.1**, the reactions involved in the galvanic cell, both written as reductions, are

$$\mathrm{Au^{3+}}(aq) + 3\,\mathrm{e^-} \longrightarrow \mathrm{Au}(s) \quad E^\circ_{\mathrm{Au^{3+}/Au}} = +1.498\ \mathrm{V}$$

$$\mathrm{Ni^{2+}}(aq) + 2\,\mathrm{e^-} \longrightarrow \mathrm{Ni}(s) \quad E^\circ_{\mathrm{Ni^{2+}/Ni}} = -0.257\ \mathrm{V}$$

Galvanic cells have positive cell potentials, and all the reduction reactions are reversible. The reaction at the anode will be the half-reaction with the smaller or more negative standard reduction potential. Reversing the reaction at the anode (to show the oxidation) but *not* its standard reduction potential gives:

$$\text{Anode (oxidation): } \mathrm{Ni}(s) \longrightarrow \mathrm{Ni^{2+}}(aq) + 2\,\mathrm{e^-} \quad E^\circ_{\text{anode}} = E^\circ_{\mathrm{Ni^{2+}/Ni}} = -0.257\ \mathrm{V}$$
$$\text{Cathode (reduction): } \mathrm{Au^{3+}}(aq) + 3\,\mathrm{e^-} \longrightarrow \mathrm{Au}(s) \quad E^\circ_{\text{cathode}} = E^\circ_{\mathrm{Au^{3+}/Au}} = +1.498\ \mathrm{V}$$

The least common factor is six, so the overall reaction is

$$3\,\mathrm{Ni}(s) + 2\,\mathrm{Au^{3+}}(aq) \longrightarrow 3\,\mathrm{Ni^{2+}}(aq) + 2\,\mathrm{Au}(s)$$

The reduction potentials are *not* scaled by the stoichiometric coefficients when calculating the cell potential, and the unmodified standard reduction potentials must be used.

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = 1.498\ \mathrm{V} - (-0.257\ \mathrm{V}) = 1.755\ \mathrm{V}$$

From the half-reactions, Ni is oxidized, so it is the reducing agent, and Au^{3+} is reduced, so it is the oxidizing agent.

Exercise 4.8.1

A galvanic cell consists of a Mg electrode in 1 *M* $Mg(NO_3)_2$ solution and a Ag electrode in 1 *M* $AgNO_3$ solution. Calculate the standard cell potential at 25 °C.

Answer

$$\mathrm{Mg}(s) + 2\,\mathrm{Ag^+}(aq) \longrightarrow \mathrm{Mg^{2+}}(aq) + 2\,\mathrm{Ag}(s) \quad E^\circ_{\text{cell}} = 0.7996\ \mathrm{V} - (-2.372\ \mathrm{V}) = 3.172\ \mathrm{V}$$

Exercise 4.8.3

True or False?

1. Hydrogen has oxidation potentials of 0.
2. The standard oxidation potential is not much like the standard reduction potential.
3. The standard reduction cell potential and the standard oxidation cell potential can never be combined.

Answer

1. True
2. False: the standard oxidation potential is much like the standard reduction potential
3. False: The standard reduction cell potential and the standard oxidation cell potential can be combined to determine the overall cell potential

Exercise 4.8.4

1. What does the standard reduction potential measure?
2. What are the differences between the standard reduction potential and standard oxidation potential, and how are the two related?
3. What conditions must be met for a potential to be standard?
4. When standard reduction potentials are measured, what are the potentials relative to?
5. How is a standard reduction potential measured?
6. Explain how the activity series is used.
7. Explain how standard reduction potentials or standard oxidation potentials are applied.
8. Draw and label a SHE.

Answer

1. Standard reduction potential measures the tendency for a given chemical species to be reduced.
2. The standard oxidation potential measures the tendency for a given chemical species to be oxidized as opposed to be reduced. For the same chemical species the standard reduction potential and standard oxidation potential are opposite in sign.
3. The cell must be at 298K, 1atm, and all solutions must be at 1M. Standard reduction potentials are measured with relativity to hydrogen which has be universally set to have a potential of zero.
4. A standard reduction potential is measured using a galvanic cell which contains a SHE on one side and an unknown chemical half cell on the other side.
5. The amount of charge that passes between the cells is measured using a voltmeter.
6. The activity series is a list of standard reduction potentials in descending order of the tendency for chemical species to be reduced. Species at the top are more likely to be reduced while species at the bottom are more likely to be oxidized.
7. Standard reduction and oxidation potentials can be applied to solve for the standard cell potential of two different non hydrogen species. Examples can be seen in Cell Potentials.
8. See Figure (2).

Exercise 4.8.5

Based on the activity series, which species will be oxidized and reduced: Zn^{2+} or H^{+}.

Answer

H^{+} is farther up on the activity series then Zn^{2+} so H^{+} is reduced while Zn^{2+} is oxidized.

Exercise 4.8.6

The standard reduction potential of Fe^{3+} is +0.77V. What is its standard oxidation potential.

Answer

The standard oxidation potential and standard reduction potential are always opposite in sign for the same species. The oxidation potential is -0.77V.

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4.9: Thermodynamic Considerations

Electrochemical Potential and Free Energy

We will now extend electrochemistry by determining the relationship between E°_{cell} and the thermodynamics quantities such as ΔG° (Gibbs free energy) and K (the equilibrium constant). In spontaneous redox reactions, chemical energy is converted into electrical energy, which can do work. The electrical work is the product of the charge transferred multiplied by the potential difference (voltage):

$$\textbf{electrical work} = \textbf{volts} \times (\textbf{charge in coulombs}) = \text{J}$$

The charge on 1 mole of electrons is given by Faraday's constant (F)

$$\begin{aligned} F &= \frac{6.022 \times 10^{23}\ e^-}{mol} \times \frac{1.602 \times 10^{-19}\ C}{e^-} \\ &= 9.648 \times 10^4\ \frac{C}{mol} \\ &= 9.648 \times 10^4\ \frac{J}{V \cdot mol} \end{aligned}$$

Therefore

$$\textbf{total charge} = (\textbf{number of moles of e}^-) \times F = nF$$

In this equation, n is the number of moles of electrons for the *balanced* oxidation-reduction reaction. The measured cell potential is the maximum potential the cell can produce and is related to the electrical work (w_{ele}) by

$$E_{\text{cell}} = \frac{-w_{\text{ele}}}{nF} \qquad \text{or} \qquad w_{\text{ele}} = -nFE_{\text{cell}}$$

The negative sign for the work indicates that the electrical work is done by the system (the galvanic cell) on the surroundings. Free energy is defined as the energy that is available to do work. In particular, the change in free energy is defined in terms of the maximum work (w_{max}), which is w_{ele} for electrochemical systems.

$$\begin{aligned} \Delta G &= w_{\text{max}} = w_{\text{ele}} \\ &= -nFE_{\text{cell}} \end{aligned}$$

We can verify the signs are correct when we realize that n and F are positive constants and that galvanic cells, which have positive cell potentials, involve spontaneous reactions. Thus, spontaneous reactions, which have $\Delta G < 0$, must have $E_{cell} > 0$. If all the reactants and products are in their standard states, this becomes

$$\Delta G^\circ = -nFE^\circ_{\text{cell}}$$

Although the sign of E°_{cell} tells us whether a particular redox reaction will occur spontaneously under standard conditions, it does not tell us to what extent the reaction proceeds, and it does not tell us what will happen under nonstandard conditions. To answer these questions requires a more quantitative understanding of the relationship between electrochemical cell potential and equilibrium constants. Since

$$\Delta G^\circ = -RT \ln K$$

$$-nFE^\circ_{\text{cell}} = -RT \ln K$$

or

$$E^\circ_{\text{cell}} = \frac{RT}{nF} \ln K$$

Most of the time, the electrochemical reactions are run at standard temperature (298.15 K). Collecting terms at this temperature yields

$$
\begin{aligned}
E^\circ_{\text{cell}} &= \frac{RT}{nF} \ln K \\
&= \frac{\left(8.314 \ \frac{\text{J}}{\text{K·mol}}\right)(298.15 \ K)}{n \times 96,485 \ \text{C/V·mol}} \ln K \\
&= \frac{0.0257 \ \text{V}}{n} \ln K
\end{aligned}
$$

where n is the number of moles of electrons. The logarithm in equations involving cell potentials is often expressed using base 10 logarithms (i.e., $\log_{10}$ or just $\log$), which changes the constant by a factor of 2.303:

$$
E^\circ_{\text{cell}} = \frac{0.0592 \ \text{V}}{n} \log K
$$

Thus, if $\Delta G°$, K, or E°_{cell} is known or can be calculated, the other two quantities can be readily determined. The relationships are shown graphically in Figure 4.9.1. Given any one of the quantities, the other two can be calculated.

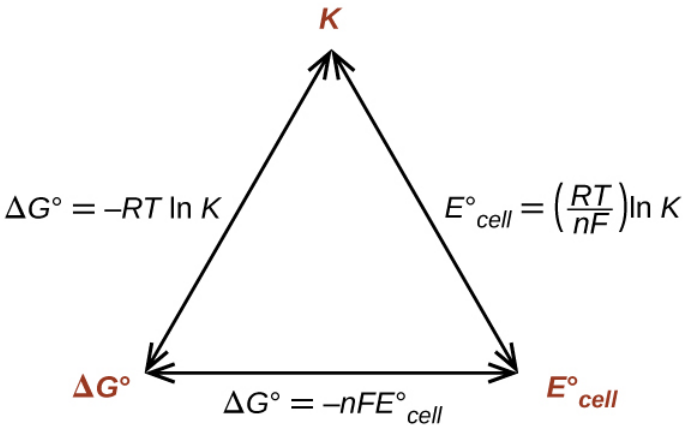


Figure 4.9.1: The relationships between ΔG°, K, and E°_{cell}. *Given any one of the three quantities, the other two can be calculated, so any of the quantities could be used to determine whether a process was spontaneous.*

Example 4.9.1: Equilibrium Constants, Potentials, & Free Energy Changes

What is the standard Gibbs free energy change and equilibrium constant for the following reaction at 25 °C?

$$
2 \ \text{Ag}^+(aq) + \text{Fe}(s) \rightleftharpoons 2 \ \text{Ag}(s) + \text{Fe}^{2+}(aq)
$$

Solution

The reaction involves an oxidation-reduction reaction, so the standard cell potential can be calculated using the data in Table P1.

$$
\begin{aligned}
&\text{anode (oxidation): } \text{Fe}(s) \longrightarrow \text{Fe}^{2+}(aq) + 2 \ \text{e}^- \qquad E^\circ_{\text{Fe}^{2+}/\text{Fe}} = -0.447 \ \text{V} \\
&\text{cathode (reduction): } 2 \times (\text{Ag}^+(aq) + \text{e}^- \longrightarrow \text{Ag}(s)) \qquad E^\circ_{\text{Ag}^+/\text{Ag}} = 0.7996 \ \text{V} \\
&E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = E^\circ_{\text{Ag}^+/\text{Ag}} - E^\circ_{\text{Fe}^{2+}/\text{Fe}} = +1.247 \ \text{V}
\end{aligned}
$$

Remember that the cell potential for the cathode is not multiplied by two when determining the standard cell potential. With n = 2, the equilibrium constant is then

$$
\begin{aligned}
E^\circ_{\text{cell}} &= \frac{0.0592 \ \text{V}}{n} \log K \\
K &= 10^{n \times E^\circ_{\text{cell}}/0.0592 \ \text{V}} \\
&= 10^{2 \times 1.247 \ \text{V}/0.0592 \ \text{V}} \\
&= 10^{42.128} \\
&= 1.3 \times 10^{42}
\end{aligned}
$$

The standard free energy is then

$$\Delta G^\circ = -nFE^\circ_{\text{cell}}$$

$$\Delta G^\circ = -2 \times 96,485 \ \frac{\text{J}}{\text{V·mol}} \times 1.247 \ \text{V} = -240.6 \ \frac{\text{kJ}}{\text{mol}}$$

Check your answer: A positive standard cell potential means a spontaneous reaction, so the standard free energy change should be negative, and an equilibrium constant should be >1.

The Nernst Equation

Thus far, we have addressed electrochemical reactions that occur under standard conditions. The Nernst Equation will be introduced to address reactions that occur under nonstandard Conditions. Recall that

$$\Delta G = \Delta G^\circ + RT \ln Q$$

where Q is the reaction quotient (see the chapter on equilibrium fundamentals). Converting to cell potentials:

$$-nFE_{\text{cell}} = -nFE^\circ_{\text{cell}} + RT \ln Q \tag{4.9.1}$$

or

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{RT}{nF} \ln Q \tag{4.9.2}$$

Equation 4.9.2 is the generalized Nernst equation that is applicable at any temperature. However, is can be simplified for reactions occuring at 25 °C (298.15 K) by rewriting it as

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0257 \ \text{V}}{n} \ln Q \tag{4.9.3}$$

or

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0592 \ \text{V}}{n} \log_{10} Q \tag{4.9.4}$$

If the temperature is not 298.15 K, it is necessary to recalculate the potential with Equation4.9.2. With the Nernst equation, it is possible to calculate the cell potential at nonstandard conditions. This adjustment is necessary because potentials determined under different conditions will have different values.

✔ Example 4.9.2: Cell Potentials at Nonstandard Conditions

Consider the following reaction at room temperature:

$$\text{Co}(s) + \text{Fe}^{2+}(aq, \ 1.94 \ M) \longrightarrow \text{Co}^{2+}(aq, \ 0.15 \ M) + \text{Fe}(s)$$

Is the process spontaneous?

Solution

There are two ways to solve the problem. If the thermodynamic information in Table T1 were available, you could calculate the free energy change. If the free energy change is negative, the process is spontaneous. The other approach, which we will use, requires information like that given in Table P1. Using those data, the cell potential can be determined. If the cell potential is positive, the process is spontaneous. Collecting information from Table P1 and the problem,

$$\text{Anode (oxidation): } \text{Co}(s) \longrightarrow \text{Co}^{2+}(aq) + 2\,\text{e}^- \qquad E^\circ_{\text{Co}^{2+}/\text{Co}} = -0.28 \ \text{V}$$
$$\text{Cathode (reduction): } \text{Fe}^{2+}(aq) + 2\,\text{e}^- \longrightarrow \text{Fe}(s) \qquad E^\circ_{\text{Fe}^{2+}/\text{Fe}} = -0.447 \ \text{V}$$
$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = -0.447 \ \text{V} - (-0.28 \ \text{V}) = -0.17 \ \text{V}$$

The process is not spontaneous under standard conditions. Using the Nernst equation and the concentrations stated in the problem and $n = 2$,

$$Q = \frac{[Co^2+]}{[Fe^2+]} = \frac{0.15\ M}{1.94\ M} = 0.077$$

Now we can insert these into the Nernst Equation at room temperature (Equation 4.9.4)

$$\begin{aligned} E_{\text{cell}} &= E^\circ_{\text{cell}} - \frac{0.0592\ \text{V}}{n} \log Q \\ &= -0.17\ \text{V} - \frac{0.0592\ \text{V}}{2} \log 0.077 \\ &= -0.17\ \text{V} + 0.033\ \text{V} = -0.14\ \text{V} \end{aligned}$$

The process is (still) nonspontaneous.

Finally, we will take a brief look at a special type of cell called a concentration cell. In a concentration cell, the electrodes are the same material and the half-cells differ only in concentration. Since one or both compartments is not standard, the cell potentials will be unequal; therefore, there will be a potential difference, which can be determined with the aid of the Nernst equation.

✔ Example 4.9.3: Concentration Cells

What is the cell potential of the concentration cell described by

$$\text{Zn}(s)\,|\,\text{Zn}^{2+}(aq,\ 0.10\ M)\,\|\,\text{Zn}^{2+}(aq,\ 0.50\ M)\,|\,\text{Zn}(s)$$

Solution

From the information given:

$$\begin{aligned} &\text{Anode: } \text{Zn}(s) \longrightarrow \text{Zn}^{2+}(aq,\ 0.10\ M) + 2\,\text{e}^- \qquad E^\circ_{\text{anode}} = -0.7618\ \text{V} \\ &\text{Cathode: } \text{Zn}^{2+}(aq,\ 0.50\ M) + 2\,\text{e}^- \longrightarrow \text{Zn}(s) \qquad E^\circ_{\text{cathode}} = -0.7618\ \text{V} \\ &\text{Overall: } \text{Zn}^{2+}(aq,\ 0.50\ M) \longrightarrow \text{Zn}^{2+}(aq,\ 0.10\ M) \qquad E^\circ_{\text{cell}} = 0.000\ \text{V} \end{aligned}$$

The standard cell potential is zero because the anode and cathode involve the same reaction; only the concentration of Zn^{2+} changes. Substituting into the Nernst equation,

$$E_{\text{cell}} = 0.000\ \text{V} - \frac{0.0592\ \text{V}}{2} \log \frac{0.10}{0.50} = +0.021\ \text{V}$$

and the process is spontaneous at these conditions.

Check your answer: In a concentration cell, the standard cell potential will always be zero. To get a positive cell potential (spontaneous process) the reaction quotient Q must be <1. $Q < 1$ in this case, so the process is spontaneous.

Problems

? Exercise 4.9.1

What is the standard Gibbs free energy change and the equilibrium constant for the following reaction at room temperature? Is the reaction spontaneous?

$$\text{Sn}(s) + 2\,\text{Cu}^{2+}(aq) \rightleftharpoons \text{Sn}^{2+}(aq) + 2\,\text{Cu}^{+}(aq)$$

Answer

Spontaneous; $n = 2$; $E^\circ_{\text{cell}} = +0.291\ \text{V}$; $\Delta G^\circ = -56.2\ \frac{\text{kJ}}{\text{mol}}$; $K = 6.8 \times 10^9$.

? Exercise 4.9.2

What is the cell potential for the following reaction at room temperature?

$$\text{Al}(s)\,|\,\text{Al}^{3+}(aq,\ 0.15\ M)\,\|\,\text{Cu}^{2+}(aq,\ 0.025\ M)\,|\,\text{Cu}(s)$$

What are the values of *n* and Q for the overall reaction? Is the reaction spontaneous under these conditions?

Answer

n = 6; *Q* = 1440; E_{cell} = +1.97 V, spontaneous.

Exercise 4.9.3

What value of *Q* for the previous concentration cell would result in a voltage of 0.10 V? If the concentration of zinc ion at the cathode was 0.50 *M*, what was the concentration at the anode?

Answer

Q = 0.00042; $[Zn^{2+}]_{cat}$ = 2.1 \times 10^{-4} *M*.

Exercise 4.9.4: Silver Sulfide

The black tarnish that forms on silver objects is primarily Ag_2S. The half-reaction for reversing the tarnishing process is as follows:

$$Ag_2S(s) + 2e^- \longrightarrow 2Ag(s) + S^{2-}(aq) \qquad E° = -0.69\,V$$

a. Referring to Table 4.9.1, predict which species—H_2O_2(aq), Zn(s), I^-(aq), Sn^{2+}(aq)—can reduce Ag_2S to Ag under standard conditions.
b. Of these species—H_2O_2(aq), Zn(s), I^-(aq), Sn^{2+}(aq), identify which is the strongest reducing agent in aqueous solution and thus the best candidate for a commercial product.
c. From the data in Table 4.9.1, suggest an alternative reducing agent that is readily available, inexpensive, and possibly more effective at removing tarnish.



Answer

We can solve the problem in one of two ways: (1) compare the relative positions of the four possible reductants with that of the Ag_2S/Ag couple in Table 4.9.1 or (2) compare E° for each species with E° for the Ag_2S/Ag couple (−0.69 V).

a. The species in Table 4.9.1 are arranged from top to bottom in order of increasing reducing strength. Of the four species given in the problem, I^-(aq), Sn^{2+}(aq), and H_2O_2(aq) lie above Ag_2S, and one [Zn(s)] lies below it. We can therefore conclude that Zn(s) can reduce Ag_2S(s) under standard conditions, whereas I^-(aq), Sn^{2+}(aq), and H_2O_2(aq) cannot. Sn^{2+}(aq) and H_2O_2(aq) appear twice in the table: on the left side (oxidant) in one half-reaction and on the right side (reductant) in another.
b. The strongest reductant is Zn(s), the species on the right side of the half-reaction that lies closer to the bottom of Table 4.9.1 than the half-reactions involving I^-(aq), Sn^{2+}(aq), and H_2O_2(aq). (Commercial products that use a piece of zinc are often marketed as a “miracle product” for removing tarnish from silver. All that is required is to add warm water and

salt for electrical conductivity.)

c. Of the reductants that lie below Zn(s) in Table **4.9.1**, and therefore are stronger reductants, only one is commonly available in household products: Al(s), which is sold as aluminum foil for wrapping foods.

? Exercise 4.9.5

Use the data in Table **4.9.1** to determine whether each reaction is likely to occur spontaneously under standard conditions:

$$\mathrm{Sn(s) + Be^{2+}(aq) \longrightarrow Sn^{2+}(aq) + Be(s)}$$

Answer

Metallic tin is oxidized to $\mathrm{Sn^{2+}(aq)}$, and $\mathrm{Be^{2+}(aq)}$ is reduced to elemental beryllium. We can find the standard electrode potentials for the latter (reduction) half-reaction (−1.99 V) and for the former (oxidation) half-reaction (−0.14 V) directly from Table **4.9.1**.

Adding the two half-reactions gives the overall reaction:

$$\begin{aligned} \mathrm{cathode: Be^{2+}(aq) + 2e^- \rightarrow Be(s)} \\ \mathrm{anode: Sn(s) \rightarrow Sn^{2+}(s) + 2e^-} \\ \hline \mathrm{overall: Sn(s) + Be^{2+}(aq) \rightarrow Sn^{2+}(aq) + Be(s)} \end{aligned}$$

with

$$\begin{aligned} E^\circ_{\text{cathode}} &= \text{-1.99 V} \\ E^\circ_{\text{anode}} &= \text{-0.14 V} \\ E^\circ_{\text{cell}} &= E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} \\ &= -1.85 \text{ V} \end{aligned}$$

The standard cell potential is quite negative, so the reaction will not occur spontaneously as written. That is, metallic tin cannot reduce Be^{2+} to beryllium metal under standard conditions. Instead, the reverse process, the reduction of stannous ions (Sn^{2+}) by metallic beryllium, which has a positive value of $E°_{cell}$, will occur spontaneously.

? Exercise 4.9.6

Use the data in Table **4.9.1** to determine whether each reaction is likely to occur spontaneously under standard conditions:

$$\mathrm{MnO_2(s) + H_2O_2(aq) + 2H^+(aq) \longrightarrow O_2(g) + Mn^{2+}(aq) + 2H_2O(l)}$$

Answer

$\mathrm{MnO_2}$ is the oxidant ($\mathrm{Mn^{4+}}$ is reduced to $\mathrm{Mn^{2+}}$), while $\mathrm{H_2O_2}$ is the reductant ($\mathrm{O^{2-}}$ is oxidized to $\mathrm{O_2}$). We can obtain the standard electrode potentials for the reduction and oxidation half-reactions directly from Table **4.9.1**.

The two half-reactions and their corresponding potentials are as follows:

$$\begin{aligned} \mathrm{cathode: MnO_2(s) + 4H^+(aq) + 2e^- \rightarrow Mn^{2+}(aq) + 2H_2O(l)} \\ \mathrm{anode: H_2O_2(aq) \rightarrow O_2(g) + 2H^+(aq) + 2e^-} \\ \hline \mathrm{overall: MnO_2(s) + H_2O_2(aq) + 2H^+(aq) \rightarrow O_2(g) + Mn^{2+}(aq) + 2H_2O(l)} \end{aligned}$$

with

$$\begin{aligned} E^\circ_{\text{cathode}} &= 1.23 \text{ V} \\ E^\circ_{\text{anode}} &= 0.70 \text{ V} \\ E^\circ_{\text{cell}} &= E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} \\ &= +0.52 \text{ V} \end{aligned}$$

The standard potential for the reaction is positive, indicating that under standard conditions, it will occur spontaneously as written. Hydrogen peroxide will reduce $\mathbf{MnO_2}$, and oxygen gas will evolve from the solution.

Exercise 4.9.7

Use the data in Table **4.9.1** to determine whether each reaction is likely to occur spontaneously under standard conditions:

a. $\mathbf{2\,Ce^{4+}\,(aq) + 2\,Cl^{-}\,(aq) \longrightarrow 2\,Ce^{3+}\,(aq) + Cl_2\,(g)}$

b. $\mathbf{4\,MnO_2\,(s) + 3\,O_2\,(g) + 4\,OH^{-}\,(aq) \longrightarrow 4\,MnO_4^{-}\,(aq) + 2\,H_2O}$

Answer a

spontaneous with $E^{o}_{cell} = 1.61\,V - 1.396\,V = 0.214\,V$

Answer b

nonspontaneous with $E^{\circ}_{cell} = -0.20\,V$

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4.10: General Trends in Redox Reactivity

Trends in the Redox Properties of the Elements

The redox properties of the elements very roughly follow the following general trends:

1. Elements on the left of the periodic table tend to act as reductants; those on the right as oxidants
2. The noble gases are inert and as elements tend not to act as good oxidants or reductants
3. As one moves towards the left of the periodic table, elements tend to act as good reductants, while those towards the right tend to act as increasingly good oxidants.
4. As one moves down a group of the periodic table, elements tend to act as either weaker oxidants or better reductants.

These trends are summarized in Figure **4.10.2**.

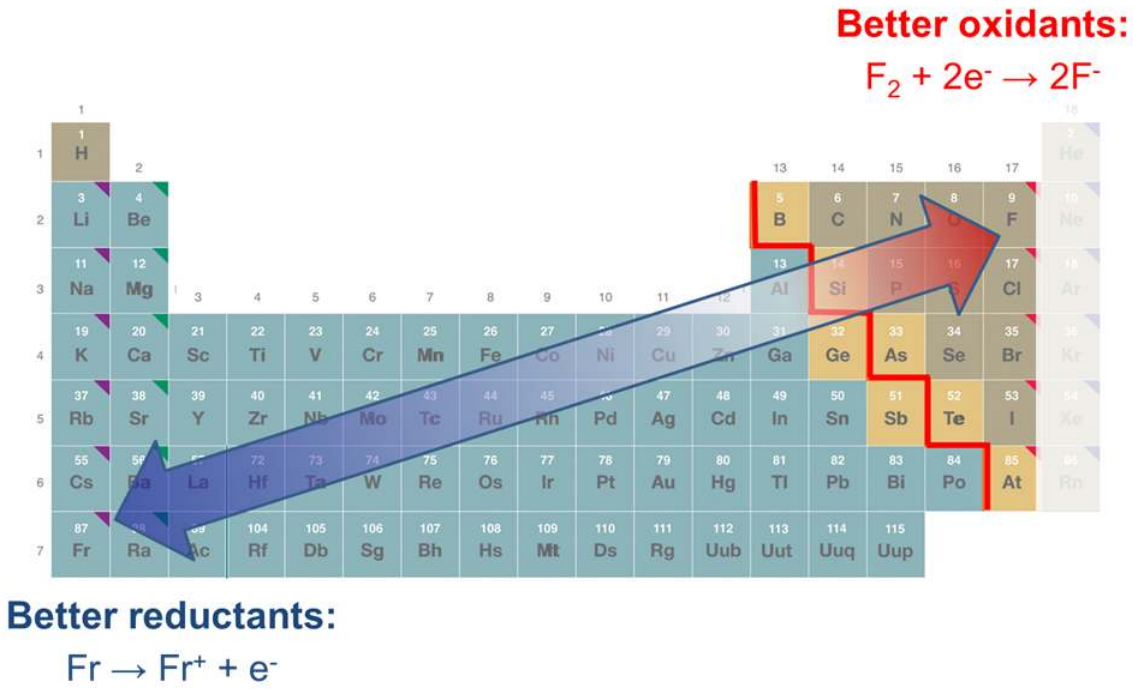


Figure **4.10.2**. Idealized scheme showing how elements' ability to act as reductants roughly increases towards the lower left of the periodic table while, noble gases excepted, their oxidizing power increases towards the upper left.

Since substances' ability to act as oxidants and reductants also depends on the stability of their oxidation and reduction products, these trends should be regarded as at best approximate. As can be seen from the data given in Table **4.10.1**, the alkali metals furnish an important exception to the general trend that substances become more reducing towards the lower left of the periodic table. Among the elements included,[2] lithium and not cesium is the most powerful reducing agent due to the high stability of the lithium cation in aqueous solution (anomalously high hydration energy). Further, from the potentials given in Table **4.10.1**, it can also be seen that on going from K^+ to Rb^+ and Cs^+ the reduction potentials do not decrease but instead remain approximately constant. In this case the decrease in ionization energy throughout this series is compensated for by a set of similar factors.[3]

Table 4.10.1 . Standard reduction potentials of aqueous alkali metal cations.

Reduction	$E°$
$Li^+(aq) + e^- \rightarrow Li(s)$	-3.040
$Na^+(aq) + e^- \rightarrow Na(s)$	-2.713
$K^+(aq) + e^- \rightarrow K(s)$	-2.924
$Rb^+(aq) + e^- \rightarrow Rb(s)$	-2.924
$Cs^+(aq) + e^- \rightarrow Cs(s)$	-2.923

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- **8.1.4: As may be seen from considering an element's redox diagrams, main group elements (aside from the noble gases) generally are more oxidizing towards the upper left of the periodic table and more reducing towards the lower right of the periodic table** by Stephen Contakes is licensed CC BY 4.0.

4.11: Latimer Diagrams

A selection of the redox reactions nitrogen is known to undergo in 1.0 *M* aqueous acid is given in Figure **4.11.1**.

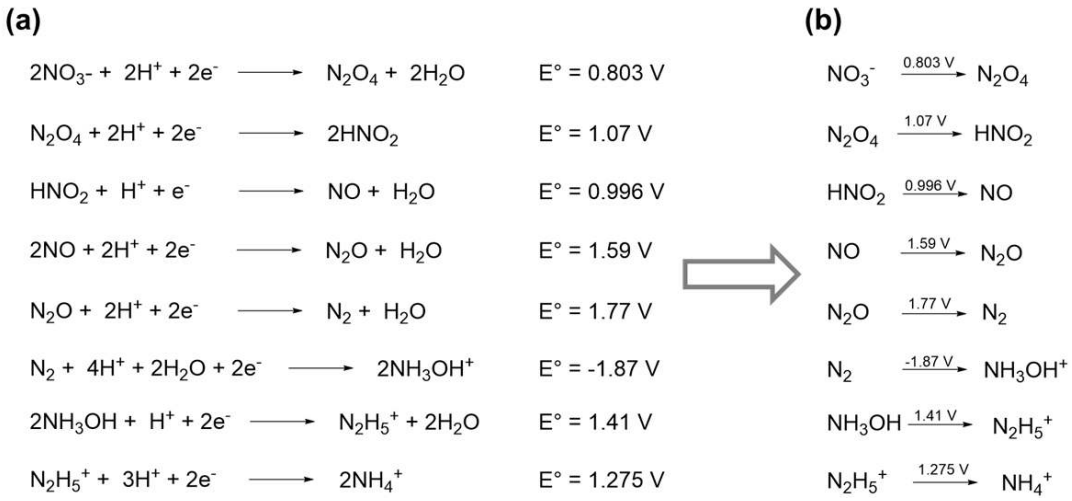


Figure **4.11.1**. (a) Full and (b) compact presentation of selected standard reduction half reactions for nitrogenous species in aqueous solution at pH 0.

The most important information in Figure **4.11.1** is the redox potentials and the identity of each nitrogen-containing species. In fact, if the latter are known, the number of electrons, water molecules, and any H^+ (in acid) or OH^- (in base) involved in the reduction may be deduced from the stoichiometry of the reaction. Consequently, the information in Figure **4.11.1** may be presented more compactly by only giving the nitrogen-containing species and the associated redox potential.

An Introduction to Latimer Diagrams

Latimer diagrams helpfully summarize elements' redox chemistry in a compact format, showing only the redox-active species and the associated redox potentials. A **Latimer diagram** is shown in Figure **4.11.2**. In a Latimer diagram, the product of each reduction half reaction is the reactant in the succeeding reduction half reaction, and the associated reduction potential is written above the reaction arrow. Because of this it is possible to represent the entire sequence of redox reactions even more compactly by writing out the reactions on a single line.

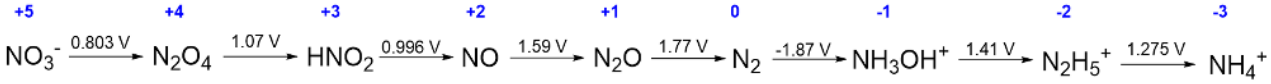


Figure **4.11.2**: Latimer diagram for nitrogen in acidic conditions.

Latimer diagrams include two additional pieces of information that are helpful for their interpretion.

1. The diagram should specify whether it represents reactivity in acidic (pH 0), basic (pH 14), or other solution conditions. In cases where it is not specified, it is customary to assume the diagram refers to behavior in pH 0 aqueous solution.
2. The oxidation state of the element is given at the top of the diagram, as shown in blue in Figure **4.11.2**. This helps to makes it easier to keep track of the number of electrons involved in each reduction reaction and to compare the redox behavior of related species.

More Complicated Latimer Diagrams

When it is possible to convert between two species by more than one pathway, the multiple pathways may be represented in the Latimer diagram. As shown in Figure **4.11.3**, additional reaction arrows can be added above or below the main pathway to represent the additional reactions that may occur. The diagram in Figure **4.11.2** presents a large number of possible interconversions. However, every possible interconversion is not represented. For example, the reduction potential for the reduction of N_2O_4 to NO is not presented. This type of selectivity is common in Latimer diagrams, but it does not necessarily mean that the missing conversions are not possible or that the potential has not been measured experimentally.

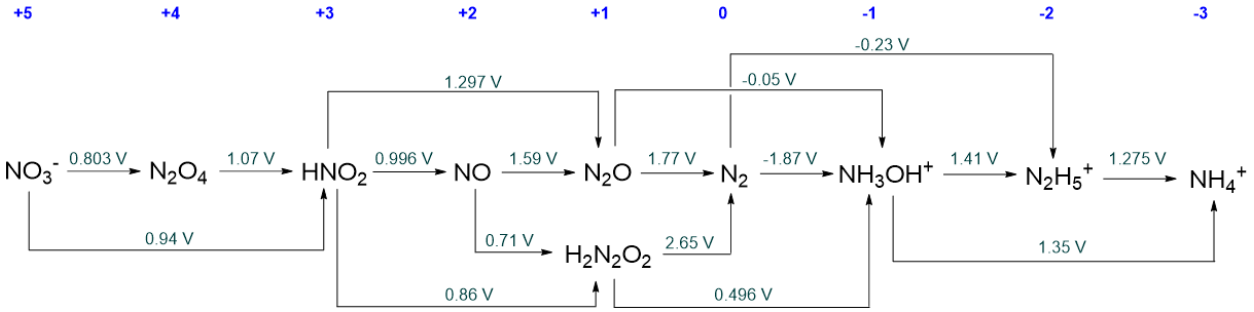


Figure **4.11.3**. Latimer Diagram for Nitrogen at pH 0. Redrawn from reference 1.

Since $\Delta G° = -nFE°$, the potentials in Latimer diagrams are thermodynamic quantities and may always be calculated from solution thermodynamic parameters. In fact, some redox potentials reported in Latimer diagrams have been only determined that way. An example is the reduction potential of fluorine,

$$F_2(g) \; + \; 2H^+ \; 2e^- \; \rightarrow \; 2HF \quad E° \; = \; 3.053 \text{ V} \;\; \text{in} \;\; \text{acid}$$

This potential has not been experimentally measured since F_2 is unstable in aqueous solution, reacting rapidly to give HF and O_2.

$$2\,F_2 \; + \; 2\,H_2O \xrightarrow{\text{fast}} 4\,HF \; + O_2$$

When a potential is missing from a Latimer diagram, it may always be calculated by constructing a thermodynamic cycle involving the known and unknown potentials, as explained in Note **4.11.1** at the bottom of this page.

Disproportionation

Latimer diagrams are useful for determining if a species is thermodynamically stable or will undergo disproportionation. **Disproportionation** occurs when a species undergoes a redox reaction with itself to produce two or more stable products. For instance, in basic solution ReO_3 can undergo disproportionation to ReO_4^- and $ReO_2{\cdot}2H_2O$.

$$2Re^{VI}O_3 + 2H_2O \rightarrow Re^{VII}O_4^- + Re^{V}O_2 \cdot 2H_2O$$

As with all redox reactions, disproportionation reactions are thermodynamically favored when they possess a positive reaction potential. To see when this will be the case it is helpful to separate the disproportionation reaction into its half reactions:

$$\text{Reduction}: Re^{VI}O_3 + H_2O + 2H^+ + e^- \rightarrow Re^{V}O_2 \cdot 2H_2O \qquad E° = -0.446V$$

$$\text{Oxidation}: Re^{VI}O_3 + H_2O \rightarrow Re^{VII}O_4^- + 2H^+ + e^- \qquad E° = +0.889V$$

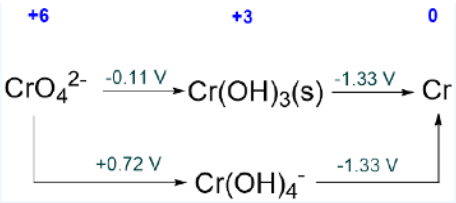
$$\text{Sum}: 2Re^{VI}O_3 + 2H_2O \rightarrow Re^{VII}O_4^- + Re^{V}O_2 \cdot 2H_2O \qquad E° = -0.446V + 0.889V = +0.443V$$

Notice that the disproportionation of ReO_3 in basic solution is favored because the favorable reaction potential for ReO_3 oxidation is larger in magnitude than the negative oxidation potential for ReO_3 reduction.

The ReO_3 disproportionation reaction is a specific instance of a general case. Any species possessing a standard reduction potential that is more positive than the standard reduction potential leading to their formation is thermodynamically unstable with respect to disproportionation. This situation is easy to recognize using a Latimer diagram; species are unstable to disproportionation (will disproportionate) if the potential on their right is more positive than that on their left.

✔ Example 4.11.1

The Latimer diagram that has been reported for Cr in pH 14 aqueous solution is given below. Which, if any, species are unstable with respect to disproportionation?



Solution

All of the species are stable with respect to disproportionation since all the potentials on the right of all the Cr^{3+} intermediates are less than those on their left.

Comparing Redox Chemistry with Latimer Diagrams

Acidic and Basic Conditions

Latimer diagrams are useful for comparing the redox chemistry of an element under different conditions (typically pH 0 and pH 14). This is well-illustrated by the Latimer diagrams of chromium explored in Examples **4.11.1** and **4.11.2** above. Another simple example involves the acidic and basic Latimer diagrams of mercury shown in Figure **4.11.4**.

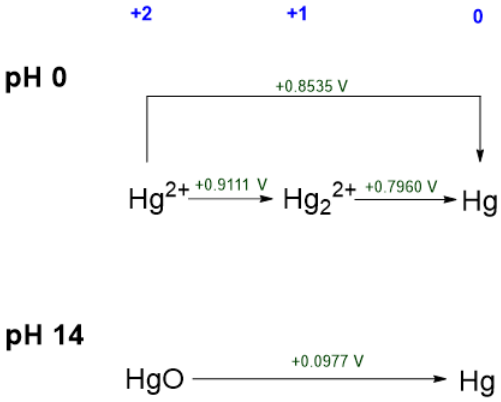


Figure**4.11.4**: Latimer diagrams for mercury in aqueous solution.

From Scheme **4.11.*IV***, several things are clear about mercury's redox chemistry under acidic and basic conditions:

- Mercury(I) ion, Hg_2^{2+}, is thermodynamically stable under acidic conditions, but it is not likely stable under basic conditions. This may be inferred from its absence in the pH 14 diagram, which suggests that it is not readily formed under basic conditions.
- Elemental mercury is the thermodynamically most stable form of the element under both acidic and basic conditions. This may be inferred because the standard reduction potential for all mercury +2 and +1 species is positive.
- In both its +1 and +2 oxidation states (Hg^{2+} and Hg_2^{2+} ions), mercury is a fairly powerful oxidant under acidic conditions (with **E°** 0.796 - 0.9111 V). In contrast, under basic conditions the +2 form of mercury (HgO) is only a weak oxidant **E°** = 0.0977 V.
- All of the mercury species represented are thermodynamically stable towards disproportionation.

Comparing Elements Under Similar Conditions

Latimer diagrams are useful for comparing the redox chemistry of different elements under similar conditions. For instance, the redox behavior of mercury and its congeners in acid solution may be easily compared using the Latimer diagrams. From Figure **4.11.5**, it is clear that Zn and Cd exhibit similar redox behavior. Both should dissolve at pH 0 to give dications. In contrast, elemental mercury should be stable towards acid. Mercury is also the only group 12 element for which the +1 oxidation state is stable.

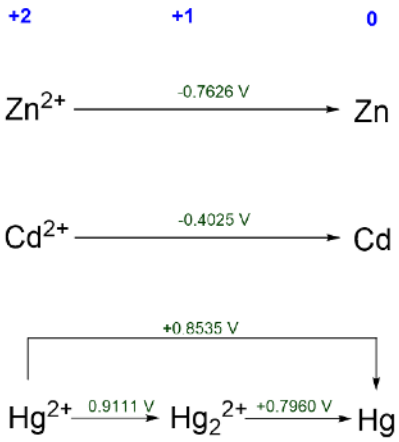


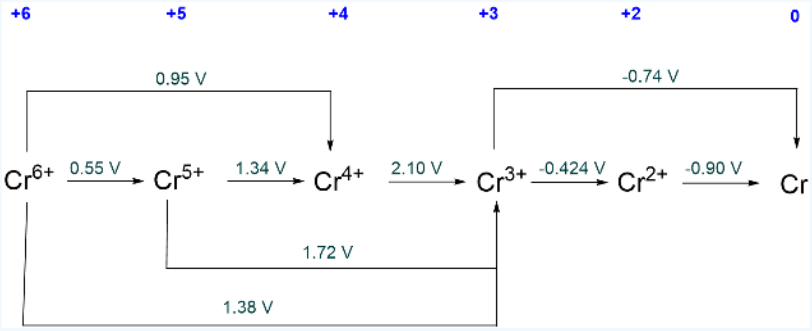
Figure **4.11.5**. Latimer diagrams for the group 12 elements in pH 0 aqueous solution.

As the examples above indicate, Latimer diagrams are helpful summaries of elements' redox chemistry, but it still requires a fair bit of careful reading to use them to make sense of trends in elements' redox chemistry or to trace out the disproportionation products of a given redox state. The published diagrams also tend to be limited to describing the redox chemistry of the elements under conditions of extreme pH. Fortunately, a variety of graphical representations of elements' redox chemistry have been developed that are particularly useful for estimating the dominant form of an element under a given set of conditions and for making sense of trends in elements' redox chemistry. These graphical methods will be described in the next two sections.

Problems

? Exercise 4.11.1

The Latimer diagram for Cr in pH 0 aqueous solution is given below. Which, if any, species are unstable with respect to disproportionation?

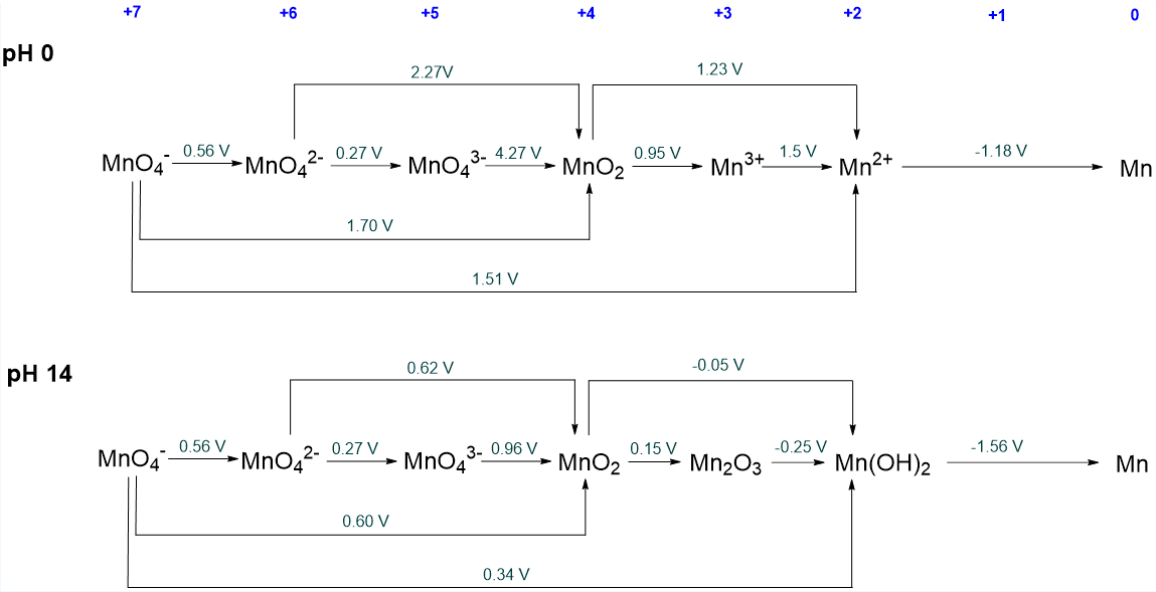


Answer

Both Cr^{5+} and Cr^{4+} are unstable towards disproportionation since the potentials on their right (for their reduction) are greater than the potentials on their left (for their formation by reduction).

? Exercise 4.11.2

Which manganese species are unstable with respect to disproportionation in aqueous solution under acidic and basic conditions? What will each of these metastable species give on disproportionation? The Latimer diagrams for manganese are given below.



Answer

Under acidic conditions the following species are unstable with respect to disproportionation:

MnO_4^{2-} is unstable with respect to disproportionation to MnO_4^- and MnO_2. MnO_4^{3-} is unstable with respect to MnO_4^{2-} and MnO_2. However, since MnO_4^{2-} is unstable with respect to disproportionation the ultimate products of the disproportionation will be MnO_4^- and MnO_2. Mn^{3+} is unstable towards disproportionation to MnO_2 and Mn^{2+}.

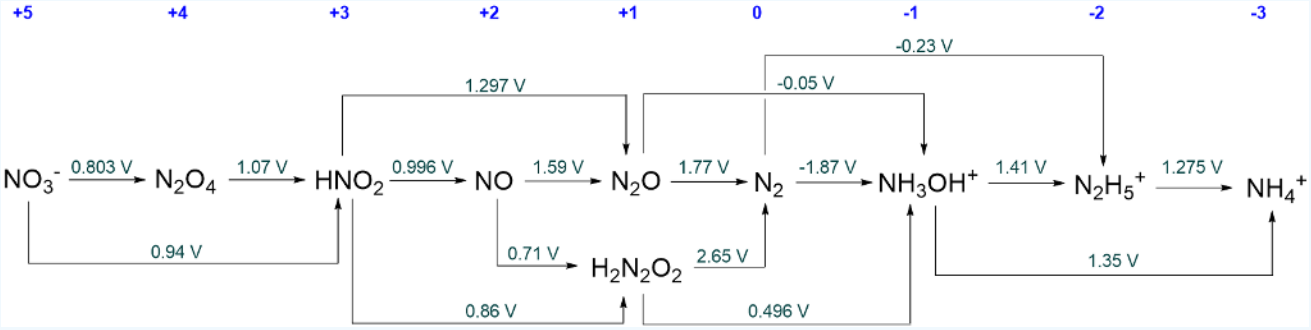
Notice that the +3 oxidation state of Mn is stable under basic conditions but not acidic ones.

MnO_4^{2-} is unstable with respect to disproportionation to MnO_4^- and MnO_2. MnO_4^{3-} is unstable with respect to MnO_4^{2-} and MnO_2. However, since MnO_4^{2-} is unstable with respect to disproportionation, the ultimate products of the disproportionation will be MnO_4^- and MnO_2.

Under basic conditions the following species are unstable with respect to disproprtionation:

? Exercise 4.11.3

Which nitrogen species in the Figure **4.11.1**, (which for convenience is reproduced below) are unstable with respect to disproportionation?



Answer

They will be all the intermediate species for which the redox potential on their right is more positive than that on their left. These are N_2O_4, HNO_2, NO, N_2O, $H_2N_2O_2$, and NH_3OH^+.

? Exercise 4.11.4

As far as you are able, determine what each metastable nitrogen species will disproportionate to at pH 0.

Answer

Initially the metastable species will disproportionate to give their immediate neighbors in the Latimer diagram.

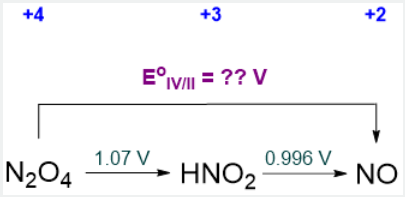
However, many of these neighbors are themselves metastable with respect to disproportionation, and so ultimately disproportionation will only stop when species that are stable towards disproportionation are reached.

In the case of N_2O_4, HNO_2, NO, N_2O, and $H_2N_2O_2$, disproportionation will ultimately give NO_3^- and N_2.

For NH_3OH^+, disproportionation will give N_2 and N_2H_5.

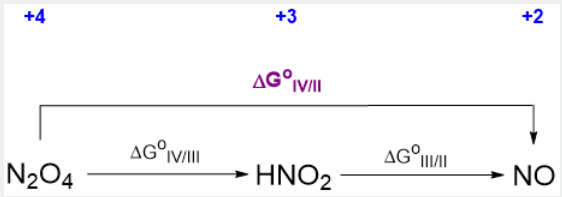
Note 4.11.1.

Potentials that are not shown in a Latimer diagram may always be calculated by constructing a **thermodynamic cycle**. Consider the interconversion of N_2O_4 to NO, $E^\circ_{IV/II}$, the value of which is not given in the standard nitrogen Latimer diagram presented in Scheme **4.11.*sfII***. Part of that diagram is reproduced as Scheme **4.11.VI** below.



Scheme **4.11.VI**. Partial Latimer diagram for nitrogen in acid.

The relevant thermodynamic cycle that may be used to calculate the unknown potential involves the free energies and is depicted in Scheme **4.11.VII**.

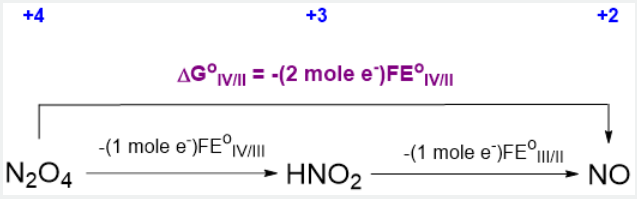


Scheme **4.11.VII**. Thermodynamic cycle that may be used to determine $E^\circ_{N_2O_4 \rightarrow NO}$.

The free energy for each conversion step in the cycle is related to the corresponding potential by the relationship

$$\Delta G^\circ = nFE^\circ$$

where n is the number of electrons involved in each step. With this substitution, the thermodynamic cycle above may be converted to the one shown in Scheme **4.11.VIII**.



Scheme **4.11.VIII**. Thermodynamic cycle expressed in terms of standard potentials.

From Scheme **4.11.VIII** it may be seen that

$$\Delta G^\circ_{IV/II} = -(2 \text{ mol } e^-)FE^\circ_{IV/II} = -(1 \text{ mol } e^-)FE^\circ_{IV/III} - (1 \text{ mol } e^-)FE^\circ_{III/II}$$

Cancelling the constant F and replacing the unknown potentials with the values in Scheme **4.11.VI** gives

$$-(2\ \text{mol}\ e^-)E^\circ_{IV/II} \quad = \quad -(1\ \text{mol}\ e^-)(1.07\ \text{V}) \quad - \quad (1\ \text{mol}\ e^-)(0.996\ \text{V})$$

from which $E^\circ_{IV/II}$ may be calculated, giving $E^\circ_{IV/II}$ = +1.033 V.

References

1. All standard reduction potentials are taken from Bard, A. J.; Parsons, R.; Jordan, J. Standard potentials in aqueous solution. M. Dekker: New York, 1985.

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- **8.1.4.1: Latimer Diagrams summarize elements' redox properties on a single line** by Stephen M. Contakes is licensed CC BY 4.0.

4.12: Pourbaix Diagrams

Pourbaix diagrams depict the most stable species or phase of an element as a function of potential and pH. Pourbaix or potential-pH/E-pH diagrams were developed and popularized by Marcel Pourbaix, who used them to study corrosion. Pourbaix diagrams depict the most stable species or phase of an element in aqueous solution as a function of potential (on the y-axis) and pH (on the x-axis). Pourbaix's *Atlas of Electrochemical Equilibria in Aqueous Solution* contains diagrams for many elements along with extensive notes on their construction.[1]

Introduction to Pourbaix Diagrams

Pourbaix diagrams are similar to phase diagrams in that they show species as a function of potential and pH. Unlike a conventional phase diagram, the regions depict the dominant species instead of the only species present under a given set of conditions (for more detail see Note 1).[1] For solution phase species, the dominant chemical species will not only depend on potential and pH as depicted in the diagram; the formal concentration of the species is important too. For the sort of corrosion applications Pourbaix envisioned, these concentrations are typically quite low, so for this reason the regions depicted in most Pourbaix diagrams correspond to 1 mM total concentration.

The lines in Pourbaix diagrams represent redox reactions that occur in neutral solutions (horizontal lines), acid-base reactions (vertical lines), and redox reactions that occur in acid or basic conditions (diagonal lines). Each lines indicate a equilibrium between two species. For example, in the Pourbaix diagram for Fe below, the horizontal line between the Fe^{3+} and Fe^{2+} regions represents the reaction $\mathbf{Fe^{3+}_{(aq)} + e^- = Fe^{2+}_{(aq)}}$, which has a standard potential of +0.77 V (Figure **4.12.1**. While we could use standard potentials for all these lines, in practice Pourbaix diagrams are usually plotted for lower ion concentrations (often 1 mM) that are more relevant to corrosion and electrochemical experiments. The areas contained by the lines represent potential and pH conditions in which a given species is stable.

Example: Iron Pourbaix diagram

Areas in the Pourbaix diagram mark regions where a single species (Fe^{2+}(aq), Fe_3O_4(s), etc.) is stable. More stable species tend to occupy larger areas.

Lines mark places where two species exist in equilibrium.

- **Pure redox** reactions are **horizontal** lines - these reactions are not pH-dependent
- **Pure acid-base** reactions are **vertical** lines - these do not depend on potential
- Reactions that are **both** acid-base and redox have a slope of -0.0592 V/pH x # H^+/# e^-)

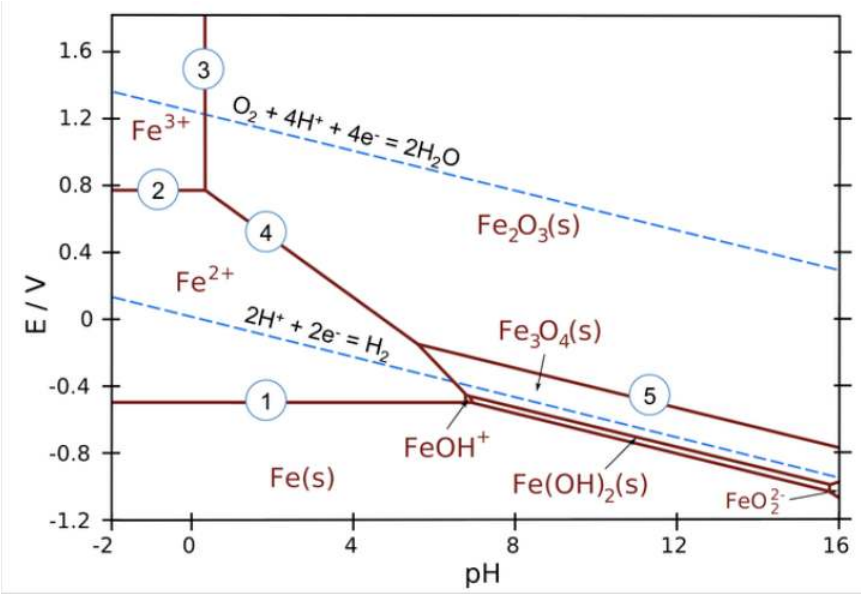


Figure **4.12.1**: Pourbaix diagram for iron at ionic concentrations of 1.0 mM. (CC BY-SA 3.0 Unported; Metallos via Wikipedia)

Examples of equilibria in the iron Pourbaix diagram (numbered in Figure 4.12.1):

1. $Fe^{2+} + 2e^- \longrightarrow Fe_{(s)}$ (pure redox reaction - no pH dependence)
2. $Fe^{3+} + e^- \longrightarrow Fe^{2+}$ (pure redox reaction - no pH dependence)
3. $2Fe^{3+} + 3H_2O \longrightarrow Fe_2O_{3(s)} + 6H^+$ (pure acid-base, no redox)
4. $2Fe^{2+} + 3H_2O \longrightarrow Fe_2O_{3(s)} + 6H^+ + 2e^-$ (slope = -59.2 x 6/2 = -178 mV/pH)
5. $2Fe_3O_{4(s)} + H_2O \longrightarrow 2H^+ + 2e^-$ (slope = -59.2 x 2/2 = -59.2 mV/pH)

Water in Pourbaix Diagrams

The water redox reactions typically are plotted as dotted lines on these more complicated Pourbaix diagrams for other elements. In Figure 4.12.1, water redox reactions are shown as the blue dotted diagonal lines. Liquid water is stable *only* in the region between the dotted lines. Above the O_2 line, water is unstable and will be oxidized:

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O.$$

Below the H_2 line, water is unstable and H^+ will be reduced:

$$2H^+ + 2e^- \rightarrow H_2$$

These lines are useful for several reasons.

- First, in cases where water oxidation and reduction are fast relative to the electrochemical phenomenon of interest, the water oxidation and reduction potentials limit the potential that the element can experience - *i.e.*, if a solution is exposed to a more extreme potential in the form of an electrode or a strong chemical or photochemical oxidant or reductant, then that substance will oxidize or reduce water instead of the element depicted in the diagram.
- Second, the oxygen reduction equilibrium is important for corrosion applications taking place in an oxygen-containing environment. In these environments, the pH-dependent standard potential of oxygen reduction depicted by the upper blue line in Figure 4.12.1 determines the potential of the system. As can be seen in Figure 4.12.1, the potential of this equilibrium is above that of the region of stability of metallic iron. This indicates that metallic iron is not thermodynamically stable at the oxygen partial pressures of the diagram; Fe^{3+} species are instead. Moreover, the precise species that metallic iron will form when it is exposed to a higher potential varies with pH. At higher pH values, an oxide will be produced - either $Fe(OH)_2$(s), Fe_3O_4(s), or Fe_2O_3(s). If these solid phases coat the surface of the iron so as to insulate it from reaction with oxygen, they will effectively prevent iron's oxidation. Such layers are said to be **passivating**, and the resulting **anodic passivation** is a form of kinetic, not thermodynamic, stabilization of the metal.

For active metals such as Fe, the region where the pure element is stable is typically below the H_2 line. This means that iron metal is unstable in contact with water, undergoing reactions:

$Fe_{(s)} + 2H^+ \longrightarrow Fe^{2+}{}_{(aq)} + H_2$ (in acid)

$fe_{(s)} + 2H_2O \longrightarrow Fe(OH)_{2(s)} + H_2$ (in base)

Iron (and most other metals) are also thermodynamically unstable in air-saturated water, where the potential of the solution is close to the O_2 line in the Pourbaix diagram. Here the spontaneous reactions are:

$4Fe_{(s)} + 3O_2 + 12H^+ \longrightarrow 4Fe^{3+} + 6H_2O$ (in acid)

\(\ce{4Fe_{(s)} + 3O2 -> 2Fe2O3_{(s)} (in base)

Straightforward applications of Pourbaix diagrams involve estimating how the potential of a system at equilibrium changes with conditions, as illustrated in Example 4.12.1.

Example 4.12.1

Metal indicator electrodes are used to measure the potential of solutions. The potential is determined by the redox equilibria taking place therein. This potential may be measured by immersing the metal indicator electrode and a reference electrode in the solution to be tested.

Use the information in Figure **4.12.2** (Do not use the information in Figure **4.12.1** since it corresponds to a different Fe concentration) to:

1. Explain how you might construct a pH-sensitive electrode from a Pt wire metal indicator electrode, $FeSO_4$ (which is water soluble) and rust, which for the purposes of this problem you may take as equivalent to $Fe_2O_3(s)$ and its hydrates.
2. What would be the pH range limits of the sensor?
3. What voltages would it read (vs. NHE) over this range?
4. Are there any limitations that should be observed when using this electrode to measure pH?

Solution

1. The electrode may be made by dissolving the $FeSO_4$ in the solution to be tested to give a solution that is ~1mM Fe^{2+}. Then enough rust would be added to give a cloudy solution, indicating that solid is present and the equilibrium between Fe^{2+} and $FeSO_4$ established. Finally, the Pt wire and a suitable reference electrode would be inserted into the solution and the potential measured.
2. The electrode would only work between pH values of ~0.5 and 7. Below pH 0.5 the Fe_2O_3 would dissolve, while above pH 7 the Fe^{2+} will precipitate.
3. The voltages should range from ~0.77 V (vs. SHE) at pH ~0.5 to ~-0.44V (vs. SHE) at pH~7.
4. There are several limitations and much would need to be done to validate this as a suitable method for the determination of pH. First, the potentials listed above assume that the iron concentration in the test solution is the same as that used to construct the diagram in Figure **4.12.1**. Thus they are at best rough estimates, and the electrode would need to be calibrated using solutions of known pH before use. Second, if the electrode is used in air, over time the Fe^{2+} will oxidize to Fe^{3+} species, shifting the response of the electrode. Because of this the electrode should either be used in an anoxic environment or prepared just before use.

What do the lines in a Pourbaix diagram mean?

The phase lines in Pourbaix diagrams correspond to switchpoints between the dominant species in solution for solution phase species or the points at which precipitation or phase change occurs for equilibria involving solid and/or pure liquid phases. To see how this works it helps to consider the three common cases:

- *Equilibria that involve electron transfer only* give rise to horizontal lines because the potential does not depend on pH. An example is the line between the Fe^{3+} and Fe^{2+} regions, marked 2 in Figure **4.12.2**. In this case the reaction potential when $\frac{Fe^{2+}}{Fe^{3+}}$=1 is $E^\circ_{Fe^{3/2+}}$:

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \quad E = E^\circ_{Fe^{3/2+}} - \frac{0.05916\ V}{1}\log\frac{[Fe^{2+}]}{[Fe^{3+}]}$$
$$= E^\circ_{Fe^{3/2+}} - (0.05916\ V)\log 1 = E^\circ_{Fe^{3/2+}}$$

- *Acid-base equilibria that do not involve changes in the redox state of the elements involved* give rise to vertical lines, the position of which depend on the stated concentration of the diagram. An example is the line between the Fe^{3+}(aq) and Fe_2O_3(s) regions, marked 3 in Figure **4.12.2**. This corresponds to the equilibrium:

$$2\ Fe^{3+} + 3\ H_2O \rightarrow Fe_2O_3(s) + 6\ H^+$$

  The equilibrium line in this case is determined by the reaction's equilibrium constant

$$K = \frac{[H^+]^6}{[Fe^{3+}]^2}$$

  From this it can be seen that the pH ($[H^+]$) is a function only of the value of $[Fe^{3+}]$ used to construct the diagram (since $[H^+] = (K[Fe^{3+}]^2)^{1/6} = constant$), so the line is vertical.

- *Equilibria that involve a combination of electron transfer and acid-base chemistry* give rise to slanted lines. An example is the equilibrium between Fe^{2+} and Fe_2O_3(s), marked 4 in Figure **4.12.2**. This corresponds to the equilibrium:

$$Fe_2O_3(s) + 6\ H^+ + 2\ e^- \rightarrow 2\ Fe^{2+} + 3\ H_2O$$

for which

$$E = E^{\circ}_{Fe_2O_3/Fe^{2+}} - \frac{0.05916\ V}{2} \log \frac{[Fe^{2+}]^2}{[H^+]^6}$$

from which it can be seen that the potential will be pH dependent.

Corrosion and Passivation

Corrosion and passivation. It certainly sounds bad for our friend Fe: unstable in water, no matter what the pH or potential. Given enough time, it will all turn into rust. But iron (and other active metals) can corrode, or can be stabilized against corrosion, depending on the conditions. Because our civilization is dependent on the use of active metals such as Fe, Al, Zn, Ti, Cr... for practically everything, it is important to understand this, and we can do so by referring to the Pourbaix diagram.

The **corrosion** of iron (and other active metals such as Al) is indeed rapid in parts of the Pourbaix diagram where the element is oxidized to a soluble, ionic product such as Fe^{3+}(aq) or Al^{3+}(aq). However, solids such as Fe_2O_3, and especially Al_2O_3, form a protective coating on the metal that greatly impedes the corrosion reaction. This phenomenon is called **passivation.**

Draw a vertical line through the iron Pourbaix diagram at the pH of tap water (about 6) and you will discover something interesting: at slightly acidic pH, iron is quite unstable with respect to corrosion by the reaction:

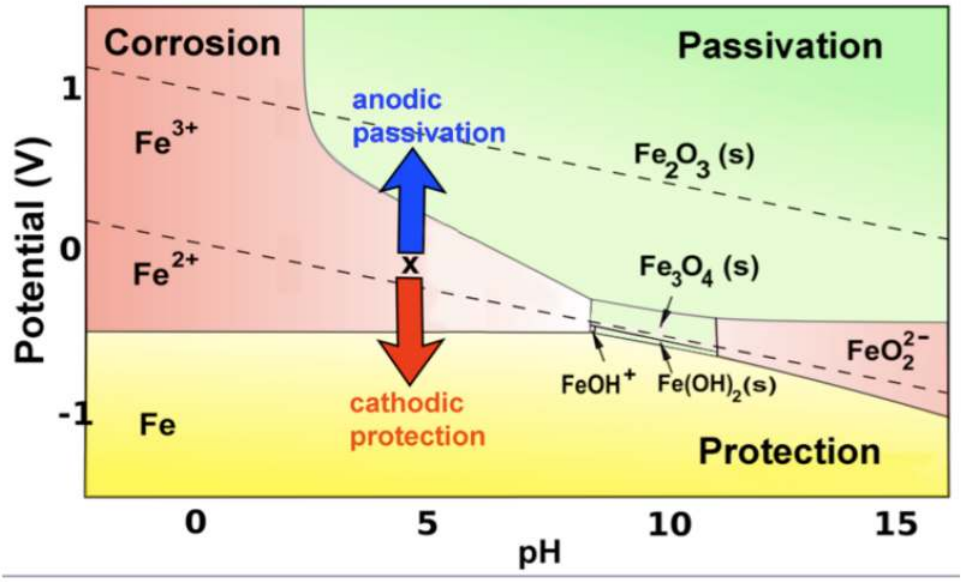
$$Fe_{(s)} + 2H^+ \longrightarrow Fe^{2+}{}_{(aq)} + H_2 \tag{4.12.1}$$

but *only in water that contains relatively little oxygen*, i.e., in solutions where the potential is near the H_2 line. Saturating the water with air or oxygen moves the system closer to the O_2 line, where the most stable species is Fe_2O_3 and the corrosion reaction is:

$$4Fe_{(s)} + 3O_2 \longrightarrow 2Fe_2O_{3\,(s)} \tag{4.12.2}$$

This oxidation reaction is orders of magnitude slower because the oxide that is formed *passivates* the surface. Therefore iron corrodes much more slowly in oxygenated solutions.

More generally, iron (and other active metals) are passivated whenever they oxidize to produce a solid product, and corrode whenever the product is ionic and soluble. This behavior can be summed up on the color-coded Pourbaix diagram below. The red and green regions represent conditions under which oxidation of iron produces soluble and insoluble products, respectively.



In the yellow part of the diagram, an active metal such as iron can be **protected** by a second mechanism, which is to bias it so that its potential is below the oxidation potential of the metal. This **cathodic protection** strategy is most frequently carried out by

connecting a more active metal such as Mg or Zn to the iron or steel object (e.g., the hull of a ship, or an underground gas pipeline) that is being protected. The active metal (which must be higher than Fe in the activity series) is also in contact with the solution and slowly corrodes, so it must eventually be replaced. In some cases a battery or DC power supply - the anode of which oxidizes water to oxygen in the solution - is used instead to apply a negative bias.



The white patches visible on the ship's hull are zinc block sacrificial anodes.

Another common mode of corrosion of iron and carbon steel is **differential aeration.** In this case, part of the iron object - e.g., the base of a bridge, or the drill in an oil rig - is under water or in an anoxic environment such as mud or soil. The potential of the solution is close to the H_2 line in the Pourbaix diagram, where Fe can corrode to Fe^{2+} (aq). Another part of the iron object is in the air, or near the surface where water is well oxygenated. At that surface oxygen can be reduced to water, $O_2 + 4H^+ + 4e^- = 2\ H_2O$. The conductive iron object completes the circuit, carrying electrons from the anode (where Fe is oxidized) to the cathode (where O_2 is reduced). Corrosion by differential aeration can be rapid because soluble ions are produced, and the reaction has a driving force of over 1 V. Iron or carbon steel that is subjected to frequent weathering, such as the cast iron bridge and lamppost shown below, is corroded on the surface by differential aeration.



Rusty cast iron bridge and lamppost, North Ayrshire, Scotland

Differential aeration is involved in the formation of a rust ring around wet areas of cast iron, e.g., an iron frying pan left partially submerged in water for a day or more. (You may have seen this mechanism of corrosion in action when you did not get to the dirty dishes right away). Under the water, Fe is oxidized to soluble Fe^{2+}, and at the water line O_2 is reduced to H_2O. As Fe^{2+} ions diffuse towards the water surface, they encounter oxygen molecules and are oxidized to Fe^{3+}. However Fe^{3+} is insoluble at neutral pH and deposits as rust, typically just below the water line, forming the rust ring.

References

1. Pourbaix, M., Atlas of electrochemical equilibria in aqueous solutions. 2nd ed. Houston: National Association of Corrosion Engineers, 1974.

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- **8.1.4.3: Pourbaix Diagrams are Redox Phase Diagrams that Summarize the most stable form of an element at a given pH and solution potential** by Stephen Contakes is licensed CC BY 4.0.

CHAPTER OVERVIEW

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5.1: The Solid State of Matter

When most liquids are cooled, they eventually freeze and form crystalline solids, solids in which the atoms, ions, or molecules are arranged in a definite repeating pattern. It is also possible for a liquid to freeze before its molecules become arranged in an orderly pattern. The resulting materials are called amorphous solids or noncrystalline solids (or, sometimes, glasses). The particles of such solids lack an ordered internal structure and are randomly arranged (Figure 5.1.1).

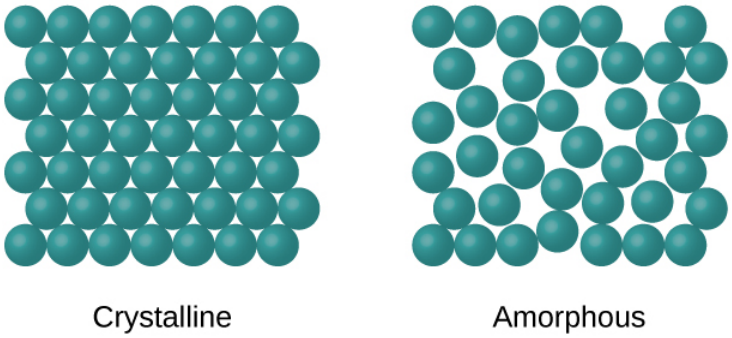


Figure 5.1.1: The entities of a solid phase may be arranged in a regular, repeating pattern (crystalline solids) or randomly (amorphous).

The crystalline arrangement shows many circles drawn in rows and stacked together tightly. The amorphous arrangement shows many circles spread slightly apart and in no organized pattern.

Metals and ionic compounds typically form ordered, crystalline solids. Substances that consist of large molecules, or a mixture of molecules whose movements are more restricted, often form amorphous solids. For examples, candle waxes are amorphous solids composed of large hydrocarbon molecules. Some substances, such as boron oxide (Figure 5.1.2), can form either crystalline or amorphous solids, depending on the conditions under which it is produced. Also, amorphous solids may undergo a transition to the crystalline state under appropriate conditions.

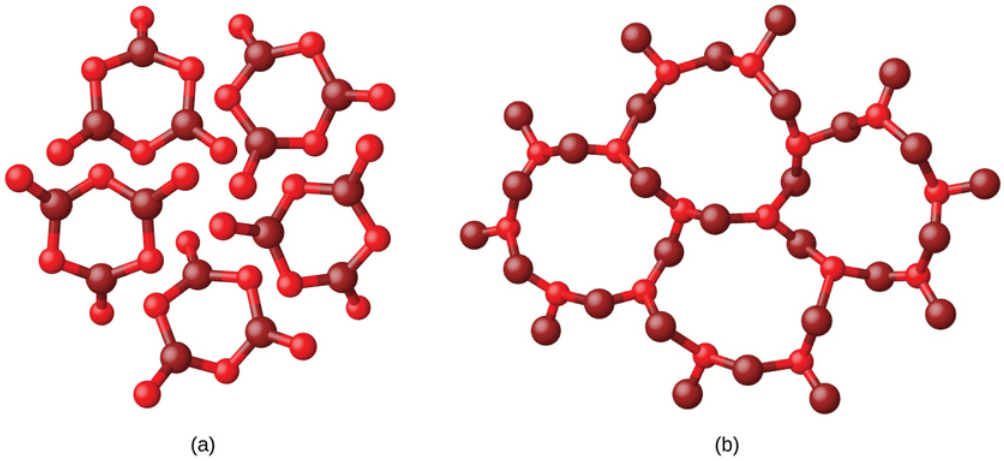


Figure 5.1.2: (a) Diboron trioxide, B_2O_3, is normally found as a white, amorphous solid (a glass), which has a high degree of disorder in its structure. (b) By careful, extended heating, it can be converted into a crystalline form of B_2O_3, which has a very ordered arrangement.

The first structure of diboron trioxide shows five identical and separated hexagonal rings. The second structure of diboron trioxide shows a more interconnected structure with four large rings forming a more stable structure.

Crystalline solids are generally classified according the nature of the forces that hold its particles together. These forces are primarily responsible for the physical properties exhibited by the bulk solids. The following sections provide descriptions of the major types of crystalline solids: ionic, metallic, covalent network, and molecular.

Metallic Solids

Metallic solids such as crystals of copper, aluminum, and iron are formed by metal atoms Figure 5.1.4. The structure of metallic crystals is often described as a uniform distribution of atomic nuclei within a “sea” of delocalized electrons. The atoms within such

a metallic solid are held together by a unique force known as *metallic bonding* that gives rise to many useful and varied bulk properties. All exhibit high thermal and electrical conductivity, metallic luster, and malleability. Many are very hard and quite strong. Because of their malleability (the ability to deform under pressure or hammering), they do not shatter and, therefore, make useful construction materials. The melting points of the metals vary widely. Mercury is a liquid at room temperature, and the alkali metals melt below 200 °C. Several post-transition metals also have low melting points, whereas the transition metals melt at temperatures above 1000 °C. These differences reflect differences in strengths of metallic bonding among the metals.

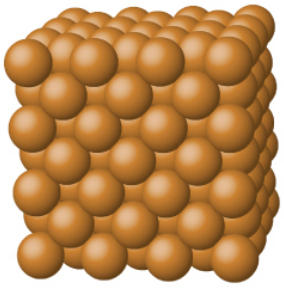


Figure **5.1.3**: Copper is a metallic solid.

Ionic Solids

Ionic solids, such as sodium chloride and nickel oxide, are composed of positive and negative ions that are held together by electrostatic attractions, which can be quite strong (Figure **5.1.3**). Many ionic crystals also have high melting points. This is due to the very strong attractions between the ions—in ionic compounds, the attractions between full charges are (much) larger than those between the partial charges in polar molecular compounds. This will be looked at in more detail in a later discussion of lattice energies. Although they are hard, they also tend to be brittle, and they shatter rather than bend. Ionic solids do not conduct electricity; however, they do conduct when molten or dissolved because their ions are free to move. Many simple compounds formed by the reaction of a metallic element with a nonmetallic element are ionic.

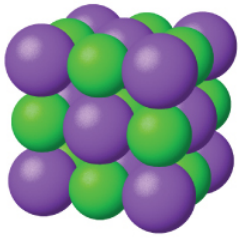


Figure **5.1.4**: Sodium chloride is an ionic solid.

A cube composed of purple and green spheres is shown. The cube has dimensions of three by three spheres. The purple spheres are slightly larger than the green spheres.

Covalent Network Solids

Covalent network solids include crystals of diamond, silicon, some other nonmetals, and some covalent compounds such as silicon dioxide (sand) and silicon carbide (carborundum, the abrasive on sandpaper). Many minerals have networks of covalent bonds. The atoms in these solids are held together by a network of covalent bonds, as shown in Figure **5.1.5**. To break or to melt a covalent network solid, covalent bonds must be broken. Because covalent bonds are relatively strong, covalent network solids are typically characterized by hardness, strength, and high melting points. For example, diamond is one of the hardest substances known and melts above 3500 °C.

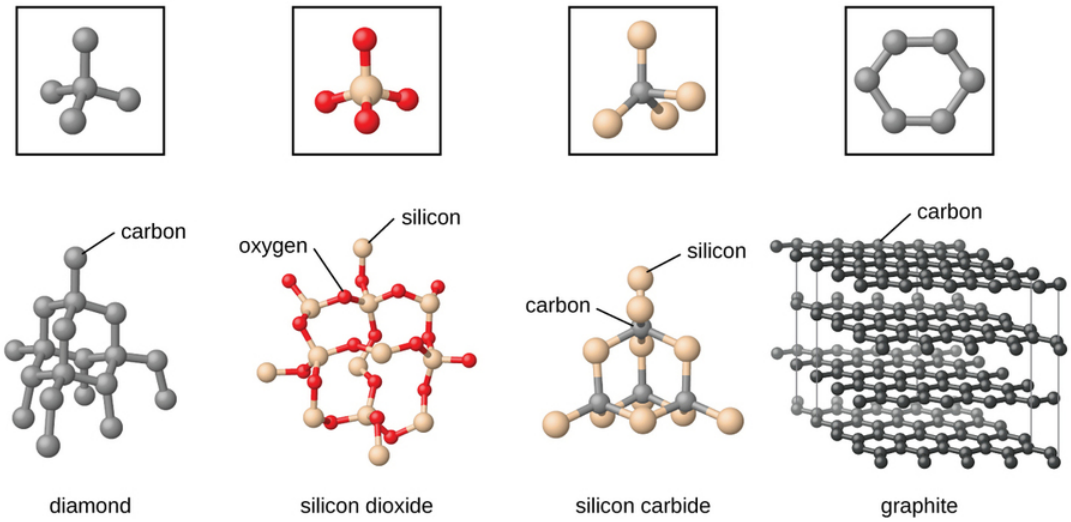


Figure **5.1.5**. A covalent crystal contains a three-dimensional network of covalent bonds, as illustrated by the structures of diamond, silicon dioxide, silicon carbide, and graphite. Graphite is an exceptional example, composed of planar sheets of covalent crystals that are held together in layers by noncovalent forces. Unlike typical covalent solids, graphite is very soft and electrically conductive.

The complex three dimensional structure of diamond, silicon dioxide, silicon carbide and graphite is shown along with a a smaller repeating unit of the structure shown above each structure.

Molecular Solids

Molecular solids, such as ice, sucrose (table sugar), and iodine, as shown in Figure **5.1.6**, are composed of neutral molecules. The strengths of the attractive forces between the units present in different crystals vary widely, as indicated by the melting points of the crystals. Small symmetrical molecules (nonpolar molecules), such as H_2, N_2, O_2, and F_2, have weak attractive forces and form molecular solids with very low melting points (below −200 °C). Substances consisting of larger, nonpolar molecules have larger attractive forces and melt at higher temperatures. Molecular solids composed of molecules with permanent dipole moments (polar molecules) melt at still higher temperatures. Examples include ice (melting point, 0 °C) and table sugar (melting point, 185 °C).

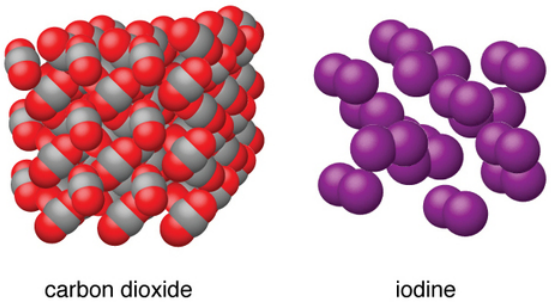


Figure **5.1.6**: Carbon dioxide (CO_2) consists of small, nonpolar molecules and forms a molecular solid with a melting point of −78 °C. Iodine (I_2) consists of larger, nonpolar molecules and forms a molecular solid that melts at 114 °C.

On the left, many red and grey molecules are densely stacked in a 3-D drawing to represent carbon dioxide. On the right, purple molecules are scattered randomly to represent iodine.

Properties of Solids

A crystalline solid, like those listed in Table **5.1.1** has a precise melting temperature because each atom or molecule of the same type is held in place with the same forces or energy. Thus, the attractions between the units that make up the crystal all have the same strength and all require the same amount of energy to be broken. The gradual softening of an amorphous material differs dramatically from the distinct melting of a crystalline solid. This results from the structural nonequivalence of the molecules in the amorphous solid. Some forces are weaker than others, and when an amorphous material is heated, the weakest intermolecular attractions break first. As the temperature is increased further, the stronger attractions are broken. Thus amorphous materials soften over a range of temperatures.

Table 5.1.1: Types of Crystalline Solids and Their Properties

Type of Solid	Type of Particles	Type of Attractions	Properties	Examples
metallic	atoms of electropositive elements	metallic bonds	shiny, malleable, ductile, conducts heat and electricity well, variable hardness and melting temperature	Cu, Fe, Ti, Pb, U
ionic	ions	ionic bonds	hard, brittle, conducts electricity as a liquid but not as a solid, high to very high melting points	NaCl, Al_2O_3
covalent network	atoms of electronegative elements	covalent bonds	very hard, not conductive, very high melting points	C (diamond), SiO_2, SiC
molecular	molecules (or atoms)	IMFs	variable hardness, variable brittleness, not conductive, low melting points	H_2O, CO_2, I_2, $C_{12}H_{22}O_{11}$

Graphene: Material of the Future

Carbon is an essential element in our world. The unique properties of carbon atoms allow the existence of carbon-based life forms such as ourselves. Carbon forms a huge variety of substances that we use on a daily basis, including those shown in Figure 5.1.7. You may be familiar with diamond and graphite, the two most common *allotropes* of carbon. (Allotropes are different structural forms of the same element.) Diamond is one of the hardest-known substances, whereas graphite is soft enough to be used as pencil lead. These very different properties stem from the different arrangements of the carbon atoms in the different allotropes.

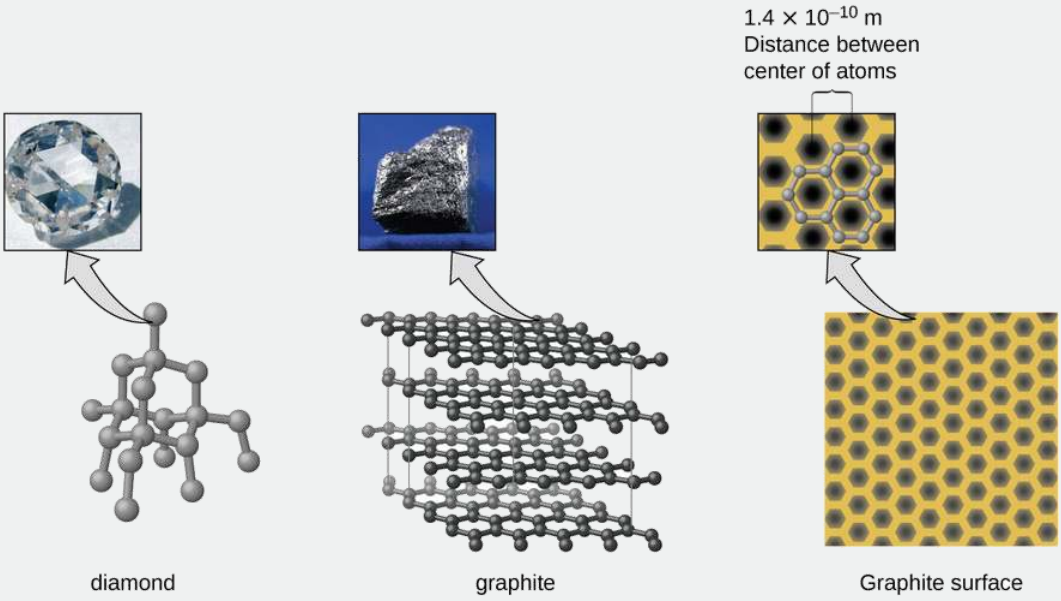


Figure **5.1.7**: Diamond is extremely hard because of the strong bonding between carbon atoms in all directions. Graphite (in pencil lead) rubs off onto paper due to the weak attractions between the carbon layers. An image of a graphite surface shows the distance between the centers of adjacent carbon atoms. (credit left photo: modification of work by Steve Jurvetson; credit middle photo: modification of work by United States Geological Survey)

A close up of a piece of diamond shows a three dimensional sturcture of a complex network of well bonded carbon atoms. A close up of a graphite shows several layers of carbon sheets. Each sheet is composed of a repeated and connected hexagonal structure of carbon atoms. The third diagram shows that the distance between the center of atoms is 1.4 times 10 to the power of negative 10 meters.

You may be less familiar with a recently discovered form of carbon: graphene. Graphene was first isolated in 2004 by using tape to peel off thinner and thinner layers from graphite. It is essentially a single sheet (one atom thick) of graphite. Graphene, illustrated in Figure **5.1.8**, is not only strong and lightweight, but it is also an excellent conductor of electricity and heat. These properties may prove very useful in a wide range of applications, such as vastly improved computer chips and circuits, better batteries and solar cells, and stronger and lighter structural materials. The 2010 Nobel Prize in Physics was awarded to Andre Geim and Konstantin Novoselov for their pioneering work with graphene.

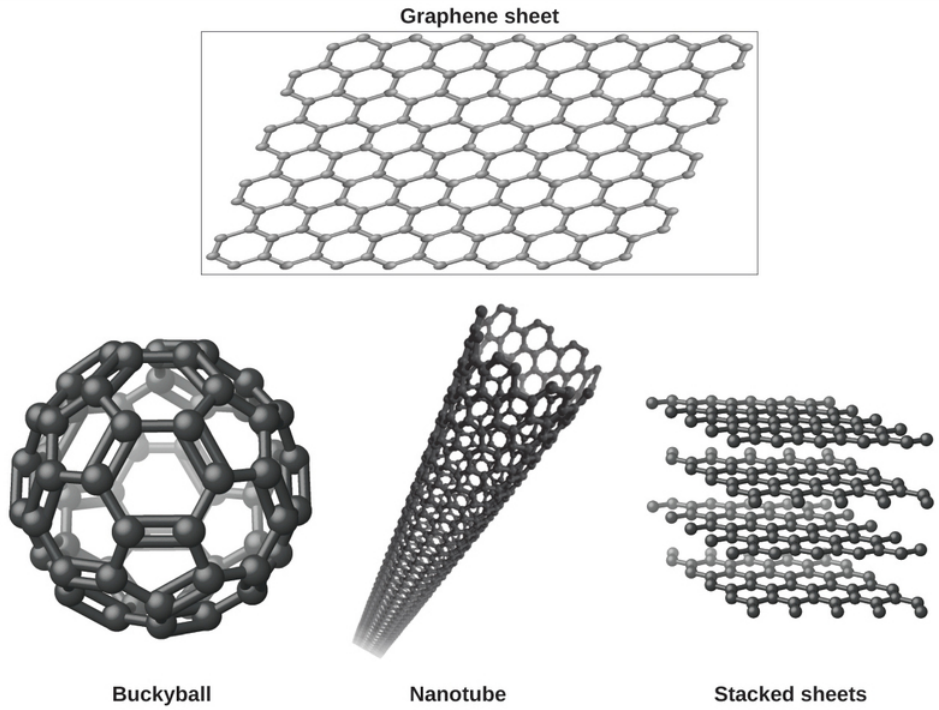


Figure **5.1.8**: Graphene sheets can be formed into buckyballs, nanotubes, and stacked layers.

A sheet of interconnected hexagonal rings is shown at the top. Below it, a bukcyball is shown which is a sphere is composed of hexagonal rings. In the lower middle image, a nanotube is shown that is made by rolling a graphene sheet into a tube. In the lower right image, stacked sheets made up of four horizontal sheets composed of joined, hexagonal rings is shown.

Summary

Some substances form crystalline solids consisting of particles in a very organized structure; others form amorphous (noncrystalline) solids with an internal structure that is not ordered. The main types of crystalline solids are ionic solids, metallic solids, covalent network solids, and molecular solids. The properties of the different kinds of crystalline solids are due to the types of particles of which they consist, the arrangements of the particles, and the strengths of the attractions between them. Because their particles experience identical attractions, crystalline solids have distinct melting temperatures; the particles in amorphous solids experience a range of interactions, so they soften gradually and melt over a range of temperatures.

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5.2: Lattice Structures in Metallic Solids

The Structures of Crystalline Metallic Solids

Over 90% of naturally occurring and man-made solids are crystalline. Most solids form with a regular arrangement of their particles because the overall attractive interactions between particles are maximized, and the total intermolecular energy is minimized, when the particles pack in the most efficient manner. The regular arrangement at an atomic level is often reflected at a macroscopic level. In this module, we will explore some of the details about the structures of metallic and ionic crystalline solids, and learn how these structures are determined experimentally.

We will begin our discussion of crystalline solids by considering elemental metals, which are relatively simple because each contains only one type of atom. A pure metal is a crystalline solid with metal atoms packed closely together in a repeating pattern. Some of the properties of metals in general, such as their malleability and ductility, are largely due to having identical atoms arranged in a regular pattern. The different properties of one metal compared to another partially depend on the sizes of their atoms and the specifics of their spatial arrangements. We will explore the similarities and differences of four of the most common metal crystal geometries in the sections that follow.

Unit Cells of Metals

The structure of a crystalline solid, whether a metal or not, is best described by considering its simplest repeating unit, which is referred to as its unit cell. The unit cell consists of lattice points that represent the locations of atoms or ions. The entire structure then consists of this unit cell repeating in three dimensions, as illustrated in Figure **5.2.1**. In general, a unit cell is defined by the lengths of three axes (*a*, *b*, and *c*) and the angles (*α*, *β*, and *γ*) between them, as illustrated in Figure **5.2.2**. The axes are defined as being the lengths between points in the space lattice. Consequently, unit cell axes join points with identical environments.

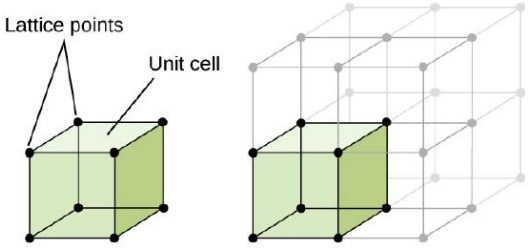


Figure **5.2.1**: A unit cell shows the locations of lattice points repeating in all directions.

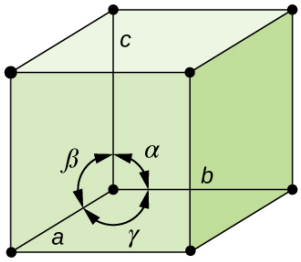


Figure **5.2.2**: A unit cell is defined by the lengths of its three axes (a, b, and c) and the angles (α, β, and γ) between the axes.

Most metal crystals are one of the four major types of unit cells. For now, we will focus on the three cubic unit cells: simple cubic , body-centered cubic unit cell, and face-centered cubic unit cell—all of which are illustrated in Figure **5.2.3**. (Note that there are actually seven different lattice systems, some of which have more than one type of lattice, for a total of 14 different types of unit cells. These are shown in Figure **5.2.4**.)

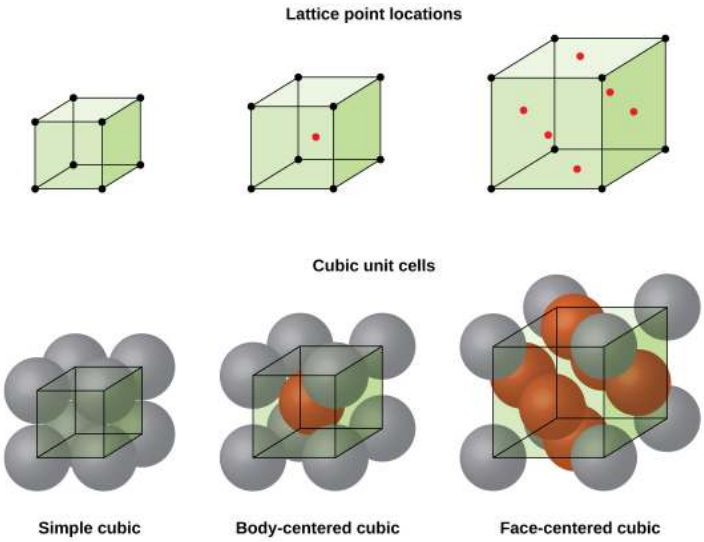


Figure **5.2.3**: Cubic unit cells of metals show (in the upper figures) the locations of lattice points and (in the lower figures) metal atoms located in the unit cell.

System/Axes/Angles	Unit Cells
Cubic $a = b = c$ $\alpha = \beta = \gamma = 90^\circ$	Simple, Face-centered, Body-centered
Tetragonal $a = b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	Simple, Body-centered
Orthorhombic $a \neq b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	Simple, Body-centered, Base-centered, Face-centered
Monoclinic $a \neq b \neq c$ $\alpha = \gamma = 90^\circ; \beta \neq 90^\circ$	Simple, Base-centered
Triclinic $a \neq b \neq c$ $\alpha \neq \beta \neq \gamma \neq 90^\circ$	
Hexagonal $a = b \neq c$ $\alpha = \beta = 90^\circ; \gamma = 120^\circ$	
Rhombohedral $a = b = c$ $\alpha = \beta = \gamma \neq 90^\circ$	

Figure **5.2.4**:There are seven different lattice systems and 14 different unit cells.

Simple Cubic (sc)

Let us begin our investigation of crystal lattice structure and unit cells with the most straightforward structure and the most basic unit cell. To visualize this, imagine taking a large number of identical spheres, such as tennis balls, and arranging them uniformly in a container. The simplest way to do this would be to make layers in which the spheres in one layer are directly above those in the layer below, as illustrated in Figure **5.2.5**. This arrangement is called simple cubic structure, and the unit cell is called the simple cubic unit cell or primitive cubic unit cell.

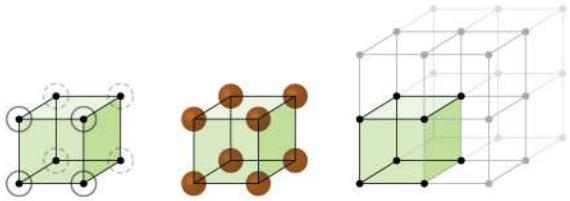


Figure **5.2.5**: .When metal atoms are arranged with spheres in one layer directly above or below spheres in another layer, the lattice structure is called simple cubic. Note that the spheres are in contact.

In a simple cubic structure, the spheres are not packed as closely as they could be, and they only "fill" about 52% of the volume of the container. This is a relatively inefficient arrangement, and only one metal (polonium, Po) crystallizes in a simple cubic structure. As shown in Figure **5.2.6**, a solid with this type of arrangement consists of planes (or layers) in which each atom contacts only the four nearest neighbors in its layer; one atom directly above it in the layer above; and one atom directly below it in the layer below. The number of other particles that each particle in a crystalline solid contacts is known as its coordination number. For a polonium atom in a simple cubic array, the coordination number is, therefore, six.

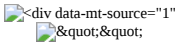


Figure **5.2.6**: An atom in a simple cubic lattice structure contacts six other atoms, so it has a coordination number of six.

In a simple cubic lattice, the unit cell that repeats in all directions is a cube defined by the centers of eight atoms, as shown in Figure **5.2.7**. Atoms at adjacent corners of this unit cell contact each other, so the edge length of this cell is equal to two atomic radii, or one atomic diameter. A cubic unit cell contains only the parts of these atoms that are within it. Since an atom at a corner of a simple cubic unit cell is contained by a total of eight unit cells, only one-eighth of that atom is within a specific unit cell. And since each simple cubic unit cell has one atom at each of its eight "corners," there is $8 \times \frac{1}{8} = 1$ atom within one simple cubic unit cell.

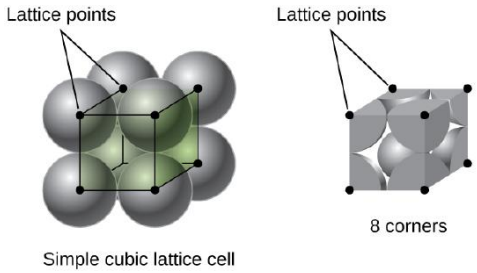
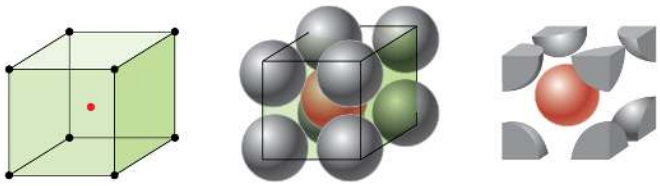


Figure **5.2.7**: A simple cubic lattice unit cell contains one-eighth of an atom at each of its eight corners, so it contains one atom total.

Body-Centered Cubic (bcc)

Some metals crystallize in an arrangement that has a cubic unit cell with atoms at all of the corners and an atom in the center, as shown in Figure **5.2.8**. This is called a body-centered cubic (BCC) solid. Atoms in the corners of a BCC unit cell do not contact each other but contact the atom in the center. A BCC unit cell contains two atoms: one-eighth of an atom at each of the eight corners ($8 \times \frac{1}{8} = 1$ atom from the corners) plus one atom from the center. Any atom in this structure touches four atoms in the layer above it and four atoms in the layer below it. Thus, an atom in a BCC structure has a coordination number of eight.



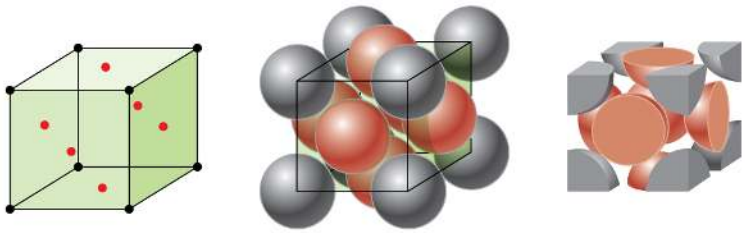
Body-centered cubic structure

Figure **5.2.8**: In a body-centered cubic structure, atoms in a specific layer do not touch each other. Each atom touches four atoms in the layer above it and four atoms in the layer below it.

Atoms in BCC arrangements are much more efficiently packed than in a simple cubic structure, occupying about 68% of the total volume. Isomorphous metals with a BCC structure include K, Ba, Cr, Mo, W, and Fe at room temperature. (Elements or compounds that crystallize with the same structure are said to be isomorphous.)

Face-centered Cubic (fcc) / Cubic Closest Packing (ccp)

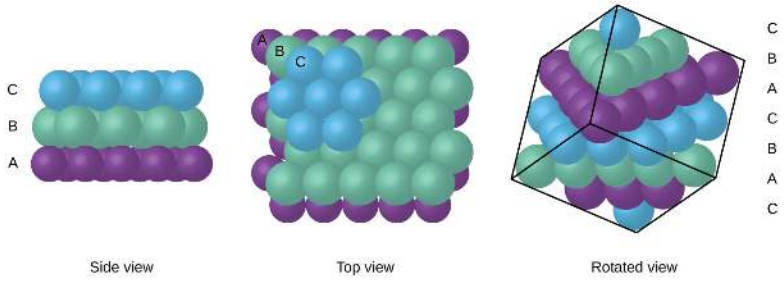
Many other metals, such as aluminum, copper, and lead, crystallize in an arrangement that has a cubic unit cell with atoms at all of the corners and at the centers of each face, as illustrated in Figure **5.2.9**. This arrangement is called a face-centered cubic (FCC) solid. A FCC unit cell contains four atoms: one-eighth of an atom at each of the eight corners ($8 \times \frac{1}{8} = 1$ atom from the corners) and one-half of an atom on each of the six faces ($6 \times \frac{1}{2} = 3$ atoms from the faces). The atoms at the corners touch the atoms in the centers of the adjacent faces along the face diagonals of the cube. Because the atoms are on identical lattice points, they have identical environments.



Face-centered cubic structure

Figure **5.2.9**:A face-centered cubic solid has atoms at the corners and, as the name implies, at the centers of the faces of its unit cells.

Atoms in an FCC arrangement are packed as closely together as possible, with atoms occupying 74% of the volume. This structure is also called cubic closest packing (CCP). In CCP, there are three repeating layers of hexagonally arranged atoms. Each atom contacts six atoms in its own layer, three in the layer above, and three in the layer below. In this arrangement, each atom touches 12 near neighbors, and therefore has a coordination number of 12. The fact that FCC and CCP arrangements are equivalent may not be immediately obvious, but why they are actually the same structure is illustrated in Figure **5.2.10**.



Cubic closest packed structure

Figure **5.2.10**: A CCP arrangement consists of three repeating layers (ABCABC…) of hexagonally arranged atoms. Atoms in a CCP structure have a coordination number of 12 because they contact six atoms in their layer, plus three atoms in the layer above and three atoms in the layer below. By rotating our perspective, we can see that a CCP structure has a unit cell with a face containing an atom from layer A at one corner, atoms from layer B across a diagonal (at two corners and in the middle of the face), and an atom from layer C at the remaining corner. This is the same as a face-centered cubic arrangement.

Because closer packing maximizes the overall attractions between atoms and minimizes the total intermolecular energy, the atoms in most metals pack in this manner. We find two types of closest packing in simple metallic crystalline structures: CCP, which we have already encountered, and hexagonal closest packing (HCP) shown in Figure **5.2.11**. Both consist of repeating layers of hexagonally arranged atoms. In both types, a second layer (B) is placed on the first layer (A) so that each atom in the second layer is in contact with three atoms in the first layer. The third layer is positioned in one of two ways. In HCP, atoms in the third layer are directly above atoms in the first layer (i.e., the third layer is also type A), and the stacking consists of alternating type A and type B close-packed layers (i.e., ABABAB⋯). In CCP, atoms in the third layer are not above atoms in either of the first two layers (i.e., the third layer is type C), and the stacking consists of alternating type A, type B, and type C close-packed layers (i.e., ABCABCABC⋯). About two–thirds of all metals crystallize in closest-packed arrays with coordination numbers of 12. Metals that crystallize in an HCP structure include Cd, Co, Li, Mg, Na, and Zn, and metals that crystallize in a CCP structure include Ag, Al, Ca, Cu, Ni, Pb, and Pt.

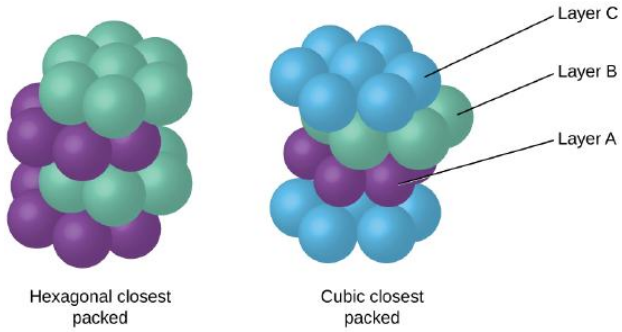


Figure **5.2.11**: In both types of closest packing, atoms are packed as compactly as possible. Hexagonal closest packing consists of two alternating layers (ABABAB…). Cubic closest packing consists of three alternating layers (ABCABCABC…).

Summary

The structures of crystalline metals and simple ionic compounds can be described in terms of packing of spheres. Metal atoms can pack in hexagonal closest-packed structures, cubic closest-packed structures, body-centered structures, and simple cubic structures.

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5.3: Lattice Structures in Ionic Solids

The Structures of Crystalline Ionic Solids

Ionic crystals consist of two or more different kinds of ions that usually have different sizes. The packing of these ions into a crystal structure is more complex than the packing of metal atoms that are the same size. Most monatomic ions behave as charged spheres, and their attraction for ions of opposite charge is the same in every direction. Consequently, stable structures for ionic compounds result (1) when ions of one charge are surrounded by as many ions as possible of the opposite charge and (2) when the cations and anions are in contact with each other. Structures are determined by two principal factors: the relative sizes of the ions and the ratio of the numbers of positive and negative ions in the compound.

Anions are generally larger than their neutral atom due to the additional electrons attracted to the nucleus. Likewise, cations are generally smaller than their neutral atom due to having fewer electrons attracted to the nucleus. In simple ionic structures, we usually find the larger anions arranged in a closest-packed array. The smaller cations commonly occupy one of two types of *holes* (or *interstices* or *interstitial sites*) that are located between the anions. The smaller type of hole is found between three anions in one plane and one anion in an adjacent plane. The four anions surrounding this hole are arranged at the corners of a tetrahedron, so the hole is called a *tetrahedral hole*. The larger type of hole is found at the center of six anions (three in one layer and three in an adjacent layer) located at the corners of an octahedron; this is called an *octahedral hole*. Figure **5.3.1** illustrates both of these types of holes.

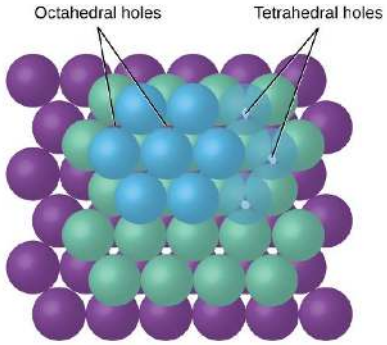


Figure **5.3.1**: Cations may occupy two types of holes between anions: octahedral holes or tetrahedral holes.

Depending on the relative sizes of the cations and anions, the cations of an ionic compound may occupy tetrahedral or octahedral holes, as illustrated in Figure **5.3.2**. Relatively small cations occupy tetrahedral holes, and larger cations occupy octahedral holes. If the cations are too large to fit into the octahedral holes, the anions may adopt a more open structure, such as a simple cubic array. The larger cations can then occupy the larger cubic holes made possible by the more open spacing.

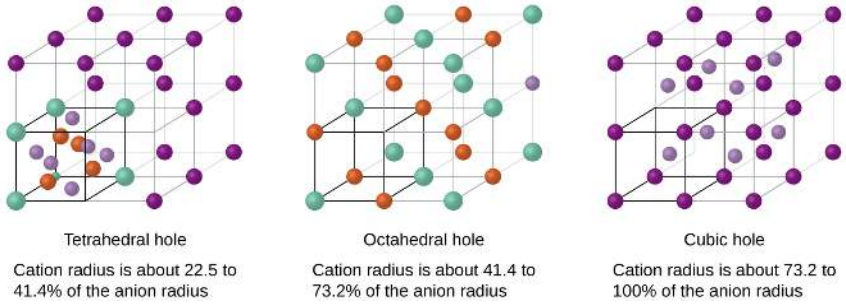


Figure **5.3.2**:A cation's size and the shape of the hole occupied by the compound are directly related.

There are two tetrahedral holes for each anion in either an HCP or CCP array of anions. A compound that crystallizes in a closest-packed array of anions with cations in the tetrahedral holes can have a maximum cation:anion ratio of 2:1; all of the tetrahedral holes are filled at this ratio. Examples include Li_2O, Na_2O, Li_2S, and Na_2S. Compounds with a ratio of less than 2:1 may also crystallize in a closest-packed array of anions with cations in the tetrahedral holes, if the ionic sizes fit. In these compounds, however, some of the tetrahedral holes remain vacant.

Therere is one octahedral hole for each anion in either an HCP or CCP structure . Thus, compounds with cations in octahedral holes in a closest-packed array of anions can have a maximum cation:anion ratio of 1:1. In NiO, MnS, NaCl, and KH, for example, all of the octahedral holes are filled. Ratios of less than 1:1 are observed when some of the octahedral holes remain empty.

In a simple cubic array of anions, there is one cubic hole that can be occupied by a cation for each anion in the array. In CsCl, and in other compounds with the same structure, all of the cubic holes are occupied. Half of the cubic holes are occupied in SrH_2, UO_2, $SrCl_2$, and CaF_2.

Example 5.3.1: Occupancy of Tetrahedral Holes

Zinc sulfide is an important industrial source of zinc and is also used as a white pigment in paint. Zinc sulfide crystallizes with zinc ions occupying one-half of the tetrahedral holes in a closest-packed array of sulfide ions. What is the formula of zinc sulfide?

Solution

Because there are two tetrahedral holes per anion (sulfide ion) and one-half of these holes are occupied by zinc ions, there must be $\frac{1}{2} \times 2$, or 1, zinc ion per sulfide ion. Thus, the formula is ZnS.

Example 5.3.2: Stoichiometry of Ionic Compounds Sapphire

Aluminum oxide crystallizes with aluminum ions in two-thirds of the octahedral holes in a closest-packed array of oxide ions. What is the formula of aluminum oxide?

Solution

Because there is one octahedral hole per anion (oxide ion) and only two-thirds of these holes are occupied, the ratio of aluminum to oxygen must be $\frac{2}{3}$:1, which would give $Al_{2/3}O$. The simplest whole number ratio is 2:3, so the formula is Al_2O_3.

Unit Cells of Ionic Compounds

Different types of ionic compounds often crystallize in the same structure when the relative sizes of their ions and their stoichiometries (the two principal features that determine structure) are similar.

Cubic Unit Cells

Many ionic compounds crystallize with cubic unit cells, and we will use these compounds to describe the general features of ionic structures. When an ionic compound is composed of cations and anions of similar size in a 1:1 ratio, it typically forms a simple cubic structure. Cesium chloride, CsCl, (Figure 5.3.3) is an example of this, with Cs^+ and Cl^- having radii of 174 pm and 181 pm, respectively. We can think of this as chloride ions forming a simple cubic unit cell, with a cesium ion in the center; or as cesium ions forming a unit cell with a chloride ion in the center; or as simple cubic unit cells formed by Cs^+ ions overlapping unit cells formed by Cl^- ions. Cesium ions and chloride ions touch along the body diagonals of the unit cells. One cesium ion and one chloride ion are present per unit cell, giving the l:l stoichiometry required by the formula for cesium chloride. Note that there is no lattice point in the center of the cell, and CsCl is not a BCC structure because a cesium ion is not identical to a chloride ion.

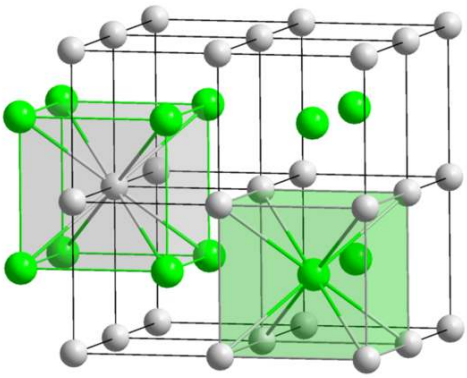


Figure 5.3.3: Ionic compounds with similar-sized cations and anions, such as CsCl, usually form a simple cubic structure. They can be described by unit cells with either cations at the corners or anions at the corners.

We have said that the location of lattice points is arbitrary. This is illustrated by an alternate description of the CsCl structure in which the lattice points are located in the centers of the cesium ions. In this description, the cesium ions are located on the lattice points at the corners of the cell, and the chloride ion is located at the center of the cell. The two unit cells are different, but they describe identical structures.

Face-Centered Cubic Unit Cells

When an ionic compound is composed of a 1:1 ratio of cations and anions that differ significantly in size, it typically crystallizes with an FCC unit cell, like that shown in Figure 5.3.4. Sodium chloride, NaCl, is an example of this, with Na^+ and Cl^- having radii of 102 pm and 181 pm, respectively. We can think of this as chloride ions forming an FCC cell, with sodium ions located in the octahedral holes in the middle of the cell edges and in the center of the cell. The sodium and chloride ions touch each other along the cell edges. The unit cell contains four sodium ions and four chloride ions, giving the 1:1 stoichiometry required by the formula, NaCl.

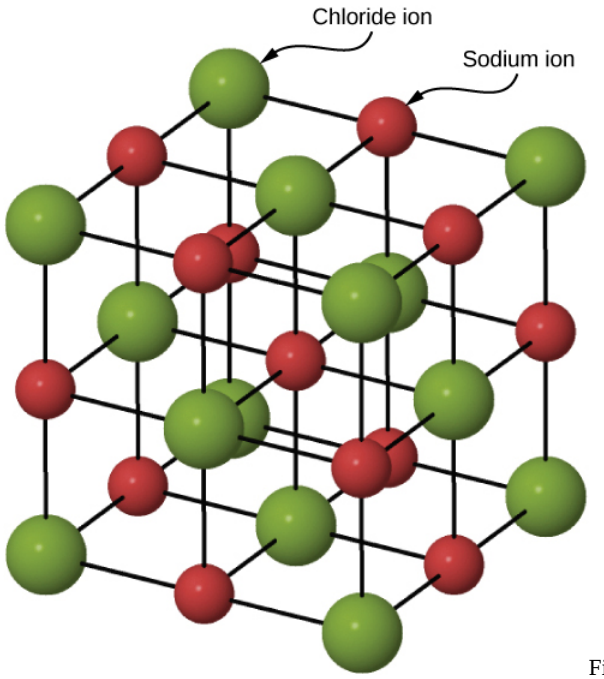
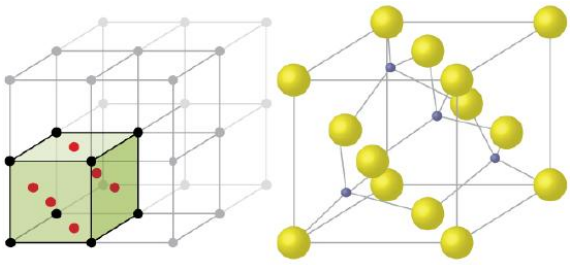


Figure 5.3.4: Ionic compounds with anions that are much larger than cations, such as NaCl, usually form an FCC structure. They can be described by FCC unit cells with cations in the octahedral holes. [LibreText]

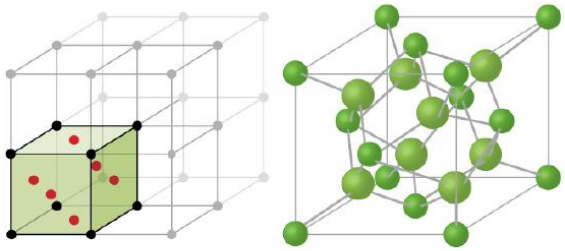
The cubic form of zinc sulfide, zinc blende, also crystallizes in an FCC unit cell, as illustrated in Figure **5.3.5**. This structure contains sulfide ions on the lattice points of an FCC lattice. (The arrangement of sulfide ions is identical to the arrangement of chloride ions in sodium chloride.) The radius of a zinc ion is only about 40% of the radius of a sulfide ion, so these small Zn^{2+} ions are located in alternating tetrahedral holes, that is, in one half of the tetrahedral holes. There are four zinc ions and four sulfide ions in the unit cell, giving the empirical formula ZnS.



ZnS face-centered unit cell

Figure **5.3.5**: ZnS, zinc sulfide (or zinc blende) forms an FCC unit cell with sulfide ions at the lattice points and much smaller zinc ions occupying half of the tetrahedral holes in the structure.

A calcium fluoride unit cell, like that shown in Figure **5.3.6**, is also an FCC unit cell, but in this case, the cations are located on the lattice points; equivalent calcium ions are located on the lattice points of an FCC lattice. All of the tetrahedral sites in the FCC array of calcium ions are occupied by fluoride ions. There are four calcium ions and eight fluoride ions in a unit cell, giving a calcium:fluorine ratio of 1:2, as required by the chemical formula, CaF_2. Close examination of Figure **5.3.6** will reveal a simple cubic array of fluoride ions with calcium ions in one half of the cubic holes. The structure cannot be described in terms of a space lattice of points on the fluoride ions because the fluoride ions do not all have identical environments. The orientation of the four calcium ions about the fluoride ions differs.



CaF_2 face-centered unit cell

Figure **5.3.6**: Calcium fluoride, CaF_2, forms an FCC unit cell with calcium ions (green) at the lattice points and fluoride ions (red) occupying all of the tetrahedral sites between them.

Summary

The structures of crystalline metals and simple ionic compounds can be described in terms of packing of spheres. The anions in simple ionic structures commonly adopt one of these structures, and the cations occupy the spaces remaining between the anions. Small cations usually occupy tetrahedral holes in a closest-packed array of anions. Larger cations usually occupy octahedral holes. Still larger cations can occupy cubic holes in a simple cubic array of anions. The structure of a solid can be described by indicating the size and shape of a unit cell and the contents of the cell.

Problems

? Exercise 5.3.1: Lithium selenide

Lithium selenide can be described as a closest-packed array of selenide ions with lithium ions in all of the tetrahedral holes. What it the formula of lithium selenide?

Answer

Li_2Se

Exercise 5.3.2

The white pigment titanium oxide crystallizes with titanium ions in one-half of the octahedral holes in a closest-packed array of oxide ions. What is the formula of titanium oxide?

Answer

TiO_2

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5.4: Alloys and Crystal Defects

Alloys

Alloys are mixtures of metals or a mixture of a metal and another element. An alloy may be a *solid solution* of metal elements (a homogeneous mixture) or a mixture of metallic phases (a heterogeneous mixture of two or more solutions). A *solid solution* can be formed by two mechanisms: (1) *atom exchange* or (2) *interstitial mechanism*. The relative size of each element in the mix plays a primary role in determining which mechanism will occur.

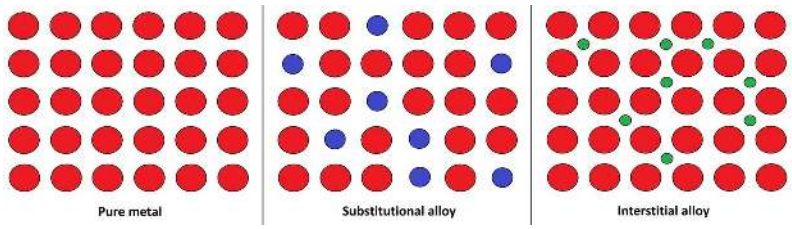


Figure **5.4.1**: Different atomic mechanisms of alloy formation, showing pure metal, substitutional, and interstitial structures. [Wikipedia]

Substitutional Alloys

When the atoms in a mixture are relatively similar in size, a solid solution usually occurs by the atom exchange method. In this case some of the atoms composing the metallic crystal are substituted with atoms another element. This is called a *substitutional alloy*. Bronze and brass are substitutional alloys in which copper atoms are substituted with tin or zinc atoms, respectively.

The bonding between two metals is best described as a combination of metallic electron "sharing" and covalent bonding, one can't occur without the other and the proportion of one to the other changes depending on the constituents involved. Metals share there electrons throughout there structure; this flow of electrons is the reason behind many of the characteristics associated with metals, including their ability to act as conductors. The different amount and strength of covalent bonds in a lattice can change depending on the specific metals involved and the ratios in which they are mixed. The covalent bonding is what is responsible for the crystal structure as well as the melting point and various other physical properties.

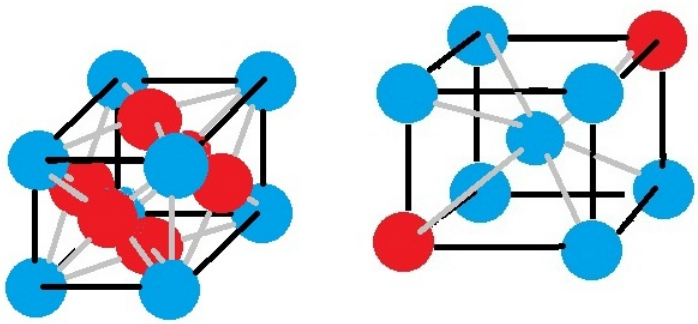


Figure **5.4.2**: Examples of Substitutional Metal Alloys. Depending on the specific type of substitutional alloy they can have multiple crystal structures. Two of the possible structures include Face Center Cubic (left), and Cubic Center Cubic (right). The structure of the metal alloy is not limited to these two structures, but combined they represent a large portion of the common alloys.

As the similarities between the electron structure of the metals involved in the alloy increase, the metallic character of the alloy decreases. Pure metals are useful but their applications are often limited to each individual metal's properties. Alloys allow metal mixtures that have increased resistance to oxidation, increased strength, conductivity, and melting point. Essentially any property can be manipulated by adjusting alloy concentrations. An example could be Brass Door fixtures, they are strong and resist corrosion better then pure zinc or copper, the two major metals that constitute a brass alloy. The combination also has a low melting point allowing it to be easily cast into many different shapes and sizes. There are many other aspects of substitutional alloys that could be explored in depth, but the basic concept is the idea that each individual metal in an alloy give the final product its chemical and physical properties.

Substitutional alloys played an important role in the development of human society and culture as we know it today. The Bronze age itself is named after the substitutional alloy consisting of tin in a metallic solution of copper. Ancient bronzes are very impure, or even mislabeled, containing large amounts of zinc and arsenic as well as lots of impurities. These many substitutional alloys allowed for stronger tools and weapons, they allowed for increased productivity in the workshop as well as on the battlefield. The need for raw materials like tin and copper for the production of bronze also spurred an increase in trade, since their ores are rarely found together. The current chemical understanding of substitutional alloys would not be so in depth if it weren't for the usefulness of the alloys to humans.

Interstitial Alloys

An interstitial mechanism usually occurs when the metal lattice atoms are much large than the other type of atom in the mixture. As such, the smaller atom cannot successfully replace an atom in the metal lattice. The smaller atoms become trapped in the *interstices* (spaces between the atoms in the metallic lattice). This is referred to as an *interstitial alloy*. Steel is an example of an interstitial alloy, because the very small carbon atoms fit into interstices of the iron matrix. Stainless steel is an example of a combination of interstitial and substitutional alloys, because the carbon atoms fit into the interstices, but some of the iron atoms are replaced with nickel and chromium atoms.

Crystal Defects

“Crystals are like people, it is the defects in them which tend to make them interesting!” - *Colin Humphreys.*

In a crystalline solid, the atoms, ions, or molecules are arranged in a definite repeating pattern, but occasional defects may occur in the pattern. Several types of defects are known, as illustrated in Figure **5.4.3**.

Vacancies are defects that occur when positions that should contain atoms or ions are vacant. Interstitial impurities occur when atoms or ions occupy positions, called interstitial sites, located between the regular positions for atoms. Substitutional impurities occur when atoms or ions occupy regular lattice positions. In some cases, the impurity atoms may be smaller than the lattice atoms (aqua atom in Figure **5.4.3**. When the impurity atom is too large to fit into the regular lattice positions, the substitutional impurity may distort the lattice structure (yellow atom in Figure **5.4.3**.

Trace amounts of impurities are sometimes added to a crystal (a process known as *doping)* in order to create defects in the structure that yield desirable changes in its properties. For example, silicon crystals are doped with varying amounts of different elements to yield suitable electrical properties for their use in the manufacture of semiconductors and computer chips.

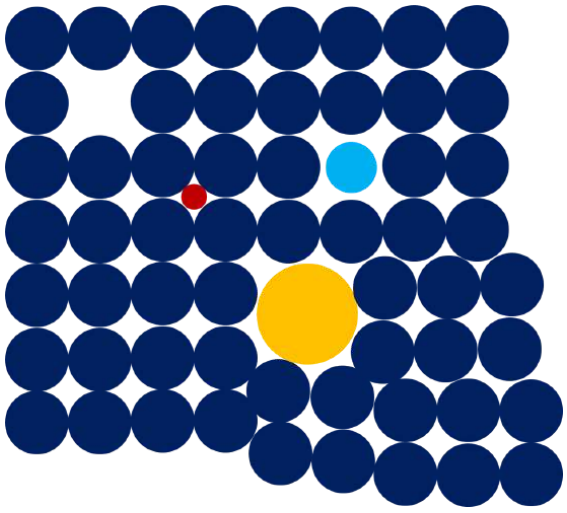


Figure **5.4.3**: Types of crystal defects include vacancies (blank space), interstitial impurities (red atom), and substitutional impurities (yellow and aqua atoms). (CC-BY-NC-SA 4.0, Kathryn A. Newton)

Because both alloys and defects can be achieved by substitutional and interstitial mechanisms, you may be wondering what the different between an alloy and a defect is. It is in part related to concentration. Generally, a defect is the result of very small concentrations of impurities, while alloys represent larger concentrations of atoms added to a structure. Alloys are usually made the

intentional incorporation of atoms into a lattice. Impurities, may or may not be intentional depending on the application of the material!

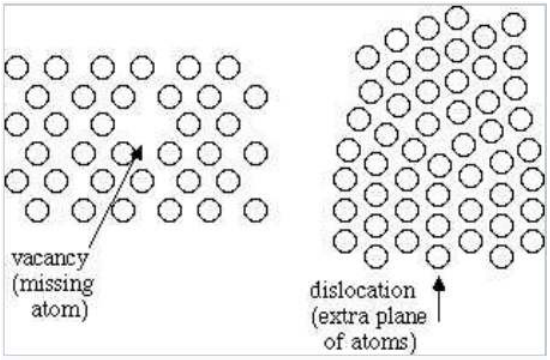


Figure 5.4.4: Vacancy and dislocation crystal defects. (CC-BY-NC, LibreText)

Metals, by virtue of their non-directional bonding, are more energetically tolerant of **defects** than are covalent network or ionic solids. Because there is no strong preference for one atomic position over another, the energy of a metallic crystal is not greatly impaired by the vacancy of a single atom or by the dislocation of a group of atoms. These kinds of "mistakes" in the packing of metal atoms within crystals are collectively called defects. The deformability of metals is the direct result of defects in the crystal structure. Defects in metals such as Al and Fe are responsible for the three orders of magnitude difference between the yield stress of annealed polycrystalline samples (i.e., normal articles of commerce) and perfect single crystals.

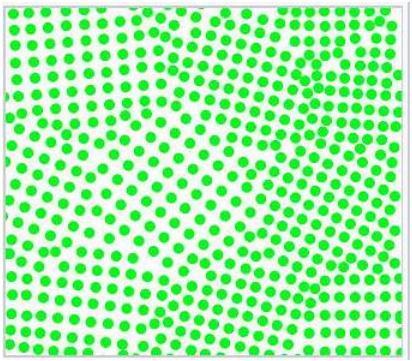


Figure 5.4.5: Grains and grain boundaries in polycrystalline material. (CC-BY-NC, LibreText)

Summary

When a molten metal is mixed with another substance, there are two mechanisms that can cause an alloy to form: (1) *atom exchange* or (2) *interstitial mechanism*. The relative size of each element in the mix plays a primary role in determining which mechanism will occur. When the atoms are relatively similar in size, the atom exchange method usually happens, where some of the atoms composing the metallic crystals are substituted with atoms of the other constituent. This is called a *substitutional alloy*. Examples of substitutional alloys include bronze and brass, in which some of the copper atoms are substituted with either tin or zinc atoms. Alloys can be also formed by inserting smaller atoms into holes in the metal lattice (interstitial alloys). Although the elemental composition of most alloys can vary over wide ranges, certain metals combine in only fixed proportions to form intermetallic compounds.

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SECTION OVERVIEW

5.5: Ionic Lattices

Topic hierarchy

5.5.1: Structure - Rock Salt (NaCl)

5.5.2: Structure - Caesium Chloride (CsCl)

5.5.3: Structure - Zinc Blende (ZnS)

5.5.4: Structure - Fluorite and Antifluorite

5.5.5: Structure - β-Cristobalite (SiO_2)

5.5.6: Spinel, Perovskite, and Rutile Structures

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5.5.1: Structure - Rock Salt (NaCl)

Rock salt also known as NaCl is an ionic compound. It occurs naturally as white cubic crystals. The structure of NaCl is formed by repeating the unit cell. It has an organized structure and has a 1:1 ratio of Na:Cl.

Introduction

Rock salt (**NaCl**) is an ionic compound that occurs naturally as white crystals. It is extracted from the mineral form halite or evaporation of seawater. The structure of NaCl is formed by repeating the face centered cubic unit cell. It has 1:1 stoichiometry ratio of Na:Cl with a molar mass of 58.4 g/mol. Compounds with the sodium chloride structure include alikali halides and metal oxides and transition-metal compounds. An important role to many important applications is structure and dynamics of water. Some applications include crystallization of proteins and conformational behavior of peptides and nucleic acids.

Structure

Figure **5.5.1.1** shows how the Na^+ and Cl^- ions occupy the space. The smaller ions are the Na^+ with has an atomic radius of 102 pm, and the larger ions are the Cl^- with an atomic radium of 181 pm. Since NaCl are one to one ratio as a compound, the coordination numbers of Na and Cl are equal. The larger green ions represent Cl^- and the smaller purple ions represent Na^+. However, the structure of this molecule allows their positions to be switched since the coordination numbers are equivalent.

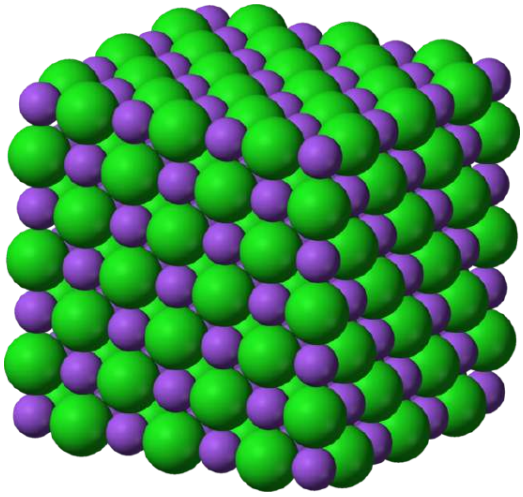


Figure **5.5.1.1**: The crystal structure of sodium chloride, **NaCl**, a typical ionic compound. The smaller purple spheres represent sodium cations, $\mathbf{Na^+}$, and the larger green spheres represent chloride anions, $\mathbf{Cl^-}$. (Public Domain; Benjah-bmm27 via Wikipedia)

A Unit Cell

The unit cell of **NaCl** consists of $\mathbf{Na^+}$ ions and $\mathbf{Cl^-}$ ions. There are four types of site: unique central position, face site, edge sites and corner site, which are used to determine the number of Na^+ ions and Cl^- ions in the unit cell of NaCl. When counting the number of ions, a corner site would be shared by 7 other unit cells. Therefore, 1 corner would be 1/8 of an ion. A similar occurrence happens with the face site and the edge sites. For a face site, it is shared by 1 other unit cell and for an edge site, the ion is shared by 3 other unit cells. **NaCl** is a face centered cubic unit cell which has four cations and four anions. This can be shown by counting the number of ions and multiplying them in relation to their position.

- $\mathbf{Na^+}$:

$$1_{center} + 12_{edge} \times \frac{1}{4} = 4 \,\text{sodium ions total per cell}$$

- $\mathbf{Cl^-}$:

$$4_{face} \times \frac{1}{2} + 8_{corner} \times \frac{1}{8} = 4 \,\text{chloride ions total per cell}$$

Each ion in this lattice has six of the other kind of ion as its nearest neighbors, and twelve of the same kind of ions as its second nearest neighbors. There are many ionic compounds that assume this structure including all other halides of Na, Li, K and Rb. CsF, AgF, AgCl, BaO, CoO, and SrS are also among many that will form similar structures to NaCl.

Outside Links

- Video about structure of NaCl: http://www.youtube.com/watch?v=csfOBynrF8E
- Unit Cell. http://www.case.edu/artsci/chem/chim...ids/xtal1.html

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5.5.2: Structure - Caesium Chloride (CsCl)

This page is going to discuss the structure of the molecule cesium chloride (**CsCl**), which is a white hydroscopic solid with a mass of 168.36 g/mol. Cesium Chloride is a type of unit cell that is commonly mistaken as Body-Centered Cubic. This misconception is easy to make, since there is a center atom in the unit cell, but CsCl is really a **non-closed packed structure** type.

Introduction

CsCl has a boiling point of 1303 degrees Celsius, a melting point of 646 degrees Celsius, and is very soluble in water. For the most part this molecule is stable, but is not compatible with strong oxidizing agents and strong acids. Although it is not hazardous, one should not prolong their exposure to CsCl. CsCl is an ionic compound that can be prepared by the reaction:

$$Cs_2CO_3 + 2\,HCl \longrightarrow 2\,CsCl + H_2O + CO_2 \tag{5.5.2.1}$$

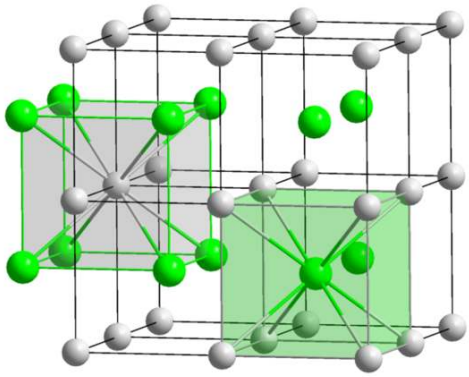


Figure **5.5.2.1**: **CsCl** Coordination Cubes. (Public Domain; Solid State via Wikipedia)

CsCl crystallize in a primitive cubic lattice which means the cubic unit cell has nodes only at its corners. The structure of CsCl can be seen as two interpenetrating cubes, one of Cs^+ and one of Cl^-. The ions are not touching one another. Touching would cause repulsion between the anion and cation. Some may mistake the structure type of CsCl with NaCl, but really the two are different. CsCl is more stable than NaCl, for it produces a more stable crystal and more energy is released.

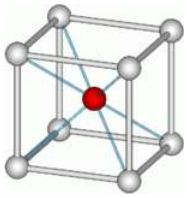


Figure **5.5.2.2**: Unit Cell of CsCl (en.Wikipedia.org/wiki/Caesium_chloride

Anions and cations have similar sizes. Each Cs^+ is surrounded by 8 Cl^- at the corners of its cube and each Cl^- is also surrounded by 8 Cs^+ at the corners of its cube. The cations are located at the center of the anions cube and the anions are located at the center of the cations cube. There is one atom in CsCl. To determine this, the following equation is given:

8 Corners of a given atom x 1/8 of the given atom's unit cell = 1 atom

Applications

Cesium chloride is used in centrifugation, a process that uses the centrifugal force to separate mixtures based on their molecular density. It is also used in the preparation of electrically conducting glasses. Radioactive CsCl is used in some types of radiation therapy for cancer patients, although it is blamed for some deaths.

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5.5.3: Structure - Zinc Blende (ZnS)

ZnS has a unique structure type compared to other molecules, having different types of unique structures. ZnS can have a zinc blende structure which is a "diamond-type network" and at a different temperature, ZnS can become the wurtzite structure type which has a hexagonal type symmetry. Structure-wise, the zinc blende structure is more thermodynamically favored, however, because of the wurtzite structures slow construction, both forms of ZnS can be found.

Summary: Zinc blend is a compound that comes in two forms: sphalerite and wurtzite. These are characterized by a 1:1 stoichiometric ratio of Zinc to Sulfur. It maintains a tetrahedral arrangement in both forms.

Introduction

Zinc sulfide (ZnS) is a unique compound that forms two types of crystalline structures. These two polymorphs are wurtzite and zincblende (also known as sphalerite). Wurtzite has a hexagonal structure, while zincblende is cubic. It is characterized by single bonds between each atom and maintenance of a 1:1 zinc to sulfur ratio.

sphalerite:

Site	Zn	S
Central	4	0
Face	0	6(1/2) = 3
Corner	0	8(1/8) = 1
Total	4	4

Since the number of atoms in a single unit cell of Zn and S is the same, it is consistent with the formula ZnS.

The ionic radius for Zn^{2+} is 74pm and for S^{2-} is 190pm. Therefore the ratio between cationic and anionic radii in zinc blend is 0.39 (74pm/190 pm) .This suggests a tetrahedral ion arrangement and four nearest neighbors from standard crystal structure prediction tables. Therefore, four sulfur atoms surround each zinc atom and four zinc atoms surround each sulfur atom.$_2$ The coordination number, the number of of electron pairs donated to a metal by its ligands, for both zinc an sulfur is four.[1,2] The difference between wurtzite and zincblende lies in the different arrangements of layers of ions.[2]

Zincblende (Sphalerite)

Zincblende is characterized as a **cubic closet packing** (ccp), also known as face-centered cubic, structure.[1,4] This crystal lattice structure is shown in Figures 1 & 2 below.

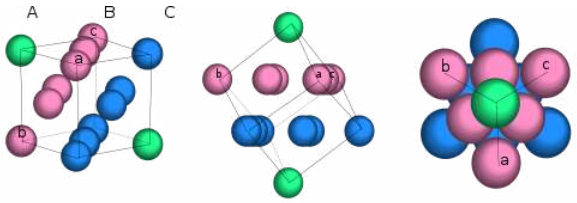


Fig. 1. A break down of cubic closest packing. (Author: Maghémite Date: May 5, 2008. Licensed under the Creative Commons Attribution-Share Alike 3.0 Unported, 2.5 Generic, 2.0 Generic and 1.0 Generic license.)

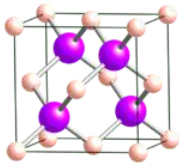


Fig. 2. A representation of ccp structure. (from Public Domain)

Notice how only half of the tetrahedral sites are occupied.

Thermal stability

Density tends to decrease as temperature increases. In this case, since ccp structures are more dense than hcp structures, so a conversion from sphalerite to wurtzite occurs naturally over time at a rate similar to that of diamond to graphite. The sphalerite structure is favored at 298k by 13kJ/mol, but at 1296K the transition to wurtzite occurs.[3]

Wurtzite

Wurtzite has a hexagonal closest packing structure (hcp), which is characterized by 12 ions in the corners of each unit that create a hexagonal prism (seen in Fig. 3).[2] As discussed previously, zincblende slowly transforms to wurtzite due to thermodynamic stability.

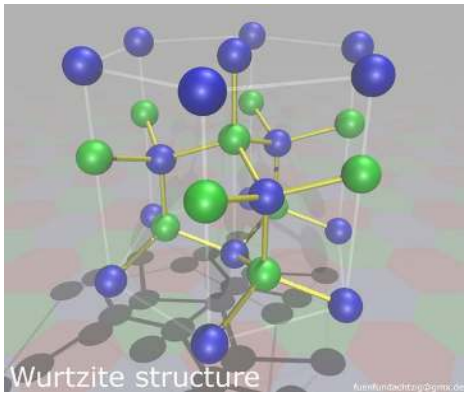


Fig 3. HCP structure of wurtzite. (Creator: Alexander Mann Date: 01/14/2006 Licensed under the Creative Commons Attribution-Share Alike 2.0 Germany license)

Calculating density of a crystal structure

Density = Mass of unit cell / volume of unit cell.

where:

Mass of unit cell = Number of atoms in a unit cell x the mass of each atom

volume of unit cell = $a^3 \times 10^{-30}$

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5.5.4: Structure - Fluorite and Antifluorite

Fluorite

Calcium Fluoride is a solid and forms a cube like structure that is centralized around the calcium molecules. The crystal lattice structure that Calcium Fluoride is also known as the fluorite structure (Figure **5.5.4.1**) where the Ca^{2+} ions are eight-coordinate, being centered in a cube of eight F^- ions. Each F^- is coordinated to four Ca^{2+} in the shape of a tetrahedron.

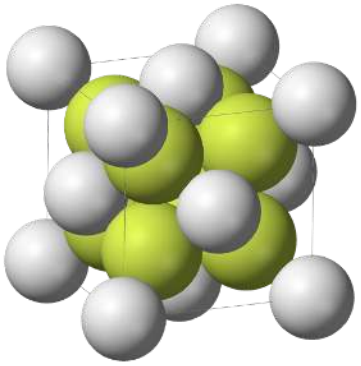


Figure **5.5.4.1**: Fluorite unit cell. (Public Domain; Benjah-bmm27 via Wikipedia)

When Calcium Fluoride is in a single molecule it forms a Quasilinear structure. Quasilinear means the molecule resonates between a linear shape and a bent shape.Calcium Fluoride is a polyatomic molecule that contains one calcium molecule and two fluoride molecules. Calcium Fluoride is a quasilinear molecule the bonds are created from the single electrons of calcium and the single electron from fluoride. $\mathbf{CaF_2}$ has its electrons contained with in the 3d orbitals and are able to move between d_{yz} and d_z^2 squared. The molecule in linear when they are in the d_z^2 orbitals the molecule is also the most stable in this shape. When the electrons are in the d_{yz} orbitals the molecule becomes bent. The molecule resonates between these two shapes making it quasilinear.

Antifluorite

Antifluorite is a mineral with a crystal structure identical with that of fluorite but with the positions of the cations and anions reversed (Figure **5.5.4.2**).

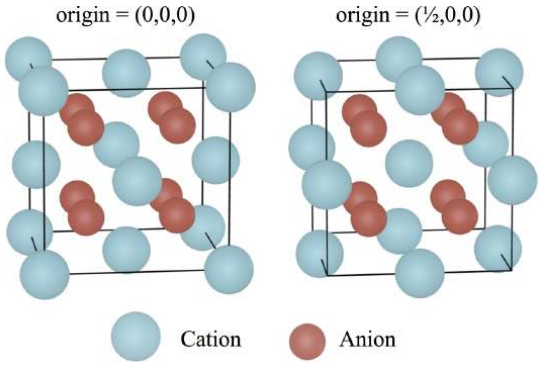


Figure **5.5.4.2**: Unit cell of the fluorite structure, from two equivalent perspectives. In the antifluorite structure, the blue positions are taken by the anion, the red positions by the cation. (CC BY-SA 4.0; Paburr via source)

The same crystal structure is found in numerous ionic compounds with formula AB2, such as ceria (CeO2), zirconia (cubic ZrO2), uranium dioxide (UO2). In the corresponding anti-structure, called the antifluorite structure, anions and cations are swapped, such as beryllium carbide (Be2C) or lithium oxide (Li2O), potassium sulfate (K2SO4).

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- en.Wikipedia.org/wiki/Anti-structure

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5.5.5: Structure - β-Cristobalite (SiO_2)

Silicon dioxide, SiO_2, also known as silica is a linear molecule that is formed by one silicon atom and two oxygen atoms with two sets of doubles bonds and 4 single bonds. Because of its main component: glass, silicon dioxide is a very common and important molecule in the construction industry. One of the forms of silicon dioxide is quartz, which is found in sand.

The Structure of Silica

SiO_2 is a 3 dimensional structure and comes from the tetrahedral structure, SiO_4. Each of the Silicon atoms are connected to each other with an oxygen atom, which creates a "diamond type network". All forms of SiO_2 possess a 3 dimensional shape and has a diamond structure. The bonding angle of Si-O-Si, which is the building block of the SiO_2 molecule, is 144 degrees. These are called polymorph and in order to be stable, 3 of these polymorph are suppose to exist. This stable unit creates a a temperature for each of the different forms of SiO_2. Forms that have (alpha) are at low temperature, while forms with (beta) are at high temperature. The structure of the different forms of SiO_2 is important because it gives each of the different forms of SiO_2 different characteristics and functions. Commercially, SiO_2 is very important in steel, electronic, and semiconductor industries because of its structure, SiO_2 is able to undergo rapid temperature changes and still maintain its shape and structure.

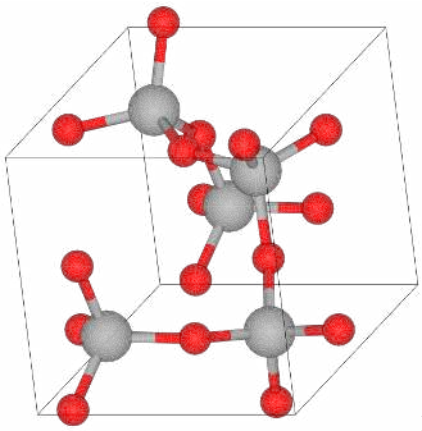


Figure 5.5.5.1: Unit cell of α-cristobalite; red spheres are oxygen atoms. (Public Domain, Wikipedia)

Different Forms of Silica **and Their Uses**

There are many different forms of SiO_2, which mainly derived quartz glass. One form that is derived from quartz is beta-cristobalite, which is found in high temperature. Some other forms are beta-quartz, alpha-quartz, beta-tridymite, alpha-tridymite, alpha=cristobalite, and many more. The alpha and beta stands for the temperature range. Alpha molecules have low temperature while beta molecules have high temperature.

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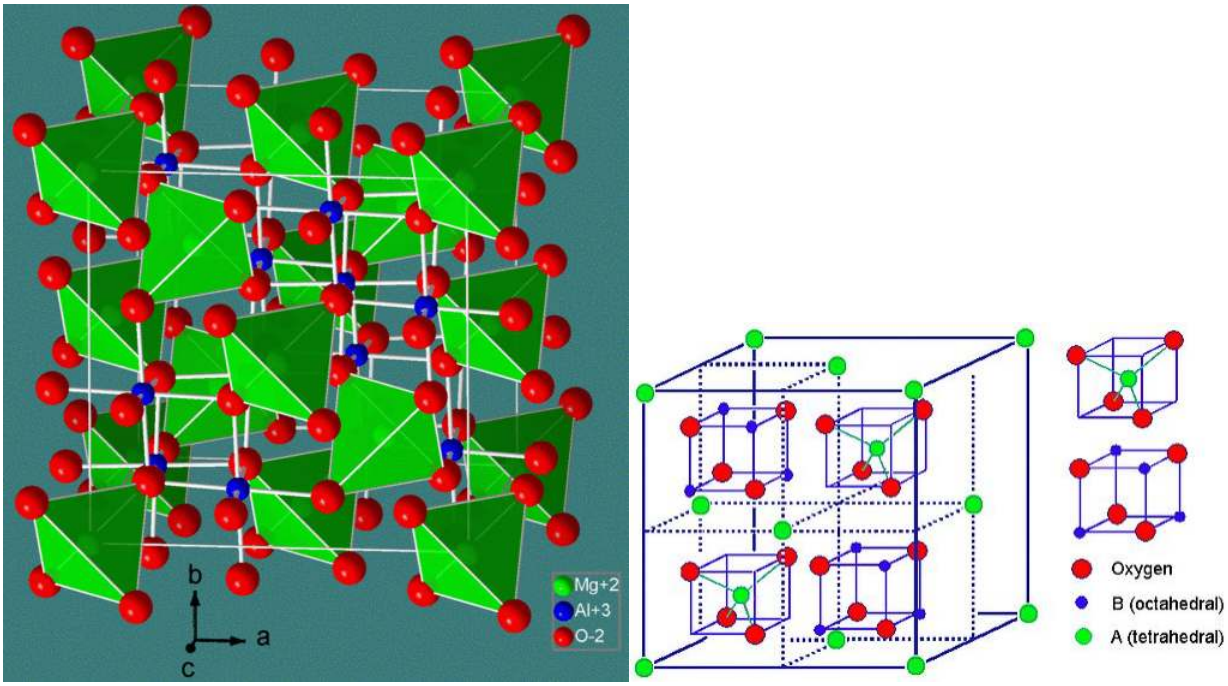
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5.5.6: Spinel, Perovskite, and Rutile Structures

There are three more structures, which are derived from close-packed lattices, that are particularly important because of the material properties of their compounds. These are the **spinel** structure, on which ferrites and other magnetic oxides are based, the **perovskite** structure, which is adopted by ferroelectric and superconducting oxides, and the **rutile** structure, which is a common binary 6:3 structure adopted by oxides and fluorides.

Spinel



The **spinel structure** is formulated MM'_2X_4, where M and M' are tetrahedrally and octahedrally coordinated cations, respectively, and X is an anion (typically O or F). The structure is named after the mineral $MgAl_2O_4$, and oxide spinels have the general formula AB_2O_4.

In the **normal spinel** structure, there is a close-packed array of anions. The A-site cations fill 1/8 of the tetrahedral holes and the B-site cations fill 1/2 of the octahedral holes. A polyhedral view of the normal spinel unit cell is shown at the left, and a simplified view (with the contents of the back half of the cell removed for clarity) is shown above. Each unit cell contains eight formula units and has a composition $A_8B_{16}O_{32}$.

Inverse spinels have a closely related structure (with the same large unit cell) in which the A-site ions and half of the B-site ions switch places. Inverse spinels are thus formulated $B(AB)O_4$, where the AB ions in parentheses occupy octahedral sites, and the other B ions are on tetrahedral sites. There are also mixed spinels, which are intermediate between the **normal** and **inverse** spinel structure.

Some spinel and inverse spinel AB combinations are:

$A^{2+}B^{3+}$, e.g., $MgAl_2O_4$ (normal spinel)

$A^{4+}B^{2+}$, e.g., $Pb_3O_4 = Pb^{II}(Pb^{II}Pb^{IV})O_4$ (inverse spinel)

$A^{6+}B^{+}$, e.g., Na_2WO_4 (normal spinel)

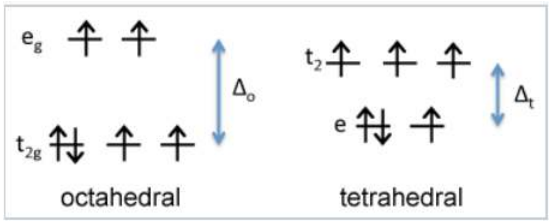
Many magnetic oxides, such as Fe_3O_4 and $CoFe_2O_4$, are spinels.

Normal vs. inverse spinel structure

For transition metal oxide spinels, the choice of the normal vs. inverse spinel structure is driven primarily by the **crystal field stabilization energy** (CFSE) of ions in the tetrahedral and octahedral sites. For spinels that contain 3d elements such as Cr, Mn, Fe,

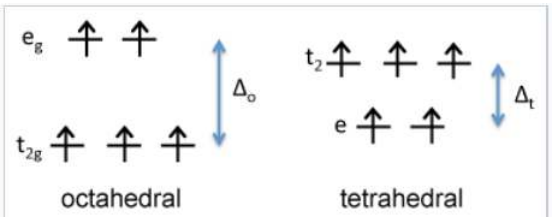
Co, and Ni, the electron configuration is typically **high spin** because O^{2-} is a **weak field ligand**.

As an example, we can consider magnetite, Fe_3O_4. This compound contains one Fe^{2+} and two Fe^{3+} ions per formula unit, so we could formulate it as a normal spinel, $Fe^{2+}(Fe^{3+})_2O_4$, or as an inverse spinel, $Fe^{3+}(Fe^{2+}Fe^{3+})O_4$. Which one would have the lowest energy?



d-orbital energy diagram for Fe^{2+}

First we consider the crystal field energy of the **Fe^{2+}** ion, which is d^6. Comparing the tetrahedral and high spin octahedral diagrams, we find that the CFSE in an **octahedral** field of O^{2-} ions is $[(4)(\frac{2}{5}) - (2)(\frac{3}{5})]\Delta_o - P = \mathbf{0.4\Delta_o - P}$. In the **tetrahedral** field, the CFSE is $[(3)(\frac{3}{5}) - (3)(\frac{2}{5})]\Delta_t - P = \mathbf{0.6\Delta_t - P}$. Since Δ_o is about 2.25 times larger than Δ_t, the octahedral arrangement has a larger CFSE and is preferred for Fe^{2+}.



d-orbital energy diagram for Fe^{3+}

In contrast, it is easy to show that **Fe^{3+}**, which is d^5, would have a CFSE of zero in either the octahedral or tetrahedral geometry. This means that Fe^{2+} has a preference for the octahedral site, but Fe^{3+} has no preference. Consequently, we place Fe^{2+} on octahedral sites and **Fe_3O_4 is an inverse spinel**, $Fe^{3+}(Fe^{2+}Fe^{3+})O_4$.

Ferrites are compounds of general formula **$M^{II}Fe_2O_4$**. We can see that magnetite is one example of a ferrite (with M = Fe). Other divalent metals (M = Mg, Mn, Co, Ni, Zn) also form ferrites. Ferrites can be normal or inverse spinels, or mixed spinels, depending on the CFSE of the M^{II} ion. Based on their CFSE, Fe^{2+}, Co^{2+}, and Ni^{2+} all have a strong preference for the octahedral site, so those compounds are all inverse spinels. $ZnFe_2O_4$ is a normal spinel because the small Zn^{2+} ion (d^{10}) fits more easily into the tetrahedral site than Fe^{3+} (d^5), and both ions have zero CFSE. $MgFe_2O_4$ and $MnFe_2O_4$, in which all ions have zero CFSE and no site preference, are mixed spinels. **Chromite** spinels, **$M^{II}Cr_2O_4$**, are always **normal spinels** because the d^3 Cr^{3+} ion has a strong preference for the octahedral site.

Examples of normal and inverse spinel structures:

> **$MgAl_2O_4$** is a **normal spinel** since both Mg^{2+} and Al^{3+} are non-transition metal ions and thus CFSE = 0. The more highly charged Al^{3+} ion prefers the octahedral site, where it is surrounded by six negatively charged oxygen atoms.
>
> **Mn_3O_4** is a **normal spinel** since the Mn^{2+} ion is a high spin d^5 system with zero CFSE. The two Mn^{3+} ions are high spin d^4 with higher CFSE on the octahedral sites (3/5 Δ_O) than on the tetrahedral site (2/5 Δ_t ~ 1/5 Δ_O).
>
> **Fe_3O_4** is an **inverse spinel** since the Fe^{3+} ion is a high spin d^5 system with zero CFSE. Fe^{2+} is a high spin d^6 system with more CFSE on an octahedral site than on a tetrahedral one.
>
> **$NiFe_2O_4$** is again an **inverse spinel** since Ni^{2+} (a d^8 ion) prefers the octahedral site and the CFSE of Fe^{3+} (a d^5 ion) is zero.
>
> **$FeCr_2O_4$** is a **normal spinel** since Fe^{2+} is high spin d^6 ion with $CFSE = [4(\frac{2}{5}) - 2(\frac{3}{5})]\Delta_o = \frac{2}{5}\Delta_o$ on an octahedral site, and Cr^{3+} is a d^3 ion with CFSE = 3(2/5) Δ_O = 6/5 Δ_O. Hence it is more energetically favorable for Cr^{3+} to occupy both of the octahedral sites.

Co_3O_4 is a **normal spinel**. Even in the presence of weak field oxo ligands, Co^{3+} is a low spin d^6 ion with very high CFSE on the octahedral sites, because of the high charge and small size of the Co^{3+} ion. Hence the Co^{3+} ions occupy both octahedral sites, and Co^{2+} occupies the tetrahedral site.

Magnetism of ferrite spinels

Ferrite spinels are of technological interest because of their magnetic ordering, which can be ferrimagnetic or antiferromagnetic depending on the structure (normal or inverse) and the nature of the metal ions. Fe_3O_4, $CoFe_2O_4$, and $NiFe_2O_4$ are all inverse spinels and are ferrimagnets. The latter two compounds are used in magnetic recording media and as deflection magnets, respectively.

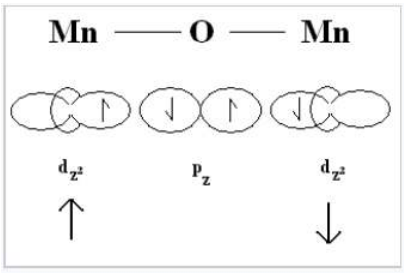
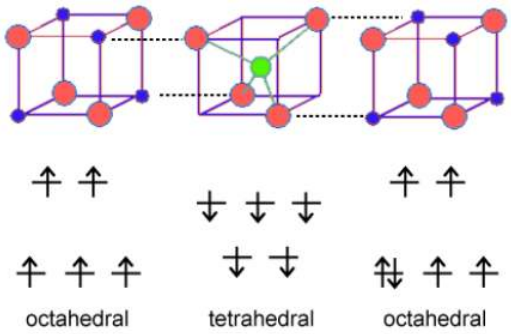


Illustration of antiferromagnetic superexchange between two transition metal cations through a shared oxygen atom.

In order to understand the magnetism of ferrites, we need to think about how the unpaired spins of metal ions are coupled in oxides. If an oxide ion is shared by two metal ions, it can mediate the coupling of spins by superexchange as shown at the right. The coupling can be antiferromagnetic, as shown, or ferromagnetic, depending on the orbital filling and the symmetry of the orbitals involved. The **Goodenough-Kanamori rules** predict the local magnetic ordering (ferromagnetic vs. antiferromagnetic) that results from superexchange coupling of the electron spins of transition metal ions. For ferrites, the strongest coupling is between ions on neighboring **tetrahedral and octahedral sites**, and the ordering of spins between these two sites is reliably **antiferromagnetic**.

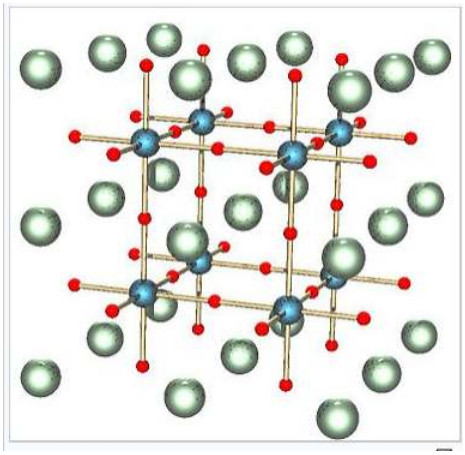


Because all the tetrahedral and octahedral sites in a spinel or inverse spinel crystal are coupled together identically, it works out that ions on the tetrahedral sites will all have one orientation (e.g., spin down) and ions on all the octahedral sites will have the opposite orientation (e.g., spin up). If the number of spins on the two sites is the same, then the solid will be antiferromagnetic. However, if the **number of spins is unequal** (as in the case of Fe_3O_4, $CoFe_2O_4$, and $NiFe_2O_4$) then the solid will be **ferrimagnetic**. This is illustrated above for Fe_3O_4. The spins on the Fe^{3+} sites cancel, because half of them are up and half are down. However, the four unpaired electrons on the Fe^{2+} ions are all aligned the same way in the crystal, so the compound is ferrimagnetic.

Perovskite

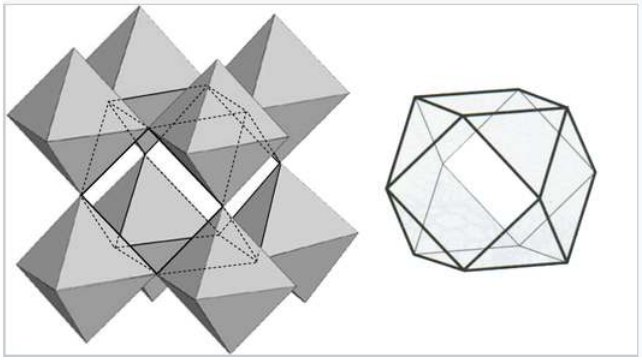
Perovskites are **ternary oxides** of general formula **ABO_3**. More generally, the perovskite formula is ABX_3, where the anion X can be **O, N, or halogen**. The A ions are typically large ions such as Sr^{2+}, Ba^{2+}, Rb^{+}, or a lanthanide 3+ ion, and the B ions are smaller transition metal ions such as Ti^{4+}, Nb^{5+}, Ru^{4+}, etc. The mineral after which the structure is named has the formula $CaTiO_3$.

The perovskite structure has simple cubic symmetry, but is related to the fcc lattice in the sense that the A site cations and the three O atoms comprise a fcc lattice. The B-site cations fill 1/4 of the octahedral holes and are surrounded by six oxide anions.



ABX_3 perovskite structure. A, B, and X are white, blue, and red, respectively.

The coordination of the A ions in perovsite and the arrangement of BO_6 octahedra is best understood by looking at the ReO_3 structure, which is the same structure but with the A-site cations removed. In the polyhedral representation of the structure shown at the right, it can be seen that the octahedra share all their vertices but do not share any octahedral edges. This makes the ReO_3 and perovskite structures flexible, like three-dimensional wine racks, in that the octahedra can **rotate and tilt cooperatively**. Eight such octahedra surround a large **cuboctahedral cavity**, which is the site of the A ions in the perovskite structure. Cations in these sites are coordinated by 12 oxide ions, as expected from the relationship between the perovskite and fcc lattices.



Polyhedral representation of the ReO_3 structure showing the large cuboctahedral cavity that is surrounded by 12 oxygen atoms

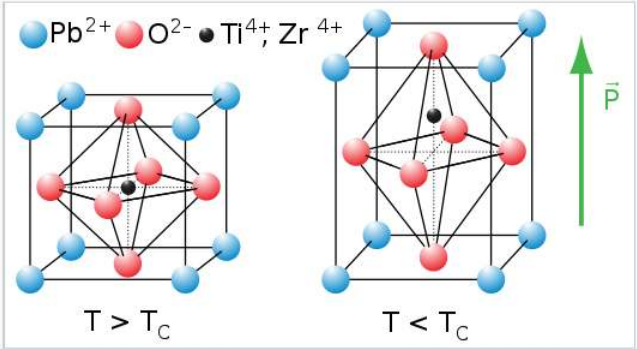
Because the A-site is empty in the ReO_3 structure, compounds with that structure can be reversibly **intercalated** by small ions such as **Li^+ or H^+**, which then occupy sites in the cuboctahedral cavity. For example, smart windows that darken in bright sunlight contain the **electrochromic** material WO_3, which has the ReO_3 structure. In the sunlight, a photovoltaic cell drives the reductive intercalation of WO_3 according to the reaction:

$$x\,H^+ + xe^- + WO_3 \leftrightharpoons H_xWO_3 \qquad (5.5.6.1)$$

WO_3 is a light yellow compound containing d^0 W(VI). In contrast, H_xWO_3, which is mixed-valent W(V)-W(VI) = d^1-d^0, has a deep blue color. Such coloration is typical of mixed-valence transition metal complexes because their d-electrons can be excited to delocalized conduction band levels by red light. Because the electrochemical intercalation-deintercalation process is powered by a solar cell, the tint of the windows can adjust automatically to the level of sunlight.

Ferroelectric perovskites

The flexibility of the network of corner-sharing BO_6 octahedra is also very important in ferroelectric oxides that have the perovskite structure. In some perovsites with small B-site cations, such as Ti^{4+} and Nb^{5+}, the cation is too small to fit symmetrically in the BO_6 octahedron. The octahedron distorts, allowing the cation to move off-center. These distortions can be **tetragonal** (as in the example shown at the right), **rhombohedral**, or **orthorhombic**, depending on whether the cation moves towards a vertex, face, or edge of the BO_6 octahedron. Moving the cation off-center in the octahedron creates an **electric dipole**. In ferroelectrics, these dipoles align in neighboring unit cells through cooperative rotation and tilting of octahedra. The crystal thus acquires a net electrical polarization.



Tetragonal distortion of the perovskite unit cell in the ferroelectric oxide PZT, $PbTi_xZr_{1-x}$

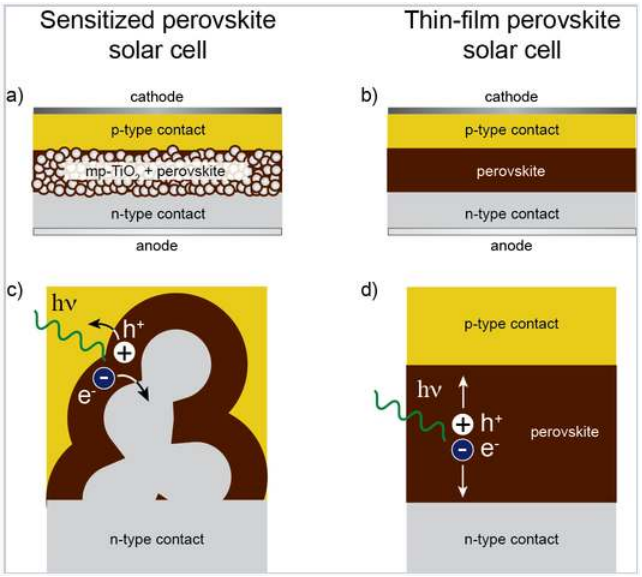
Ferroelectricity behaves analogously to **ferromagnetism**, except that the polarization is electrical rather than magnetic. In both cases, there is a **critical temperature (T_c)** above which the **spontaneous polarization** of the crystal disappears. Below T_c, the electric polarization of a ferroelectric can be switched with a coercive field, and hysteresis loop of polarization vs. field resembles that of a ferromagnet. Above T_c, the crystal is **paraelectric** and has a high dielectric permittivity.

Ferroelectric and paraelectric oxides (along with piezoelectrics and pyroelectrics) have a wide variety of applications as switches, actuators, transducers, and dielectrics for capacitors. **Ferroelectric capacitors** are important in memory devices (FRAM) and in the tuning circuits of cellular telephones. **Multiferroics**, which are materials that are simultaneously ferroelectric and ferromagnetic, are rare and are being now intensively researched because of their potential applications in electrically adressable magnetic memory.

Halide perovskites (ABX_3, X = Cl, Br, I) can be made by combining salts of monovalent A ions ($A^+ = Cs^+$, NH_4^+, RNH_3^+) and divalent metal salts such as $PbCl_2$ or PbI_2. These compounds have sparked recent interest as light absorbers for **thin film solar cells** that produce electricity from sunlight. Lead and tin halide perovskites can be grown as thin films from solution precursors or by thermal evaporation at relatively low temperatures. In some lead halide perovskites, the mobility of electrons and holes is very high, comparable to that of more expensive III-V semiconductors such as GaAs, which must be grown as very pure single crystals at high temperatures for use in solar cells. Because of their high carrier mobility, some lead halide perovskites are also electroluminescent and are of interest as inexpensive materials for light-emitting diodes (LEDs).

Tin and lead halide perovskites were first studied in the 1990s as materials for thin film electronics,[4] and more recently as light absorbers in dye-sensitized solar cells. Soon after the results on dye-sensitized perovskite cells were reported, it was discovered that halide perovskites could also be used in thin film solid state solar cells. The structures of these solar cells are shown schematically at the right. The highest reported solar power conversion efficiencies of perovskite solar cells have jumped from 3.8% in 2009 [5] to

10.2% in 2012[6] and a certified 20.1% in 2014.[7]. The highest performing cells to date contain divalent lead in the perovskite B cation site and a mixture of methylammonium and formamidinium ions in the perovskite A cation site.

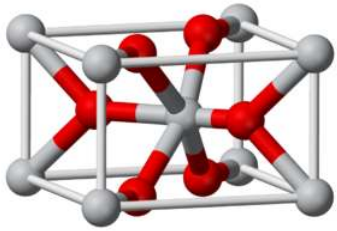


a) Solar cell architecture in which a lead halide perovskite absorber coats a layer of nanocrystalline anatase TiO_2. b) Thin-film solar cell, with a layer of lead halide perovskite sandwiched between two selective contacts. c) Charge generation and extraction in the sensitized architecture and d) in the thin-film architecture.

Despite their very impressive efficiency, perovskite solar cells are stable for relatively short periods of time and are sensitive to air and moisture. Current research is focused on understanding the degradation mechanisms of these solar cells and improving their stability under operating conditions.

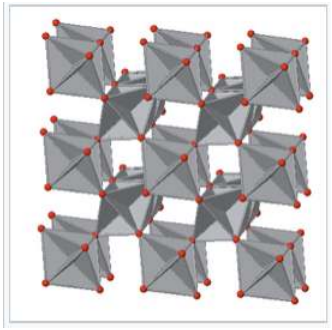
Rutile

The **rutile structure** is an important MX_2 (X = O, F) structure. It is a 6:3 structure, in which the cations are octahedrally coordinated by anions, and as such is intermediate in polarity between the CaF_2 (8:4) and SiO_2 (4:2) structures. The mineral rutile is one of the polymorphs of TiO_2, the others (anatase and brookite) also being 6:3 structures.



The rutile structure can be described as a distorted version of the NiAs structure with half the cations removed. Recall that compounds with the NiAs structure were typically metallic because the metal ions are eclipsed along the stacking axis and thus are in relatively close contact. In rutile, the MO_6 **octahedra share edges** along the tetragonal c-axis, and so some rutile oxides, such as

NbO_2, RuO_2 and IrO_2, are also **metallic** because of **d-orbital overlap** along that axis. These compounds are important as electrolyzer catalysts and catalyst supports because they combine high catalytic activity with good electronic conductivity.



View down the tetragonal c-axis of the rutile lattice, showing edge-sharing MO_6 octahedra.

Rutile TiO_2, because of its high refractive index, is the base pigment for white paint. It is a wide bandgap semiconductor that has also been extensively researched as an electrode for water splitting solar cells and as a photocatalyst (primarily as the anatase polymorph) for degradation of pollutants in air and water. Self-cleaning glass exploits the photocatalytic properties of a thin film of TiO_2 to remove oily substances from the glass surface and improve the wetting properties of the glass.

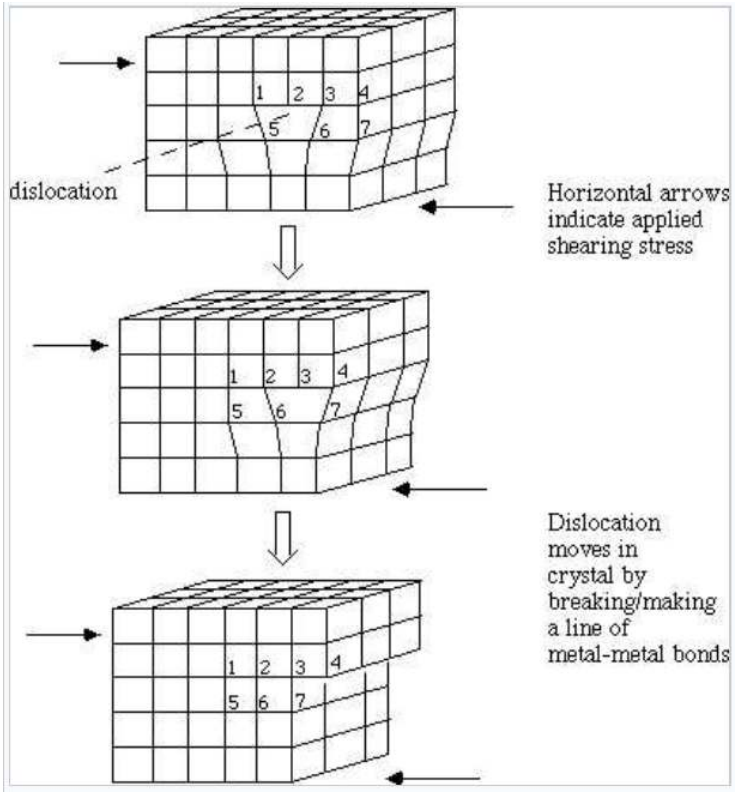
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5.6: Work Hardening, Alloying, and Annealing

One of the questions we would like to ask is, why are the yield stresses of normal (polycrystalline) metal samples so much lower (by a factor of 1000) than they are in perfect single crystals? The answer has to do with the motion of dislocations. Consider the picture below, which shows planes of metal atoms near a dislocation (the individual atoms are numbered to help you see which bonds are broken and which are formed). The arrows indicate force applied under shear stress. Notice how the dislocation moves by breaking/making metal-metal bonds.

The key point here is that we can induce plastic deformation (shear) by breaking only one line of metal-metal bonds at a time along the dislocation line. This involves far less force than breaking an entire plane of bonds, as we would need to do to shear a perfect crystal. In a given polycrystalline sample, there are many dislocation lines that run perpendicular to all possible shear directions, so their motion can be used to "tear" the metal apart. Turbine rotors on large jets are made of very expensive **single crystal** nickel-titanium alloys, so that these shearing deformations can be avoided.[1]



We can see that motion of dislocations is basically bad news if we want a metal to be strong and hard (e.g., if we want a structural material, or a knife that can hold a decent edge). There are several ways we can overcome (to some extent) this problem:

1. Use **single crystals** and anneal out all the dislocations (expensive - especially with large items like turbine blades, and impossible with very large items like airplane wings or bridges).

2. **Work hardening** of the metal - this moves all dislocations to grain boundaries (the dislocation essentially becomes part of the grain boundary). Since a grain boundary is a planar defect, it is much less responsive to stress than a line defect.

3. Introduce **impurity atoms** (that is alloying elements) or impurity phases that "pin" the motion of defects. An impurity atom stops the motion because it is a different size, or makes stronger bonds, than the other metal atoms; the line defect has a hard time moving away from rows of such atoms. An impurity phase (like Fe_3C in iron) makes extra grain boundaries that can stop the motion of defects. This effect is analogous to the graphite fibers in fiber-reinforced cross-linked polymers (used, e.g., in tennis rackets) that stop the propagation of cracks.

A simple illustration of work hardening can be done with a piece of copper wire. When struck many times with a hammer, the copper wire becomes stiffer, and it is possible to hang a weight from it. Dislocations move to the crystal grain boundaries during work hardening, effectively halting their motion and at the same time making the individual crystal grains smaller. Because the crystal grains are now smaller, the amount of grain boundary area has increased, and with it the free energy of the material. Annealing reverses the process by lowering the free energy. When the wire is annealed in a flame (heated so that atoms can move and rearrange), the crystal grains grow, and the dislocations reappear. The copper again becomes ductile, and bends easily. Cold-working (work hardening) of metals is important for strengthening structural materials (e.g., iron beams) and for making brittle, hard edges (this is why blacksmiths hammer on knives and swords when they are making them. If you have ever watched them, they do the same thing to horseshoes, when they cool down, to make them stiff).



Blacksmith, 1606

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5.7: Properties of Unit Cells

Size of a Metallic Unit Cell

The size of a cubic unit cell is describe by the length of the side of the unit cell and by the volume of the unit cell. The length of the side of the unit cell depends on the radius of the atoms contained in the unit cell and on the arrangement of the atoms in the unit cell (the structure of the unit cell). The mathemetical relationship between side length and atomic radius is derived below for the simple cubic, face-centered cubic, and body-centered cubic unit cells.

The sides of a cubic unit cell are all equal in length. Therefore, the volume of the unit cell is given by the volume of a cube: $V = l^3$.

A note on units

Atomic and ionic radii are typically reported in units of picometers (pm, 10^{-12} m) or angstroms (Å, 10^{-10} m).

Simple Cubic

In a simple cubic unit cell, the corner atoms are in physical contact along the edge of the unit cell. Each side length is made up of two radii.

The length of a side is given as: $l = 2r$.

Volume of the unit cell is given as: $V = (2r)^3 = 8r^3$.

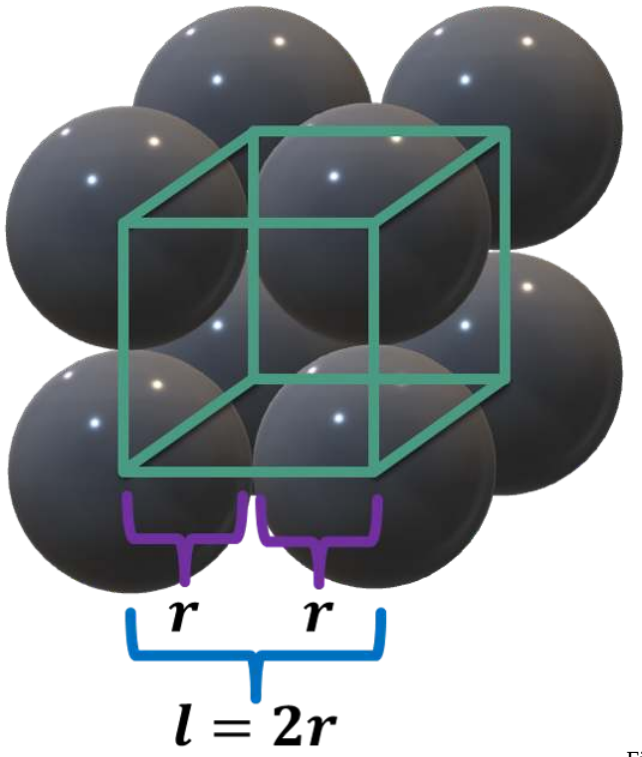


Figure 5.7.1: Simple cubic unit cell demonstrating the relationship between atomic radius and side length. (CC-BY-NC-SA 4.0; Kathryn A. Newton)

Face-Centered Cubic

In a face-centered cubic unit cell, each corner atom is in physical contact the face atoms, and therefore, is not in physical contact with any of the other corner atoms. The diagonal across each face of the unit cell is made up of four radii (two corner atom radii and two face atom radii). The length of the face diagonal is given as: $d = 4r$. Two edges of the unit cell make a right triangle with the diagonal across the face of the unit cell. Thus, the relationship between atomiside length of the unit cell can be derived using the Pythagorean theorem:

$$d^2 = l^2 + l^2 = 2l^2$$

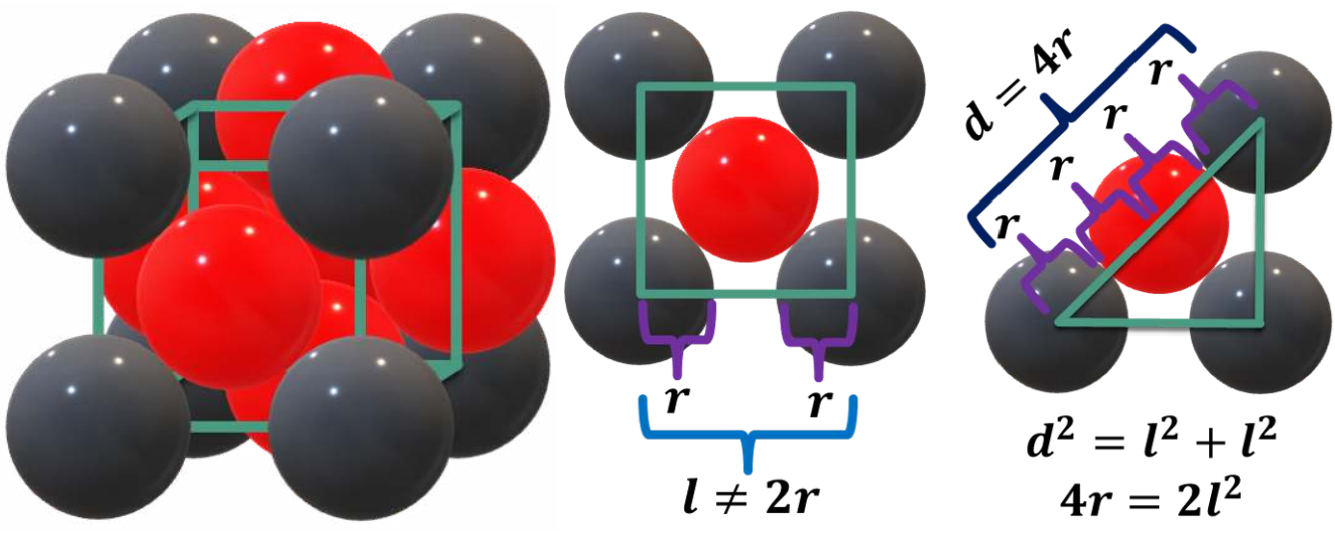
$$(4r)^2 = 2l^2$$

$$16r^2 = 2l^2$$

$$\sqrt{8r^2} = \sqrt{l^2}$$

The length of a side is given as: $\sqrt{8}r = l$.

Volume of the unit cell is given as: $V = l^3 = (\sqrt{8}r)^3 = 8\sqrt{8}r^3$.



(a) (b) (c)

Figure 5.7.2: Face-centered cubic unit cell (a) demonstrating the relationship between atomic radius and side length (b) and the length of the face diagonal (c). (CC-BY-NC-SA 4.0; Kathryn A. Newton)

Body-Centered Cubic

In a body-centered cubic unit cell, each corner atom is in physical contact the body atom, and therefore, is not in physical contact with any of the other corner atoms. Two sides of the unit cell make a right triangle with the diagonal across the face of the unit cell. The diagonal through the body of the unit cell is made up of four radii (two corner atom radii and two body atom radii) and is the hypotenuse of the right triangle made by one edge of the unit cell and the diagonal across the face of the unit cell. The body hypotenuse is given as: $h = 4r$. Using these two right triangles, the relationship between atomic radius and side length of the unit cell can be derived using the Pythagorean theorem:

$$d^2 = l^2 + l^2 = 2l^2$$

$$h^2 = l^2 + d^2$$

$$h^2 = l^2 + 2l^2$$

$$(4r)^2 = 3l^2$$

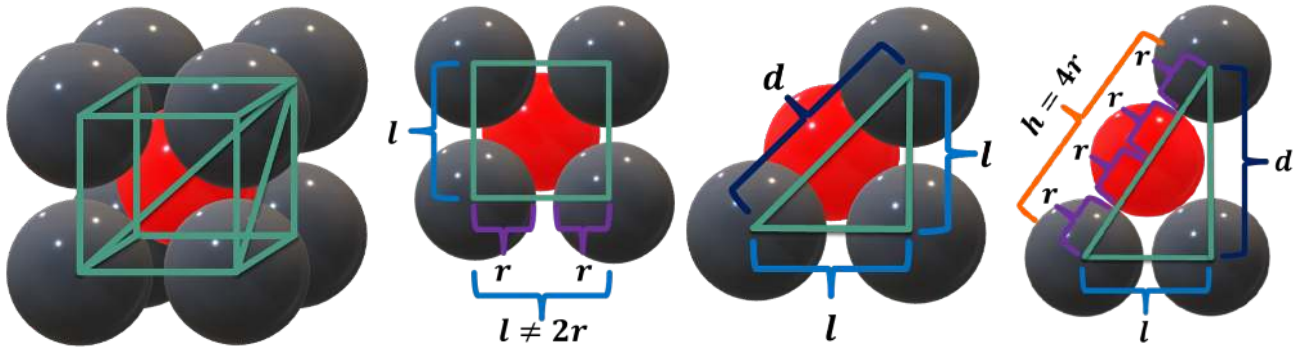
$$16r^2 = 3l^2$$

$$\sqrt{16r^2} = \sqrt{3l^2}$$

$$4r = \sqrt{3}l$$

The length of a side is given as: $\frac{4r}{\sqrt{3}} = l$.

Volume of the unit cell is given as: $V = l^3 = (\frac{4r}{\sqrt{3}})^3 = \frac{64}{3\sqrt{3}}r^3$.



(a) (b) (c) (c)

Figure **5.7.3**: Body-centered cubic unit cell (a) demonstrating the relationship between atomic radius and side length (b) and the length of the face diagonal (c) and the length of the body hypotenuse (d). (CC-BY-NC-SA 4.0; Kathryn A. Newton)

Example 5.7.1: Calculating Atomic Radius

The edge length of the unit cell of alpha polonium is 336 pm. Determine the radius of a polonium atom.

Solution

Alpha polonium crystallizes in a simple cubic unit cell. Two adjacent Po atoms contact each other, so the edge length of this cell is equal to two Po atomic radii: $l = 2r$. Therefore, the radius of Po is

$$r = \frac{l}{2} = \frac{336\ \text{pm}}{2} = 168\ \text{pm}$$

Example 5.7.2: Calculating Atomic Radius

Calcium crystallizes in a face-centered cubic structure. The edge length of its unit cell is 558.8 pm. What is the atomic radius of Ca in this structure?

Solution

In an FCC structure, Ca atoms contact each other across the diagonal of the face, so the length of the diagonal is equal to four Ca atomic radii (d = 4r).

Two adjacent edges and the diagonal of the face form a right triangle, with the length of each side equal to 558.8 pm and the length of the hypotenuse equal to four Ca atomic radii:

$$a^2 + a^2 = d^2$$

$$(558.8\ \text{pm})^2 + (558.5\ \text{pm})^2 = (4r)^2$$

Solving this gives

$$r = \sqrt{\frac{(558.8\ \text{pm})^2 + (558.5\ \text{pm})^2}{16}} = 197.6\ \text{pmg for a Ca radius.}$$

Size of an Ionic Unit Cell

Similar to a metallic unit cell, the length of the side of an ionic unit cell depends on the radius of the atoms contained in the unit cell and on the arrangement of the atoms in the unit cell (the structure of the unit cell). There are two difference when finding the size of an ionic unit cell. First, there will be two or more radii to consider, and second, the location of each atom (type of radii) needs to be considered. The relationship between side length and atomic radii can be derived by drawing analogy to the metallic unit cell structures and adjusting for having multiple values for the radii. A few derivations are shown below for various ionic unit cells.

It is important to realize that values for ionic radii calculated from the edge lengths of unit cells depend on numerous assumptions, such as a perfect spherical shape for ions, which are approximations at best. Hence, such calculated values are themselves approximate and comparisons cannot be pushed too far. Nevertheless, this method has proved useful for calculating ionic radii from experimental measurements such as X-ray crystallographic determinations.

Cesium Chloride (CsCl)

In a cesium chloride structure, the chloride ions form a simple cubic lattice and the cesium ions occupy 100% of the cubic interstitial sites. Each chloride corner is in contact with the cesium body atom in a structure analogous to the body-centered cubic unit cell (Figure **5.7.3**). The diagonal through the body of the unit cell is made up of four radii: two chloride corner atom radii and two cesium body atom radii. The body diagonal is the hypotenuse of a right triangle made by one edge of the unit cell and the diagonal across the face of the unit cell. The body hypotenuse is given as: $h = 2r_1 + 2r_2$, where r_1 and r_2 are the radii of the anions and cations. Using these two right triangles, the relationship between atomic radius and side length of the unit cell can be derived using the Pythagorean theorem:

$$d^2 = l^2 + l^2 = 2l^2$$

$$h^2 = l^2 + d^2$$

$$h^2 = l^2 + 2l^2$$

$$(2r_1 + 2r_2)^2 = 3l^2$$

$$\sqrt{(2r_1 + 2r_2)^2} = \sqrt{3l^2}$$

$$2r_1 + 2r_2 = \sqrt{3}l$$

The length of a side is given as: $\frac{(2r_1+2r_2)}{\sqrt{3}} = l$.

Volume of the unit cell is given as: $V = l^3 = (\frac{(2r_1+2r_2)}{\sqrt{3}})^3 = \frac{(2r_1+2r_2)^3}{3\sqrt{3}}$.

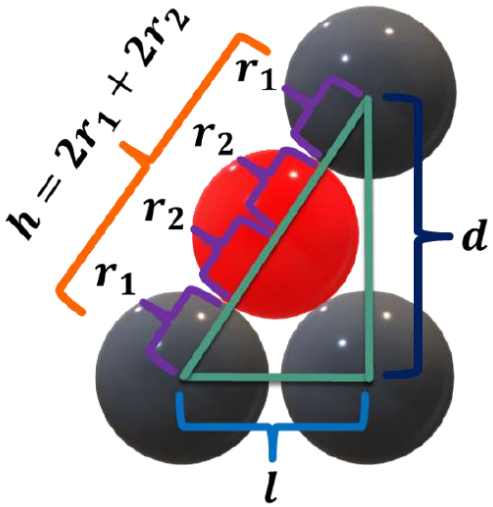


Figure **5.7.4**: Cesium chloride unit cell analogy to a body-centered cubic unit cell demonstrating the relationship between ionic radius, side length, the length of the face diagonal, and the length of the body hypotenuse. (CC-BY-NC-SA 4.0; Kathryn A. Newton)

Lithium Chloride (LiCl)

In a lithium chloride structure, the chloride ions form a face-centered cubic lattice and the lithium ions occupy 100% of the octahedral interstitial sites. When looking at a unit cell, there will be a lithium ion in the body position and on each edge of the unit cell. The lithium ions are small enough that the corner chloride ions are in physical contact with the face chloride ions. The corner chloride ions are not in physical contact with any of the other corner ions.

The diagonal across each face of the unit cell is made up of four radii (two corner chloride ion radii and two face chloride ion radii). The length of the face diagonal is given as: $d = 4r_1$, where r_1 is the ionic radius of the corner ion (chloride). Two edges of the unit cell make a right triangle with the diagonal across the face of the unit cell. Thus, the relationship between the ionic radii and the side length of the unit cell can be derived using the Pythagorean theorem:

$$d^2 = l^2 + l^2 = 2l^2$$

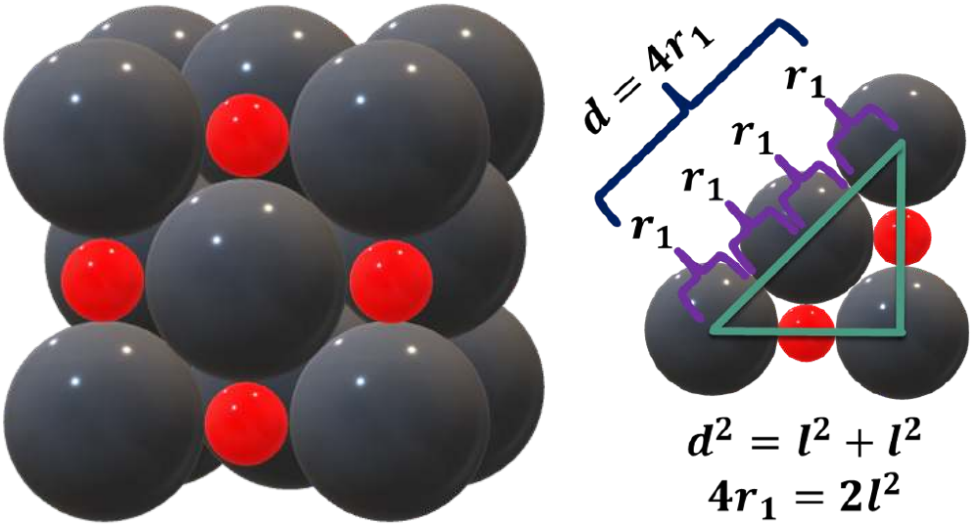
$$(4r_1)^2 = 2l^2$$

$$16r_1^2 = 2l^2$$

$$\sqrt{8r_1^2} = \sqrt{l^2}$$

The length of a side is given as: $\sqrt{8}r_1 = l$.

Volume of the unit cell is given as: $V = l^3 = (\sqrt{8}r_1)^3 = 8\sqrt{8}r_1^3$.



(a) (b)

Figure 5.7.5: Lithium chloride unit cell with fcc chloride ions and lithium ions in octahedral holes (a) demonstrating the relationship between ionic radius, side length, and the length of the face diagonal (b). (CC-BY-NC-SA 4.0; Kathryn A. Newton)

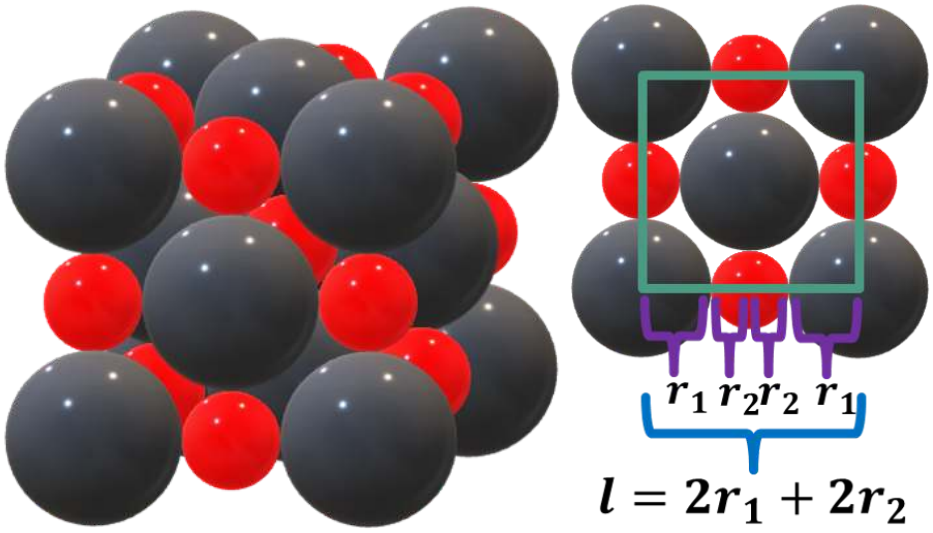
Sodium Chloride (NaCl)

In a sodium chloride structure, the chloride ions form a face-centered cubic lattice and the sodium ions occupy 100% of the octahedral interstitial sites. When looking at a unit cell, there will be a sodium ion in the body position and on each edge of the unit cell. The sodium ions are large enough that the corner chloride ions are not in physical contact with the face chloride ions but do make contact with the edge sodium ions.

The edge of the unit cell is made up of four radii (two corner chloride ion radii and two edge sodium ion radii).

The length of a side of the unit cells is given as: $l = 2r_1 + 2r_2 = 2(r_1 + r_2)$, where r_1 is the ionic radius of the corner ion (chloride) and r_2 is the ionic radius of the edge ion (sodium).

Volume of the unit cell is given as: $V = l^3 = (2(r_1 + r_2))^3 = 8(r_1 + r_2)^3$.



(a) (b)

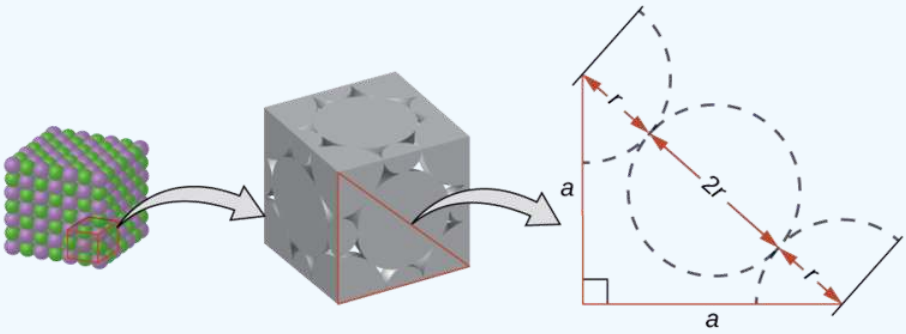
Figure **5.7.6**: Sodium chloride unit cell with fcc chloride ions and sodium ions in octahedral holes (a) demonstrating the relationship between ionic radii and side length (b). (CC-BY-NC-SA 4.0; Kathryn A. Newton)

Example 5.7.3: Calculation of Ionic Radii

The edge length of the unit cell of LiCl (NaCl-like structure, FCC) is 0.514 nm or 5.14 Å. Assuming that the lithium ion is small enough so that the chloride ions are in contact, calculate the ionic radius for the chloride ion. Note: The length unit angstrom, Å, is often used to represent atomic-scale dimensions and is equivalent to 10^{-10} m.

Solution

On the face of a LiCl unit cell, chloride ions contact each other across the diagonal of the face:



Drawing a right triangle on the face of the unit cell, we see that the length of the diagonal is equal to four chloride radii (one radius from each corner chloride and one diameter—which equals two radii—from the chloride ion in the center of the face), so $d = 4r$. From the Pythagorean theorem, we have:

$$a^2 + a^2 = d^2$$

which yields:

$$(0.514\ \text{nm})^2 + (0.514\ \text{nm})^2 = (4r)^2 = 16r^2$$

Solving this gives:

$$r = \sqrt{\frac{(0.514\ \text{nm})^2 + (0.514\ \text{nm})^2}{16}} = 0.182\ \text{nm}\ (1.82\ \text{Å})\ \text{for a}\ Cl^-\ \text{radius.}$$

Density of a Unit Cell

By definition, the density of an object is equal to the mass of the object divided by its volume and is given by the equation:

$$d = \frac{m}{V}$$

For a crystalline solid, the volume of the unit cell, and therefore the density of the solid, depend on the arrangement of atoms in in the lattice structure. Methods to calculate the volume of a cubic unit cells are discussed above. The mass of a cubic unit cell depends on the number of atoms contained in the unit cell and the mass of those atoms.

The steps to find the mass of a unit cell are as follows:

1. Determine the mass of a single atom of each element in the unit cell by dividing the respective molar mass by Avogadro's number.
2. Determine how many atoms or ions are contained in the unit cell structure.
3. Multiply the mass of one atom by the number of atoms in the unit cell structure for each element in the structure.
4. Sum the collected masses of all elements to find the overall mass of the unit cell.

The mass of the unit cell can then be used to calculate the density of the unit cell by dividing by the unit cell volume.

Example 5.7.4

Platinum crystallizes in a face-centered cubic structure. The molar mass of platinum is 195.084 g/mol. Calculate the mass of one unit cell of platinum.

Solution

1. Calculate mass of one atom of Pt.

$$\frac{195.084g}{mol} \times \frac{mol}{6.022 \times 10^{24} atoms} = 3.240 \times 10^{-23} g/atom$$

2. Determine how many atoms are in the unit cell.

Face-centered cubic structures contain 4 lattice atoms (8 x 1/8 corner atoms, 6 x 1/2 face atoms)

3. Calculate the mass of atoms in the unit cell.

$$\frac{3.240 \times 10^{-23} g}{atom} \times 4\ atoms = 1.30 \times 10^{-22} g$$

The mass of one unit cell of platinum is 1.30 x 10^{-22} g

Example 5.7.1: Calculating Density for Metals

Determine the mass of one unit cell of sodium chloride. Sodium chloride crystallizes in a face-centered cubic lattice with the sodium atoms occupying 100% of the octahedral interstitial sites.

Solution

1. Calculate mass of one atom of Na and one atom of Cl.

$$m_Na = \frac{22.99g}{mol} \times \frac{mol}{6.022 \times 10^{24} atoms} = 3.818 \times 10^{-23} g/atom$$

$$m_Cl = \frac{35.45g}{mol} \times \frac{mol}{6.022 \times 10^{24} atoms} = 5.887 \times 10^{-23} g/atom$$

2. Determine how many atoms are in the unit cell.

Face-centered cubic structures contain 4 lattice atoms (8 x 1/8 corner atoms, 6 x 1/2 face atoms) and 4 octahedral interstitial sites. There will be 4 chloride ions and 4 sodium ions (100% occupancy).

3. Calculate the mass of atoms in the unit cell.

$$m_{unit\ cell} = (4 \times\ m_{Na}) + (4 \times\ m_{Cl})$$

$$m_{unit\ cell} = (4 \times\ 3.818 \times\ 10^{-23} g) + (4 \times\ 5.887 \times\ 10^{-23} g)$$

$$m_{unit\ cell} = 9.704 \times\ 10^{-23} g$$

The mass of one unit cell of platinum is 9.704 x 10^{-23} g

Problems

Exercise 5.7.1

Silver crystallizes in an FCC structure. The edge length of its unit cell is 409 pm.

a. What is the atomic radius of Ag in this structure?
b. Calculate the density of Ag.

Answer a

144 pm

Answer b

10.5 g/cm^3

Exercise 5.7.2

The edge length of the unit cell for nickel is 0.3524 nm. The density of Ni is 8.90 g/cm^3. Does nickel crystallize in a simple cubic structure? Explain.

Answer

No. If Ni were simple cubic, its density would be given by:

$$1\ \text{Ni atom} \times \frac{1\ \text{mol Ni}}{6.022 \times 10^{23}\ \text{Ni atoms}} \times \frac{58.693\ \text{g}}{1\ \text{mol Ni}} = 9.746 \times 10^{-23}\ \text{g}$$

$$V = l^3 = (3.524 \times 10^{-8}\ \text{cm})^3 = 4.376 \times 10^{-23}\ \text{cm}^3$$

Then the density of Ni would be

$$(= \frac{9.746 \times 10^{-23}\ \text{g}}{4.376 \times 10^{-23}\ \text{cm}^3} = 2.23\ \text{g/cm}^3$$

Since the actual density of Ni is not close to this, Ni does not form a simple cubic structure.

Exercise 5.7.3

The edge length of the unit cell of KCl (NaCl-like structure, FCC) is 6.28 Å. Assuming anion-cation contact along the cell edge, calculate the radius of the potassium ion. The radius of the chloride ion is 1.82 Å.

Answer

The radius of the potassium ion is 1.33 Å.

Exercise 5.7.4

Calcium crystallizes in a face-centered cubic structure. The edge length of its unit cell is 558.8 pm. Calculate the density of Ca.

Answer

Density is given by $\text{density} = \dfrac{\text{mass}}{\text{volume}}$. The density of calcium can be found by determining the density of its unit cell: for example, the mass contained within a unit cell divided by the volume of the unit cell. A face-centered Ca unit cell has one-eighth of an atom at each of the eight corners ($8 \times \dfrac{1}{8} = 1\text{atom}$) and one-half of an atom on each of the six faces $6 \times \dfrac{1}{2} = 3$ atoms), for a total of four atoms in the unit cell.

The mass of the unit cell can be found by:

$$1\ \text{Ca unit cell} \times \frac{4\ \text{Ca atoms}}{1\ \text{Ca unit cell}} \times \frac{1\ \text{mol Ca}}{6.022 \times 10^{23}\ \text{Ca atoms}} \times \frac{40.078\ \text{g}}{1\ \text{mol Ca}} = 2.662 \times 10^{-22}\ \text{g}$$

The volume of a Ca unit cell can be found by:

$$V = a^3 = (558.8 \times 10^{-10}\ \text{cm})^3 = 1.745 \times 10^{-22}\ \text{cm}^3$$

(Note that the edge length was converted from pm to cm to get the usual volume units for density.)

Then, the density of polonium:

$$\text{Po} = \frac{2.662 \times 10^{-22}\ \text{g}}{1.745 \times 10^{-22}\ \text{cm}^3} = 1.53\ \text{g/cm}^3$$

Exercise 5.7.5

The edge length of the unit cell of alpha polonium is 336 pm. Determine the density of alpha polonium.

Answer

Density is given by

$$\text{density} = \frac{\text{mass}}{\text{volume}}.$$

The density of polonium can be found by determining the density of its unit cell (the mass contained within a unit cell divided by the volume of the unit cell). Since a Po unit cell contains one-eighth of a Po atom at each of its eight corners, a unit cell contains one Po atom.

The mass of a Po unit cell can be found by:

$$1\ \text{Po unit cell} \times \frac{1\ \text{Po atom}}{1\ \text{Po unit cell}} \times \frac{1\ \text{mol Po}}{6.022 \times 10^{23}\ \text{Po atoms}} \times \frac{208.998\ \text{g}}{1\ \text{mol Po}} = 3.47 \times 10^{-22}\ \text{g}$$

The volume of a Po unit cell can be found by:

$$V = l^3 = (336 \times 10^{-10}\ \text{cm})^3 = 3.79 \times 10^{-23}\ \text{cm}^3$$

(Note that the edge length was converted from pm to cm to get the usual volume units for density.)

Therefore, the density of

$$\text{Po} = \frac{3.471 \times 10^{-22}\ \text{g}}{3.79 \times 10^{-23}\ \text{cm}^3} = 9.16\ \text{g/cm}^3$$

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5.8: Enthalpy of Hydration

The formation of a solution involves the interaction of solute with solvent molecules. Many different liquids can be used as solvents for liquid solutions, and water is the most commonly used solvent. When water is used as the solvent, the dissolving process is called **hydration**. The interaction between water molecules and sodium ion is illustrated in Figure **5.8.1**. This is a typical **ion-dipole interaction**. At the molecular level, the ions interact with water molecules from all directions in a 3-dimensional space. Figure **5.8.1** also shows **hydrogen-bonding, dipole-dipole, ion-induced dipole**, and **dipole-induced dipole** interactions. In the absence of these interactions, solvation takes place due to **dispersion**.

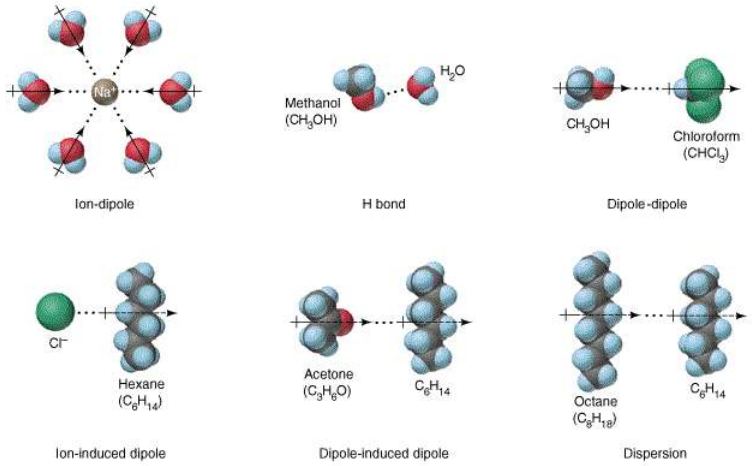


Figure **5.8.1**: Intermolecular interactions.

Enthalpy of Hydration

Enthalpy of hydration, ΔH_{hyd}, of an ion is the amount of heat *released* when a mole of the ion dissolves in a large amount of water forming an infinitely dilute solution in the process,

$$M^{z+}_{(g)} + mH_2O \rightarrow M^{z+}_{(aq)} \tag{5.8.1}$$

where $M^{z+}(aq)$ represents ions surrounded by water molecules and dispersed in the solution. The approximate hydration energy of some common ions are listed in Table **5.8.1**.

Figure **5.8.1**: Enthalpy of Hydration (ΔH_{hyd} kJ/mol) of Some Typical Ions

Ion	ΔH_{hyd}	Ion	ΔH_{hyd}	Ion	ΔH_{hyd}
H^+	-1130	Al^{3+}	-4665	Fe^{3+}	-4430
Li^+	-520	Be^{2+}	-2494	F^-	-505
Na^+	-406	Mg^{2+}	-1921	Cl^-	-363
K^+	-322	Ca^{2+}	-1577	Br^-	-336
Rb^+	-297	Sr^{2+}	-1443	I^-	-295
Cs^+	-276	Ba^{2+}	-1305	ClO_4^-	-238
Cr^{2+}	-1904	Mn^{2+}	-1841	Fe^{2+}	-1946
Co^{2+}	-1996	Ni^{2+}	-2105	Cu^{2+}	-2100
Zn^{2+}	-2046	Cd^{2+}	-1807	Hg^{2+}	-1824

Hydration of an ion occurs in two steps. First, the solvent coordinates with the ion as energy is released. The energy released is called the **enthalpy of ligation**, ΔH_{lig}. Second, the hydrated ions are dispersed into the solvent. The energy change associated with

this step is called **energy of dispersion**, ΔH_{disp}.

$$M^{z+} + nL \rightarrow ML_n^{z+} \quad \Delta H_{lig} \tag{5.8.2}$$

$$ML_n^{z+} + solvent \rightarrow ML_{n(sol)}^{z+} \quad \Delta H_{disp} \tag{5.8.3}$$

$$\Delta H_{hyd} = \Delta H_{disp} + \Delta H_{lig} \tag{5.8.4}$$

Factors affecting the size of hydration enthalpy

Hydration enthalpy is a measure of the energy released when attractions are set up between positive or negative ions and water molecules.

- With positive ions, there may only be loose attractions between the slightly negative oxygen atoms in the water molecules and the positive ions, or there may be formal dative covalent (co-ordinate covalent) bonds.
- With negative ions, hydrogen bonds are formed between lone pairs of electrons on the negative ions and the slightly positive hydrogen atoms in water molecules.

The size of the hydration enthalpy is governed by the amount of attraction between the ions and the water molecules.

- The attractions are stronger the smaller the ion. For example, hydration enthalpies fall as you go down a group in the Periodic Table. The small lithium ion has by far the highest hydration enthalpy in Group 1, and the small fluoride ion has by far the highest hydration enthalpy in Group 7. In both groups, hydration enthalpy falls as the ions get bigger.
- The attractions are stronger the more highly charged the ion. For example, the hydration enthalpies of Group 2 ions (like Mg^{2+}) are much higher than those of Group 1 ions (like Na^{+}).

Contributors and Attributions

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5.9: Enthalpy of Solution

Enthalpy of Solution

The enthalpy change of solution is the enthalpy change when 1 mole of an ionic substance dissolves in water to give a solution of infinite dilution. Enthalpies of solution may be either positive or negative - in other words, some ionic substances dissolved endothermically (for example, NaCl); others dissolve exothermically (for example NaOH).

An infinitely dilute solution is one where there is a sufficiently large excess of water that adding any more does not cause any further heat to be absorbed or evolved. So, when 1 mole of sodium chloride crystals are dissolved in an excess of water, the enthalpy change of solution is found to be +3.9 kJ mol^{-1}. The change is slightly endothermic, and so the temperature of the solution will be slightly lower than that of the original water.

The process of forming a solution, or of dissolving a solid, is often referred to as the *dissolution process*. In the dissolution process, the solid must separate into ions and become dispersed with solvent molecules between the ions. The overall process of dissolving a solid can be treated as an energy cycle.

Dissolving as an Energy Cycle

Why is heat sometimes evolved and sometimes absorbed when a substance dissolves in water? To answer that it is useful to think about the various enthalpy changes that are involved in the process of dissolving a solid. First, the crystal lattice is first broken up into its separate gaseous ions. Then those ions become surrounded by water molecules, which is how they exist in the final solution. The energy change associated with this overall process is the molar enthalpy of solution, ΔH_{sol}.

The energy change associated with assembling a lattice from its component gaseous ions is referred to as the *lattice energy*, $\Delta H_{lattice}$, and it typically has a negative value, indicating that energy is released to assemble ions into a lattice. The process of breaking a lattice apart into its component ions, is the opposite of the lattice energy and has a value of $-\Delta H_{lattice}$, indicating that energy is required to break the lattice apart. In order to dissolve a solid, the lattice must break apart; thus, the negative of the lattice energy is used in this cycle.

The hydration enthalpy is the energy released when new bonds are made between the ions and water molecules that surround them. The hydration enthalpy is the enthalpy change when 1 mole of gaseous ions dissolve in sufficient water to give an infinitely dilute solution. Hydration enthalpies are always negative.

The enthalpy of solution is then equal to the enthalpy of hydration minus the lattice energy.

$$\Delta H_{sol} = \Delta H_{lattice} + \Delta H_{hydration}$$

The cycle relating solution enthalpy, hydration enthalpy, and lattice energy is shown in Figure 5.9.1 using the salt NaCl as an example.

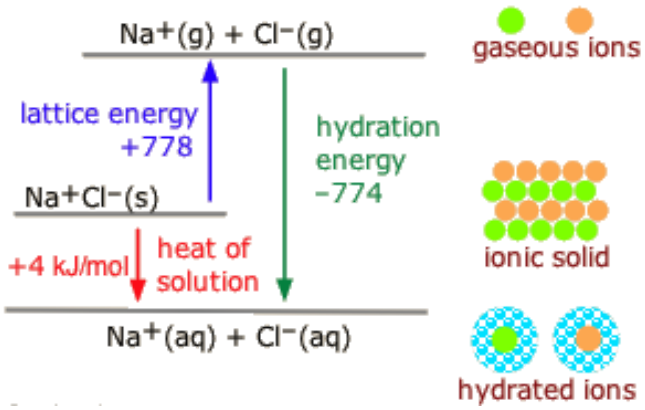


Figure 5.9.1: Thermodynamic cycle for dissolving sodium chloride in water. (CC-BY-NC-SA 4.0, Chung (Peter) Chieh)

The enthalpies of solution for some salts can be positive values, in these cases the temperatures of the solution decrease as the substances dissolve; the dissolving is an endothermic reaction. The energy levels of solids and solutions reverse in order of

height. The values in Table 5.9.1 indicate that when aluminum chloride and sulfuric acid are dissolved in water, much heat is released. Due to the very small value of enthalpies of solution, the temperature changes are hardly noticed when $LiNO_3$ and NaCl are dissolving.

Table 5.9.1: Enthalpy of Solution ΔH_{sol} kJ/mol) of Some Common Electrolytes

Substance	ΔH_{sol}	Substance	ΔH_{sol}
$AlCl_3$(s)	-373.63	H_2SO_4(l)	-95.28
$LiNO_3$(s)	-2.51	LiCl(s)	-37.03
$NaNO_3$(s)	20.50	NaCl(s)	3.88
KNO_3(s)	34.89	KCl(s)	-17.22
NaOH(s)	-44.51	NH_4Cl(s)	14.77

Calculating Enthalpy of Solution

The hydration enthalpies for calcium and chloride ions are given by the equations:

$$Ca^{2+}(g) + H_2O \rightarrow \ Ca^{2+}(aq), \Delta H_{hyd} = -1650 kJ/mol$$

$$Cl^{-}(g) + H_2O \rightarrow \ Cl^{-}(aq), \Delta H_{hyd} = -364 kJ/mol$$

The following cycle is for calcium chloride, and includes a lattice energy of -2258 kJ mol^{-1} (+2258 kJ mol^{-1} to disassemble the lattice). We have to use double the hydration enthalpy of the chloride ion because we are hydrating 2 moles of chloride ions.

$$\Delta H_{sol} = -\Delta H_{lattice} + \Delta H_{hyd,Ca} + 2 \times \Delta H_{hyd,Cl}$$

$$\Delta H_{sol} = -(-2258\ kJ/mol) + (-1650\ kJ/mol) + (2 \times -364\ kJ/mol)$$

Whether an enthalpy of solution turns out to be negative or positive depends on the relative sizes of the lattice enthalpy and the hydration enthalpies. In this particular case, the negative hydration enthalpies more than made up for the positive lattice dissociation enthalpy.

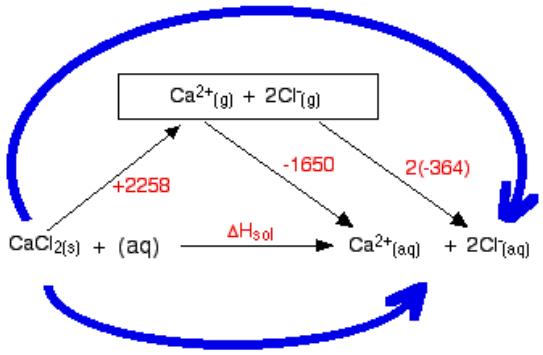


Figure 5.9.2: Thermodynamic cycle for dissolving calcium chloride in water. (CC-BY-NC 4.0, Jim Clark)

Problems

? Exercise 5.9.1

The lattice energy of NaCl is +788 kJ/mol. The estimated enthalpy of hydration for sodium and chloride ions are -406 and -363 kJ/mol respectively. Estimate the enthalpy of solvation for NaCl.

Answer

Using the cycle in Figure 5.9.2, we have

$$\Delta H_{hyd} = \Delta H_{lattice} + \Delta H_{sol}$$

$$\Delta H_{sol} = -769 - (788)\ kJ = -19\ kJ/mol$$

A positive value indicates an endothermic reaction. However, the value is small, and depending on the source of data, the estimated value may change. This value of 19 kJ/mol is too high compared to the value given earlier for NaCl of 3.88 kJ/mol, due to a high value of lattice energy used.

? Exercise 5.9.2

The enthalpy of crystallization for KCl is -715 kJ/mol. The enthalpies of hydration for potassium and chloride are -322 and -363 kJ/mol respectively. From these values, estimate the enthalpy of solution for KCl.

Answer

The enthalpy of hydration for KCl is estimated to be

$$\Delta H_{hyd} = -322 + (-363) = -685 kJ/mol$$

Thus, the enthalpy of solution is

$$\Delta H_{sol} = -685 - (-715) = 30 kJ/mol$$

The enthalpy of solution given above is -17.22. The two values here indicates that dissolving **KCl** into water is an endothermic reaction or change. Should temperature decrease or increase when **KCl** dissolves?

Contributors and Attributions

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5.10: Lattice Energy - The Born-Haber cycle

Ionic solids tend to be very stable compounds. The enthalpies of formation of the ionic molecules cannot alone account for this stability. These compounds have an additional stability due to the lattice energy of the solid structure. However, lattice energy cannot be directly measured. The Born-Haber cycle allows us to understand and determine the lattice energies of ionic solids. Lattice Energy is used to explain the stability of ionic solids. Some might expect such an ordered structure to be less stable because the entropy of the system would be low. However, the crystalline structure allows each ion to interact with multiple oppositely charge ions, which causes a highly favorable change in the enthalpy of the system. A lot of energy is released as the oppositely charged ions interact. It is this that causes ionic solids to have such high melting and boiling points. Some require such high temperatures that they decompose before they can reach a melting and/or boiling point.

Lattice Energy

Lattice Energy is a type of potential energy. Although there are two commonly used ways of defining lattice enthalpy which directly contradict each other, and we will primarily use the first of these:

- The lattice energy is the energy required to break apart an ionic solid and convert its component atoms into gaseous ions. This definition causes the value for the lattice energy to always be positive, since this will always be an endothermic reaction. In other words, you are looking at a downward arrow on Figure **5.10.1**.

$$\mathrm{M}_a\,\mathrm{L}_b\,(\mathrm{s}) \;\rightarrow a\,\mathrm{M}^{b+}\,(\mathrm{g}) + b\,\mathrm{X}^{a-}\,(\mathrm{g})$$

- The lattice energy is the energy released when gaseous ions bind to form an ionic solid. As implied in the definition, this process will always be exothermic, and thus the value for lattice energy will be negative. Its values are usually expressed with the units kJ/mol. In other words, you are looking at an upward arrow on Figure \(\PageIndex{1}).

$$a\,\mathrm{M}^{b+}\,(\mathrm{g}) + b\,\mathrm{X}^{a-}\,(\mathrm{g}) \;\rightarrow \mathrm{M}_a\mathrm{L}_b\,(\mathrm{s})$$

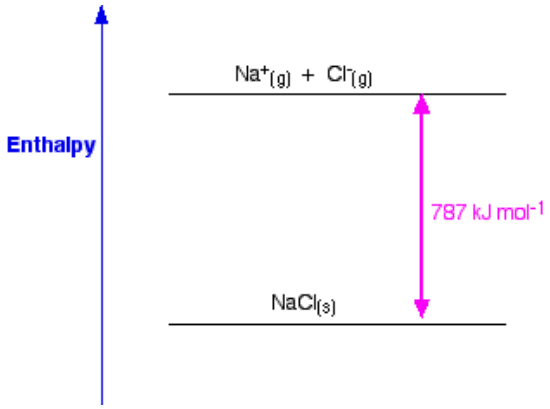


Figure **5.10.1**: Enthalpy diagram for NaCl(s); for sodium chloride, the solid is more stable than the gaseous ions by 787 kJ mol^{-1}. (CC-BY-NC-SA; Jim Clark)

Definitions

You may prefer to refer to the lattice enthalpy associated with *dissociation* or *formation* of the lattice

- The *lattice dissociation enthalpy* is the enthalpy change needed to convert 1 mole of solid crystal into its scattered gaseous ions. Lattice dissociation enthalpies are **always positive**.
- The *lattice formation enthalpy* is the enthalpy change when 1 mole of solid crystal is formed from its separated gaseous ions. Lattice formation enthalpies are **always negative**.

Values of lattice energies for various solids have been given in the literature, especially for some common solids. A few are provided in Table **5.10.1**.

Table **5.10.1**: Lattice Energies (kJ/mol) of Some Salts

Solid	*U*	Solid	*U*	Solid	*U*	Solid	*U*
LiF	1036	LiCl	853	LiBr	807	LiI	757
NaF	923	NaCl	786	NaBr	747	NaI	704
KF	821	KCl	715	KBr	682	KI	649
MgF_2	2957	$MgCl_2$	2526	$MgBr_2$	2440	MgI_2	2327

Factors Affecting Lattice Enthalpy

The following trends are obvious at a glance of the data in Table **5.10.1**:

- As the ionic radii of either the cation or anion increase, the lattice energies decrease.
- The solids consists of divalent ions have much larger lattice energies than solids with monovalent ions.

Lattice enthalpy is a measure of the strength of the forces between the ions in an ionic solid. Those forces are only completely broken when the ions are present as gaseous ions, scattered so far apart that there is negligible attraction between them. The greater the lattice enthalpy, the stronger the forces.The force of attraction between oppositely charged particles is described by Coulomb's law

The charges on the ions

Sodium chloride and magnesium oxide have exactly the same arrangements of ions in the crystal lattice, but the lattice enthalpies are very different. You can see that the lattice enthalpy of magnesium oxide is much greater than that of sodium chloride. That's because in magnesium oxide, 2+ ions are attracting 2- ions; in sodium chloride, the attraction is only between 1+ and 1- ions.

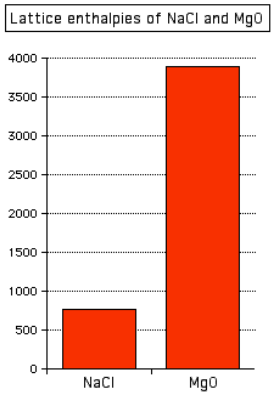


Figure **5.10.2**: A comparison of the lattice enthalpies of NaCl and MgO. (CC-BY-NC-SA; Jim Clark)

The Radius of the Ions

The lattice enthalpy of magnesium oxide is also increased relative to sodium chloride because magnesium ions are smaller than sodium ions, and oxide ions are smaller than chloride ions. That means that the ions are closer together in the lattice, and that increases the strength of the attractions.

This effect of ion size on lattice enthalpy is clearly observed as you go down a Group in the Periodic Table. For example, as you go down Group 7 of the Periodic Table from fluorine to iodine, you would expect the lattice enthalpies of their sodium salts to fall as the negative ions get bigger - and that is the case:

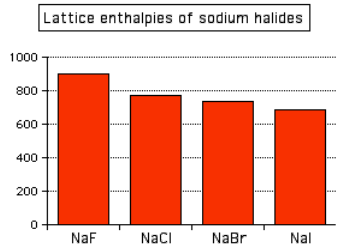


Figure **5.10.3**: Lattice enthalpies of sodium halides. (CC-BY-NC-SA; Jim Clark)

Attractions are governed by the distances between the centers of the oppositely charged ions, and that distance is obviously greater as the negative ion gets bigger. And you can see exactly the same effect if as you go down Group 1. The next bar chart shows the lattice enthalpies of the Group 1 chlorides.

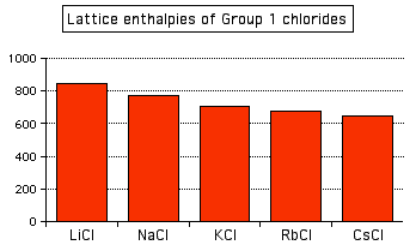


Figure **5.10.4**: Lattice enthalpies of Group 1 chlorides. (CC-BY-NC-SA; Jim Clark)

The Born-Haber Cycle

The Born-Haber cycle is used to estimate the lattice energy of an ionic solid. The Born-Haber Cycle uses several familiar concepts to determine the lattice energy of an ionic solid: ionization energy, electron affinity, dissociation energy, sublimation energy, heat of formation, and Hess's Law.

- **Ionization Energy** is the energy required to remove an electron from a neutral atom or an ion. This process always requires an input of energy, and thus will always have a positive value. In general, ionization energy increases across the periodic table from left to right, and decreases from top to bottom. There are some excepts, usually due to the stability of half-filled and completely filled orbitals.
- **Electron Affinity** is the energy released when an electron is added to a neutral atom or an ion. Usually, energy released would have a negative value, but due to the definition of electron affinity, it is written as a positive value in most tables. Therefore, when used in calculating the lattice energy, we must remember to subtract the electron affinity, not add it. In general, electron affinity increases from left to right across the periodic table and decreases from top to bottom.
- **Dissociation energy** is the energy required to break apart a compound. The dissociation of a compound is always an endothermic process, meaning it will always require an input of energy. Therefore, the change in energy is always positive. The magnitude of the dissociation energy depends on the electronegativity of the atoms involved.
- **Atomization energy** is the energy required to cause a change of phase from solid to gas, bypassing the liquid phase. This is an input of energy, and thus has a positive value. It may also be referred to as the sublimation energy.
- **The heat of formation** is the change in energy when forming a compound from its elements. This may be positive or negative, depending on the atoms involved and how they interact.
- **Hess's Law** states that the overall change in energy of a process can be determined by breaking the process down into steps, then adding the changes in energy of each step. The Born-Haber Cycle is essentially Hess's Law applied to an ionic solid.

Enthalpy of Atomization

The standard atomization enthalpy, ΔH_a°, is the enthalpy change when 1 mole of gaseous atoms is formed from the element in its standard state. Enthalpy change of atomization is always positive. You are always going to have to supply energy to break an element into its separate gaseous atoms. All of the following equations represent changes involving atomization enthalpy:

$$\frac{1}{2}Cl_2(g) \rightarrow Cl(g) \quad \Delta H_a^o = +122\,kJ\,mol^{-1}$$

$$\frac{1}{2}Br_2(l) \rightarrow Br(g) \quad \Delta H_a^o = +122\,kJ\,mol^{-1}$$

$$Na(s) \rightarrow Na(g) \quad \Delta H_a^o = +107\,kJ\,mol^{-1}$$

Notice particularly that the "mol^{-1}" is per mole of atoms **formed** - NOT per mole of element that you start with. You will quite commonly have to write fractions into the left-hand side of the equation. Getting this wrong is a common mistake.

How to Use the Born-Haber Cycle

Consider the Born-Haber cycle for sodium chloride (Figure **5.10.5**).The values used in the Born-Haber Cycle are all predetermined changes in enthalpy for the processes described above. Hess' Law allows us to add or subtract these values, which allows us to determine the lattice energy.

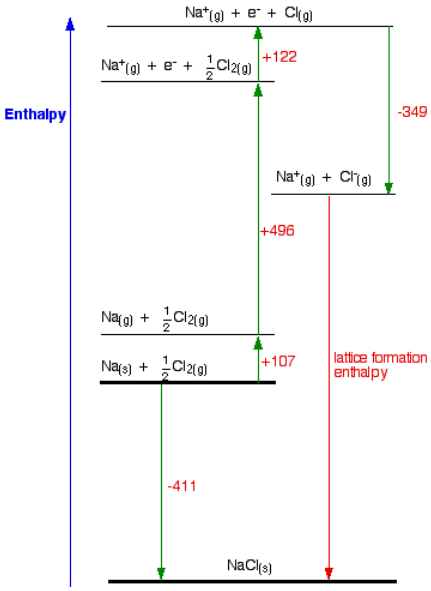


Figure **5.10.5**: Born-Haber Cycle for NaCl. (CC-BY-NC-SA; Jim Clark)

Step 0

Start with the balanced chemical equation for the formation of NaCl(s) from its elements in their standard states:

$$Na(s) + \frac{1}{2}Cl_2(g) \rightarrow NaCl(s), \Delta H_{formation} = -411kJ/mol$$

Elements in their standard states have an enthalpy of zero, and energy is released when a compound is formed from its elements in their standard states. This is the energy of formation, and will be used at the end of the process to determine the lattice energy. The energy of formation is not directly determined, thus the a series of reactions will be used to convert the elements in their standard states into non-standard states and then eventually into the compound. The sum of the energy changes in these steps will be equal to the heat of formation of the compound.

Step 1

The Born-Haber Cycle requires that the elements involved in the reaction are in their gaseous forms.

$$Na(s) \rightarrow Na(g), \Delta H_{atom,\,Na} = 107kJ/mol$$

Step 2

Although Cl_2 exists as a gas in its standard state, however, it also exists as a polyatomic species. The energy associated with changing Cl_2 into 2Cl must also be considered.

Extra close brace or missing open brace

Step 3

The gaseous atoms need to be changed into their ionic forms, as they would exist in the ionic solid. The Na(g) must be ionized to its cation form.

$$Na(g) \rightarrow Na^{+}(g) + e^{-}, \Delta H_{IE_1,\,Na} = 496 kJ/mol$$

Step 4

The chlorine must lose an electron to form its anion.

$$Cl(g) + e^{-} \rightarrow Cl^{-}(g), \Delta H_{EA_1\,Cl} = -349 kJ/mol$$

Step 5

Now the cation and anion will be combined to form the ionic solid. This will cause a release of energy, which is called the lattice energy.

$$Na^{+}(g) + Cl^{-}(g) \rightarrow NaCl(s), \Delta H_{lattice}$$

Step 6

Steps the energy changes for steps 0 through 5 can be combined into one equation:

$$\Delta H_{formation} = \Delta H_{atom,\,Na} + \Delta H_{atom,\,Cl} + \Delta H_{IE_1,\,Na} + \Delta H_{EA_1\,Cl} + \Delta H_{lattice}$$

$$-411\frac{kJ}{mol} = 107\frac{kJ}{mol} + 122\frac{kJ}{mol} + 496\frac{kJ}{mol} + (-340\frac{kJ}{mol}) + \Delta H_{lattice}$$

Rearrangement to solve for lattice energy gives the equation:

$$\Delta H_{lattice} = \Delta H_{formation} - (\Delta H_{atom,\,Na} + \Delta H_{atom,\,Cl} + \Delta H_{IE_1,\,Na} + \Delta H_{EA_1\,Cl})$$

$$\Delta H_{lattice} = -411\frac{kJ}{mol} - (107\frac{kJ}{mol} + 122\frac{kJ}{mol} + 496\frac{kJ}{mol} + (-340\frac{kJ}{mol}))$$

$$\Delta H_{lattice} = -411\frac{kJ}{mol} - 107\frac{kJ}{mol} - 122\frac{kJ}{mol} - 496\frac{kJ}{mol} + 340\frac{kJ}{mol}$$

\[\ce_\Delta H_{lattice}=-787

Example 5.10.1: Born-Haber Cycle for $MgCl_2$

Why is magnesium chloride $MgCl_2$ rather than MgCl or $MgCl_3$ (or any other formula you might like to choose)?

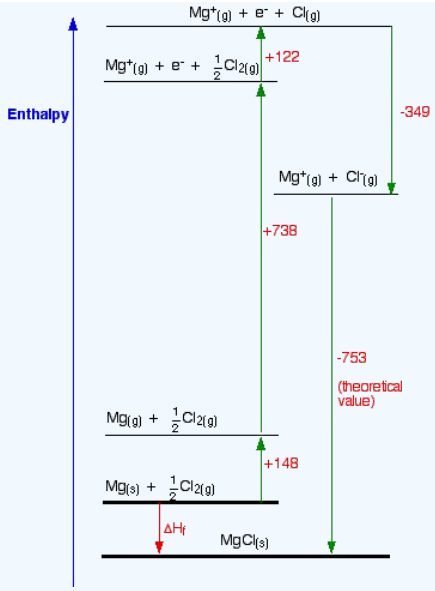
It turns out that $MgCl_2$ is the formula of the compound which has the most negative enthalpy of formation - in other words, it is the most stable one relative to the elements magnesium and chlorine. Let's look at this in terms of Born-Haber cycles of the imaginary compounds MgCl and $MgCl_3$.

This will require us to use theoretical values for their lattice enthalpies. We cannot use experimental ones, because these compounds do not exist! The exact values do not matter too much anyway, because the results are so dramatically clear-cut.

Solution

Born-Haber cycle for MgCl

$$\mathrm{Mg\,(s) + \tfrac{1}{2}\,Cl_2\,(g) \;\rightarrow MgCl\,(s)}$$



$$\Delta H_f = +148 + 738 + 122 - 349 - 753$$

$$\Delta H_f = -94 \text{ kJ mol}^{-1}$$

The compound MgCl is definitely energetically more stable than its elements. This cycle is drawn very roughly to scale, but that is going to become more and more difficult as we look at the other two possible formulae. You can see from the diagram that the enthalpy change of formation can be found just by adding up all the other numbers in the cycle, and we can do this just as well in a table:

	kJ
atomization enthalpy of Mg	+148
1st IE of Mg	+738
atomization enthalpy of Cl	+122
electron affinity of Cl	-349
lattice enthalpy	-753
calculated ΔH_f	-94

1. The Born-Haber cycle for $MgCl_2$

The equation for the enthalpy change of formation this time is

$$Mg\,(s) + Cl_2\,(g) \rightarrow MgCl_2\,(s)$$

So how does that change the numbers in the Born-Haber cycle?

- You need to add in the second ionization energy of magnesium, because you are making a 2+ ion.
- You need to multiply the atomization enthalpy of chlorine by 2, because you need 2 moles of gaseous chlorine atoms.
- You need to multiply the electron affinity of chlorine by 2, because you are making 2 moles of chloride ions.
- You obviously need a different value for lattice enthalpy.

	kJ
atomization enthalpy of Mg	+148
1st IE of Mg	+738
2nd IE of Mg	+1451
atomization enthalpy of Cl (x 2)	+244
electron affinity of Cl (x 2)	-698
lattice enthalpy	-2526
calculated ΔH_f	-643

You can see that much more energy is released when you make $MgCl_2$ than when you make MgCl. Why is that? You need to put in more energy to ionize the magnesium to give a 2+ ion, but a lot more energy is released as lattice enthalpy. That is because there are stronger ionic attractions between 1- ions and 2+ ions than between the 1- and 1+ ions in MgCl. So what about $MgCl_3$? The lattice energy here would be even greater.

3. The Born-Haber cycle for $MgCl_3$

The equation for the enthalpy change of formation this time is

$$\mathrm{Mg\,(s) + \tfrac{3}{2}\,Cl_2\,(g) \rightarrow MgCl_3\,(s)}$$

So how does that change the numbers in the Born-Haber cycle this time?

- You need to add in the third ionization energy of magnesium, because you are making a 3+ ion.
- You need to multiply the atomization enthalpy of chlorine by 3, because you need 3 moles of gaseous chlorine atoms.
- You need to multiply the electron affinity of chlorine by 3, because you are making 3 moles of chloride ions.
- You again need a different value for lattice enthalpy.

	kJ
atomization enthalpy of Mg	+148
1st IE of Mg	+738
2nd IE of Mg	+1451
3rd IE of Mg	+7733
atomization enthalpy of Cl (x 3)	+366
electron affinity of Cl (x 3)	-1047
lattice enthalpy	-5440
calculated ΔH_f	+3949

This time, the compound is hugely energetically unstable, both with respect to its elements, and also to other compounds that could be formed. You would need to supply nearly 4000 kJ to get 1 mole of $MgCl_3$ to form! Look carefully at the reason for this. The lattice enthalpy is the highest for all these possible compounds, but it is not high enough to make up for the very large third ionization energy of magnesium. Why is the third ionization energy so big? The first two electrons to be removed from magnesium come from the 3s level. The third one comes from the 2p. That is closer to the nucleus, and lacks a layer of screening as well - and so much more energy is needed to

remove it. The 3s electrons are screened from the nucleus by the 1 level and 2 level electrons. The 2p electrons are only screened by the 1 level (plus a bit of help from the 2s electrons).

Conclusion

Magnesium chloride is $MgCl_2$ because this is the combination of magnesium and chlorine which produces the most energetically stable compound - the one with the most negative enthalpy change of formation.

Theoretical Estimates of Lattice Energies

Let's assume that a compound is fully ionic. Let's also assume that the ions are point charges - in other words that the charge is concentrated at the center of the ion. By doing physics-style calculations, it is possible to calculate a theoretical value for what you would expect the lattice energy to be. Calculations of this sort end up with values of *lattice energy*, and not *lattice enthalpy*. If you know how to do it, you can then fairly easily convert between the two.

There are several different equations, of various degrees of complication, for calculating lattice energy in this way. There are two possibilities:

- There is reasonable agreement between the experimental value (calculated from a Born-Haber cycle) and the theoretical value. Sodium chloride is a case like this - the theoretical and experimental values agree to within a few percent. That means that for sodium chloride, the assumptions about the solid being ionic are fairly good.
- The experimental and theoretical values do not agree. A commonly quoted example of this is silver chloride, AgCl. Depending on where you get your data from, the theoretical value for lattice enthalpy for AgCl is anywhere from about 50 to 150 kJ mol^{-1} less than the value that comes from a Born-Haber cycle. In other words, treating the AgCl as 100% ionic underestimates its lattice enthalpy by quite a lot.

The explanation is that silver chloride actually has a significant amount of covalent bonding between the silver and the chlorine, because there is not enough electronegativity difference between the two to allow for complete transfer of an electron from the silver to the chlorine. Comparing experimental (Born-Haber cycle) and theoretical values for lattice enthalpy is a good way of judging how purely ionic a crystal is.

Problems

? Exercise 5.10.1

Find the lattice energy of KF(s).
Note: Values can be found in standard tables.

Answer

Lattice Energy= [-436.68-89-(0.5*158)-418.8-(-328)] kJ/mol= **-695.48 kJ/mol**

? Exercise 5.10.2

Find the lattice energy of $MgCl_2$(s).

Answer

Lattice Energy= [-641.8-146-243-(737.7+1450.6)-(2*-349)] kJ/mol= **-2521.1 kJ/mol**

? Exercise 5.10.3

Which one of the following has the greatest lattice energy?

a. MgO
b. NaC
c. LiCl

d. $MgCl_2$

Answer

MgO. It has ions with the largest charge.

? Exercise 5.10.4

Which one of the following has the greatest Lattice Energy?

NaCl

a. $CaCl_2$
b. $AlCl_3$
c. KCl

Answer

$AlCl_3$. According to the periodic trends, as the radius of the ion increases, lattice energy decreases.

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5.11: Lattice Energy - Madelung Constants

When determining lattice energy, there are many factors to be considered such as the covalent character and the electron-electron interactions in ionic solids. For simplicity, let us consider ionic solids to be a collection of cations and anions. In this simple view, the appropriate number of cations and anions come together to form a solid. The cations experience attraction to the anions and repulsion from the other cations. The closer the cation is to an anion, the stronger the degree of attraction between the cation and anion. Likewise, the closer the cation is to another cation, the stronger the repulsive force between the two positively charge ions. The *Madelung constant* takes in to account the total attractive and repulsive forces between all ions in a solid; it accounts for the differences in attractive and repulsive forces that result from the distance between ions. It is a property of the crystal structure and depends on the type of lattice, the distance between anions and cations, and the volume of the unit cell.

The Madelung constant is incorporated into the Born-Landé equation, which is used to calculate the lattice energy of a compound. The Born-Landé equation is a concept originally formulated in 1918 by the scientists Born and Landé. This expression takes into account Coulomb attractions between ions and the Born repulsive interactions between ions. Using the Madelung constant, this equation considers how the attractive and repulsive forces differ depending on the distance between ions.

Madelung Constants

1D Crystal

Before considering a three-dimensional crystal lattice, we shall discuss the calculation of the energetics of a linear chain of ions of alternate signs (Figure 5.11.1).

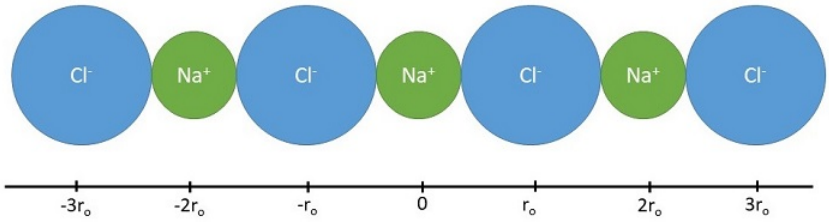


Figure 5.11.1: A hypothetical one-dimensional NaCl lattice.

Let sodium cation in the middle (at $x = 0$) be the reference and let r_0 be the shortest distance between adjacent ions (the sum of ionic radii). The energy of attraction (Coulomb energy) between this sodium cation and all others in this 1D lattice can be calculated by summing the energy of attraction for ions in the same "shells" (at the same distance or proximity).

- **Nearest Neighbors (first shell):** The sodium cation has two negative chloride ions as its neighbors on either side at $\pm r_0$ so the Coulombic energy of these interactions is

$$\underbrace{\frac{-e^2}{4\pi\epsilon_o r_o}}_{\text{left chloride ion}} + \underbrace{\frac{-e^2}{4\pi\epsilon_o r_o}}_{\text{right chloride ion}} = -\frac{2e^2}{4\pi\epsilon_o r_o} \tag{5.11.1}$$

- **Next Nearest Neighbors (second shell)**: Similarly the repulsive energy due to the next two positive sodium ions at a distance of $2r_0$ is

$$\underbrace{\frac{+e^2}{4\pi\epsilon_o (2r_o)}}_{\text{left sodium ion}} + \underbrace{\frac{+e^2}{4\pi\epsilon_o (2r_o)}}_{\text{right sodium ion}} = +\frac{2e^2}{4\pi\epsilon_o (2r_o)} \tag{5.11.2}$$

- **Next Next Nearest Neighbors (third shell)**: The attractive Coulomb energy due to the next two chloride ions neighbors at a distance $3r_0$ is

$$\underbrace{\frac{-e^2}{4\pi\epsilon_o (3r_o)}}_{\text{left chloride ion}} + \underbrace{\frac{-e^2}{4\pi\epsilon_o (3r_o)}}_{\text{right chloride ion}} = -\frac{2e^2}{4\pi\epsilon_o (3r_o)} \tag{5.11.3}$$

and so on. Thus the total energy due to all the ions in the linear array is

$$E = -\frac{2e^2}{4\pi\epsilon_o r_o} + \frac{2e^2}{4\pi\epsilon_o (2r_o)} - \frac{2e^2}{4\pi\epsilon_o (3r_o)} - \ldots \tag{5.11.4}$$

or

$$E = \frac{e^2}{4\pi\epsilon_o r_o}\left[2\left(1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \ldots\right)\right] \tag{5.11.5}$$

We can use the following Maclaurin expansion

$$\ln(1+x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^3}{4} + \cdots \tag{5.11.6}$$

to simplify the sum in the parenthesis of Equation 5.11.5 as $\ln(1+1)$ to obtain

$$E = \frac{e^2}{4\pi\epsilon_o r_o}[2\ln 2] \tag{5.11.7}$$

$$= \frac{e^2}{4\pi\epsilon_o} M \tag{5.11.8}$$

The first factor of Equation 5.11.7 is the Coulomb energy for a single pair of sodium and chloride ions, while the $2\ln 2$ factor is the *Madelung constant* ($M \approx 1.38$) per molecule. The Madelung constant is named after Erwin Madelung and is a geometrical factor that depends on the arrangement of ions in the solid. If the lattice were different (when considering 2D or 3D crystals), then this constant would naturally differ.

3D Crystal

In three dimensions the series does present greater difficulty and it is not possible to sum the series conveniently as in the case of one-dimensional lattice. As an example, let us consider the the NaCl crystal. In the following discussion, assume r be the distance between Na^+ and Cl^- ions. The nearest neighbors of Na^+ are six Cl^- ions at a distance $1r$, 12 Na^+ ions at a distance $2r$, eight Cl^- ions at $3r$, six Na^+ ions at $4r$, 24 Na^+ ions at $5r$, and so on. Thus, the electrostatic potential of a single ion in a crystal by approximating the ions by point charges of the surrounding ions:

$$E_{ion-lattice} = \frac{Z^2 e^2}{4\pi\epsilon_o r} M \tag{5.11.9}$$

For NaCl is a poorly converging series of interaction energies:

$$M = \frac{6}{1} - \frac{12}{2} + \frac{8}{3} - \frac{6}{4} + \frac{24}{5} \ldots \tag{5.11.10}$$

with

- Z is the number of charges of the ions, (e.g., 1 for NaCl),
- e is the charge of an electron ($1.6022 \times 10^{-19}\ C$),
- $4\pi\epsilon_o$ is 1.11265x10^{-10} C^2/(J m).

Derived Values

The Madelung constant depends on the structure type and Equation 5.11.10 is applicable only for the sodium chloride (ei.g, rock salt) lattice geometry. Other values for other structural types are given in Table 5.11.1. A is the number of anions coordinated to cation and C is the numbers of cations coordinated to anion.

Table 5.11.1: Madelung Constants

Compound	*Crystal Lattice*	*M*	*A : C*	*Type*
NaCl	NaCl	1.74756	6 : 6	Rock salt
CsCl	CsCl	1.76267	6 : 6	CsCl type
CaF_2	Cubic	2.51939	8 : 4	Fluorite
$CdCl_2$	Hexagonal	2.244		
MgF_2	Tetragonal	2.381		
ZnS (wurtzite)	Hexagonal	1.64132		
TiO_2 (rutile)	Tetragonal	2.408	6 : 3	Rutile
$bSiO_2$	Hexagonal	2.2197		
Al_2O_3	Rhombohedral	4.1719	6 : 4	Corundum

A is the number of anions coordinated to cation and *C* is the numbers of cations coordinated to anion.

The Born-Landé Equation

There are other factors to consider for the evaluation of lattice energy and the treatment by Max Born and Alfred Lande led to the formula for the evaluation of lattice energy for a mole of **crystalline solid**. The Born–Landé equation (Equation 5.11.11) is a means of calculating the lattice energy of a crystalline ionic compound and derived from the electrostatic potential of the ionic lattice and a repulsive potential energy term

$$U = \frac{N_A M Z^2 e^2}{4\pi\epsilon_o r}\left(1 - \frac{1}{n}\right) \tag{5.11.11}$$

where

- N_A is Avogadro constant;
- M is the Madelung constant for the lattice
- z^+ is the charge number of cation
- z^- is the charge number of anion
- e is elementary charge, 1.6022×10^{-19} C
- ε_0 is the permittivity of free space
- r_0 is the distance to closest ion
- n is the **Born exponent** that is typically between 5 and 12 and is determined experimentally. n is a number related to the electronic configurations of the ions involved (Table 5.11.2).

Table 5.11.2: n values for select solids

Atom/Molecule	*n*
He	5
Ne	7
Ar	9
Kr	10
Xe	12
LiF	5.9
LiCl	8.0
LiBr	8.7
NaCl	9.1
NaBr	9.5

Derivation of the Born-Landé Equation

To solve for the Born-Landé equation, you must have a basic understanding of lattice energy:

- Lattice energy decreases as you go down a group (as atomic radii goes up, lattice energy goes down).
- Going across the periodic table, atomic radii decreases, therefore lattice energy increases.

The Born-Landé equation was derived from these two following equations. the first is the electrostatic potential energy:

$$\Delta U = -\frac{N_A M |Z^+||Z^-| e^2}{4\pi\epsilon_o r} \tag{5.11.12}$$

with

- M_A is Avogadro's constant (6.022×10^{23})
- M is the Madelung Constant (a constant that varies for different structures)
- e is the charge of an electron (1.6022×10^{-19} C)
- Z^+ is the cation charge
- Z^- is the anion charge
- ϵ_o is the permittivity of free space

The second equation is the repulsive interaction:

$$\Delta U = \frac{N_A B}{r^n} \tag{5.11.13}$$

with

- B is the repulsion coefficient and
- n is the Born Exponent (typically ranges between 5-12) that is used to measure how much a solid compresses

These equations combine and simplify to form the Born-Landé equation:

$$\Delta U(0K) = \frac{N_A M |Z^+||Z^-| e^2}{4\pi\epsilon_o r_o}\left(1 - \frac{1}{n}\right) \tag{5.11.14}$$

with

- r_0 is the closest ion distance

Problems

Exercise 5.11.1

Which compound has the greatest lattice energy?

- AlF_3
- NACl
- LiF
- $CaCl_2$

Answer

This question requires basic knowledge of lattice energy. Since F_3 gives the compound a +3 positive charge and the Al gives the compound a -1 negative charge, the compound has large electrostatic attraction. The bigger the electrostatic attraction, the greater the lattice energy.

Exercise 5.11.2

Estimate the lattice energy for **NaCl**.

Answer

Using the values giving in the discussion above, the estimation is given by

$$U_{NaCl} = \frac{(6.022 \times 10^{23}/mol)(1.74756)(1.6022 \times 10^{-19})^2}{4\pi\,(8.854 \times 10^{-12} C^2/m)(282 \times 10^{-12}\ m)}\left(1 - \frac{1}{9.1}\right)$$
$$= -766\ kJ/mol$$

Much more should be considered in order to evaluate the lattice energy accurately, but the above calculation leads you to a good start. When methods to evaluate the energy of crystallization or lattice energy lead to reliable values, these values can be used in the Born-Hable cycle to evaluate other chemical properties, for example the electron affinity, which is really difficult to determine directly by experiment.

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SECTION OVERVIEW

5.12: Basic Science of Nanomaterials

Learning Objectives

- Understand the physical basis of mesoscopic behavior in nanoscale semiconducting and magnetic particles.
- Describe how the particle-in-a-box equation applies to electrons in quantum wells.
- Use the Brus formula to calculate the band gap energy of nanoscale semiconductor particles.
- Use the surface energy concept to calculate changes in the melting point and vapor pressure of nanoparticles.
- Describe the methods used to make semiconducting and metal nanocrystals of uniform size.
- Explain the origin of the localized surface plasmon resonance effect in metal nanoparticles.
- Describe the emerging analytical and biomedical applications of metal nanoparticles.

Nanomaterials describe materials of which a single unit is sized (in at least one dimension) between 1 and 1000 nanometers, but is usually 1—100 nm. Nanomaterials research takes a materials science-based approach to nanotechnology, leveraging advances in materials metrology and synthesis which have been developed in support of microfabrication research. Materials with structure at the nanoscale often have unique optical, electronic, or mechanical properties. In this chapter we will learn about the basic science of nanomaterials, i.e., what it is about their size that makes them different.

5.12.1: Prelude to Basic Science of Nanomaterials

5.12.2: Physics and Length Scales- Cavity Laser, Coulomb Blockade, Nanoscale Magnets

5.12.3: Semiconductor Quantum Dots

5.12.4: Synthesis of Semiconductor Nanocrystals

5.12.5: Surface Energy

5.12.6: Nanoscale Metal Particles

5.12.7: Applications of Nanomaterials

5.12.8: Discussion Questions

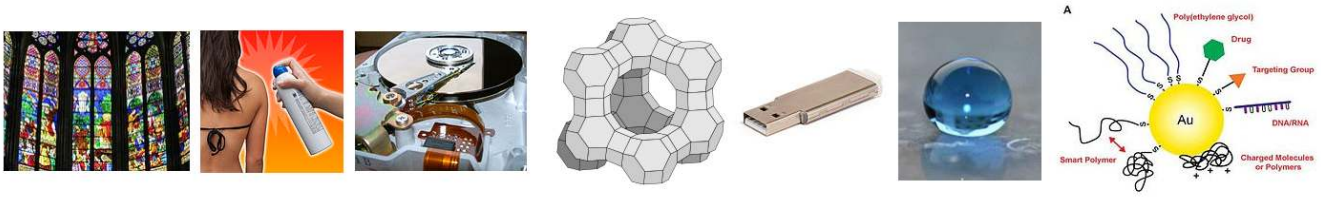
5.12.9: Problems

5.12.10: References

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5.12.1: Prelude to Basic Science of Nanomaterials

What do stained glass, sunscreen, magnetic hard drives, heterogeneous catalysts, consumer electronics, stain-resistant clothing, self-cleaning glass, and medical diagnostics all have in common? All of them derive some special property and utility from **nanoscale materials**: ordinary elements and inorganic compounds such as gold, silver, TiO_2, chromium, SiO_2, and silicon that acquire different properties when their characteristic dimensions are somewhere between **1 and 100 nm**. In this chapter we will learn about the basic science of nanomaterials, i.e., what it is about their size that makes them different.



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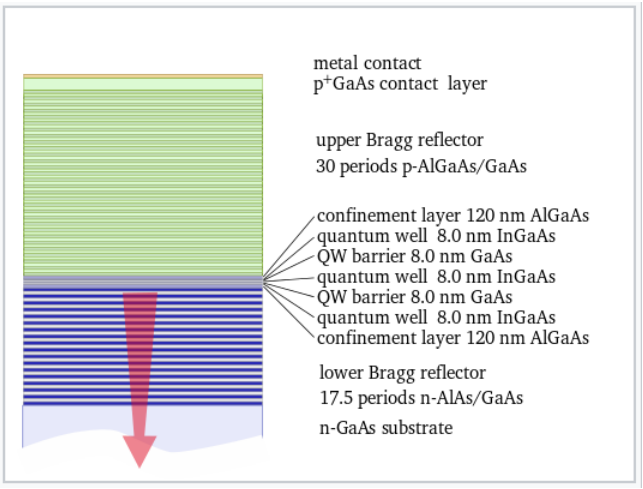
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5.12.2: Physics and Length Scales- Cavity Laser, Coulomb Blockade, Nanoscale Magnets

The special properties of nanomaterials do not derive from different laws of physics, which are the same for objects large and small. For example, Newton's second law ($F = ma$), Coulomb's law ($E = \frac{q_1 q_2}{4\pi\varepsilon_0 r}$), and the laws of energy and momentum conservation are the same for buckyballs (C_{60}) and full-size soccer balls. Nevertheless, the physics of electrons, atoms, and photons naturally produce **characteristic length scales**, some of which we have already seen. For example, in Chapter 6 we discovered that the mean free path of an electron in a good metal is about 40 nm. In Chapter 10, we learned that the Bohr radius of an electron or hole in doped Si is about 4 nm, and that the coherence length of Cooper pairs in semiconductors is somewhere between a few nm and 1 μm. When objects become small relative to these characteristic lengths, their physical properties change in interesting ways. Materials that exist at the relevant length scale are called ***mesoscopic*** (meso = "between," scopic = "size") meaning that they cross over from one kind of behavior - the bulk behavior of large objects - to another. This length scale is different for different kinds of properties, but for many it happens between 1 and 100 nm. We illustrate this point with a few examples.

The cavity laser

A vertical cavity surface-emitting laser (or VCSEL) is a semiconductor-based device that emits light in the vertical direction relative to the plane of the chip. These devices are being developed and used for high power applications such as laser surgery, infrared illumination for military surveillance, and laser cutting tools. The basic design of a VCSEL is shown at the right. The VCSEL is basically a light-emitting diode, incorporating p-type and n-type regions of the III-V semiconductor (Al,Ga)As. However, it has two special features. First, the refractive index of the semiconductor is modulated above and below the junction to make Bragg mirrors. These mirrors reflect light emitted in the junction, so that the photon density becomes very high there, a necessary condition for stimulated emission and lasing. The Bragg mirror stack is asymmetric (thinner on the bottom), so that light can escape from the junction in one direction only. Second, the junction itself consists of a thin "quantum well" layer of (In,Ga)As, a III-V semiconductor with a smaller band gap than the surrounding (Al,Ga)As layers.

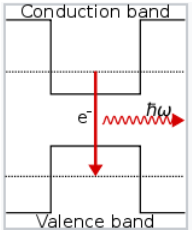


A VCSEL device structure. This is a *bottom-emitting multiple-quantum-well* VCSEL.

The **quantum well** structure, the band diagram of which is illustrated at the left, is the nanoscale part of the laser. The energies of the conduction and valence bands of (Al,Ga)As flank those of the thin (In,Ga)As layer. Therefore, electrons and holes injected into that layer cannot escape: electrons in (In,Ga)As do not have enough energy to climb "up" to the conduction band of (Al,Ga)As and holes cannot climb "down." Electrons confined to such a small well behave as a particle-in-a-box (as we learned in the context of electrides in Chapter 9).

The electron has a kinetic energy defined by the equation:

$$KE = \frac{h^2 n^2}{8mL^2} \tag{5.12.2.1}$$



We can calculate the energy difference between the lowest (n=1) and next lowest (n=2) levels, which is inversely proportional to the square of the thickness (L) of the (In,Ga)As layer. In this calculation we need to use the effective mass of the electron in (In,Ga)As, which is about 7% of the electron rest mass[1]. With an 8 nm thick layer, this energy is:

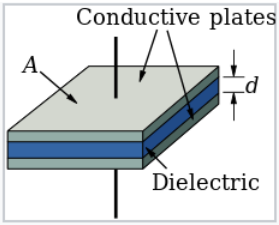
$$E = \frac{(2^2 - 1^2)(6.626 \cdot 10^{-34} Js)^2}{8 \cdot 0.07 \cdot (9.1 \cdot 10^{-31} kg)(8 \cdot 10^{-9} m)^2} = 4.0 \cdot 10^{-20} J = 0.25 eV \tag{5.12.2.2}$$

The VCSEL cavity will thus have a resonant energy of 0.25 eV and emit photons at this energy in the infrared (λ ≈ 5000 nm). Note that because of the inverse square dependence of the cavity energy on layer thickness, lasers based on this design can only function at nanoscale dimensions. When the cavity is three times thicker, its resonant energy becomes comparable to the thermal energy at room temperature (kT = 0.026 eV), and the lasing effect is thermally "washed out."

Coulomb blockade

A capacitor is a (macroscopic) device that stores electrical charge. The basic structure of a capacitor is shown at the right. When a voltage is applied to such a device, it develops a charge (± Q) on the two plates that is proportional to the voltage:

$$C = \frac{Q}{V} \tag{5.12.2.3}$$



Basic design of a parallel plate capacitor of area *A* and with a dielectric thickness of *d*

The magnitude of the capacitance C is determined by the permittivity ε and the dimensions of the dielectric layer, A and d.

$$C = \frac{\varepsilon A}{d} \tag{5.12.2.4}$$

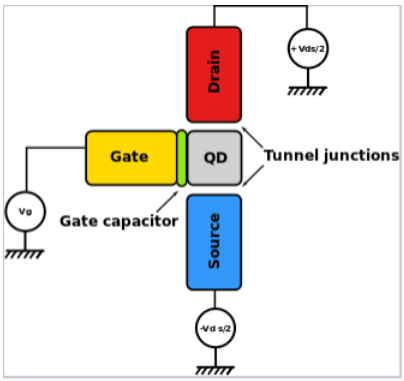
We can also calculate the work done in charging the capacitor up (i.e., the energy stored by charging the capacitor) by integrating the voltage times the charge:

$$E = int_0^Q V(q)dq = \int_0^Q \frac{q}{C} dq = \frac{1}{2}\frac{Q^2}{C} = \frac{1}{2}CV^2 = \frac{1}{2}VQ \tag{5.12.2.5}$$

Now it is interesting to ask, what happens to a capacitor when we make it very small? This is of particular interest in a device called a **single electron transistor**, a schematic diagram of which is shown at the right. The metallic gate lead is separated from a "quantum dot," which can be a metal or semiconductor particle, by a thin dielectric layer. This metal-dielectric-metal sandwich acts as a capacitor, and from the equation above, the energy needed to charge it by a single electron (Q = e) is:

$$E = \frac{e^2}{2C} \tag{5.12.2.6}$$

where e is the charge of the electron, 1.602 x 10^{-19} Coulomb. If the gate width and lateral dimensions are very small - say 2 nm as is readily achievable in self-assembled Coulomb blockade devices[2][3] - then for a typical insulating dielectric, a voltage of about 200 mV is needed to charge the quantum dot by a single electron. Again, this effect is unique to the nanoscale, because a 10 times larger device area would make the single-electron charging voltage about 20 mV, which is smaller than the thermal energy kT (26 meV). Thus for devices larger than about 5-6 nm, individual electron charging events are washed out at room temperature by thermal fluctuations.

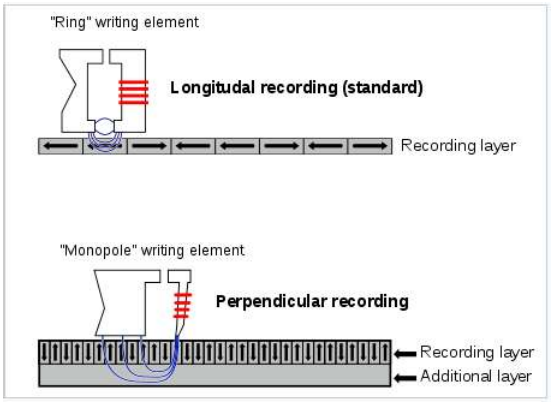


Schematic of a single-electron transistor.

How can a **nanoscale capacitor** like this act as a **transistor**, which functions as a switch in an electrical circuit? The effect comes from the mutual repulsion of electrons. An electron on the quantum dot repels any other electron that would be forced onto it by applying a small voltage between the source and the drain. Hence the conductance of the quantum dot is very low at a gate bias of zero volts, or at any gate bias (200, 400, 600 mV...) that places an integer number (1, 2, 3,...) of electrons on the dot. But halfway in between these voltages (e.g., at 100, 300, 500 mV) the energy is the same whether there are n or n+1 electrons on the dot. This means that electrons can hop on and off without changing their energy, i.e., they can tunnel through the dot from source to drain. This effect gives peaks in the conductance of the dot at regular steps in the gate voltage. In effect, the gate can act as a switch, as in a conventional field-effect transistor. Single-electron transistors are being researched as ultra-sensitive electrometers and single-molecule chemical sensors, since a tiny change in the electrostatic environment of the dot can switch the device on or off.

Nanoscale magnets

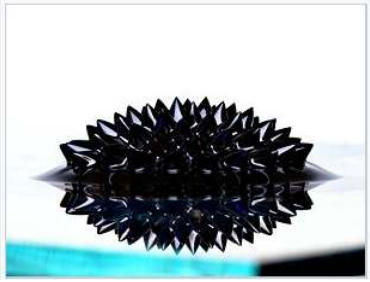
Ferro- and ferrimagnetic materials such as iron and chromium oxide are used for digitial storage of information in hard disks. The individual memory bits, which can be oriented perpendicular or parallel to the plane of the disk as shown at the right, store a logical "0" or "1" depending on the orientation of their magnetic dipole. To be useful, this information must be non-volatile, i.e., the magnetic bit must retain its polarization in the absence of an applied field from the read/write head.



Longitudinal and perpendicular recording, two types of writing heads on a hard disk.

The storage density of such magnetic memories is impressive. A 2.5" hard drive can now store 1 TB of information, using rod-shaped magnetic grains that are approximately 0.5 µm long. We now have good synthetic methods for making these same materials as crystals with dimensions of only a few nanometers. Why aren't those nanocrystals used to make even more dense memory disks?

The reason is that the energy needed to flip the magnetization (i.e., to turn a "0" into a "1" and vice-versa) is strongly size-dependent. For a ferro- or ferrimagnet this energy is equal to Mr^3, where M is the magnetic energy per unit volume and r is the characteristic dimension (e.g., the length of the edge of a cube, or the diameter of a sphere) of the magnetic grain. For typical materials such as iron, this energy becomes comparable to kT when r is about 3-5 nm. Such small particles are superparamagnetic, meaning that they still have a large magnetic moment because of the ordering of their spins, but they do not retain a permanent polarization in the absence of an applied magnetic field. Superparamagnetic particles are thus not useful for magnetic memories, but they are interesting and practical in other ways, for example in ferrofluids, magnetic resonance imaging (MRI), and some emerging medical diagnostic and therapeutic applications.



A ferrofluid containing superparamagnetic Fe_3O_4 nanoparticles, which are coated with oleic acid and suspended in oil, in the field of a strong permanent magnet.

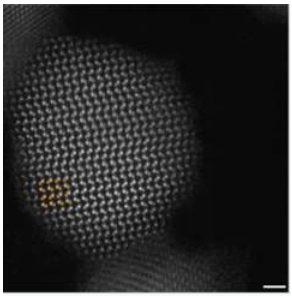
In these three illustrative examples (involving light emission, electronic conduction, and magnetic behavior), the transition to new properties involves a crossover in which the characteristic energy of the system is comparable to the thermal energy kT. It just so happens that for many physical phenomena, this crossover occurs on the length scale of nanometers.

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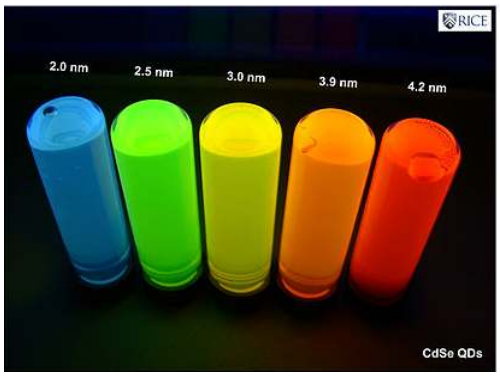
5.12.3: Semiconductor Quantum Dots

One of the most fascinating and well-studied mesoscopic effects occurs with semiconductor particles of various shapes when one or more of their dimensions is in the range of a few nanometers. These so-called "quantum dots" (0D), "quantum rods" (1D) and "nanosheets" (2D) acquire striking new electronic and optical properties.



Atomic resolution image of a CdSe nanoparticle.

The synthesis of semiconductor quantum dots, which is discussed in more detail below, is sufficiently well controlled to give essentially perfect crystals of a few thousand atoms, something that is statistically impossible in a macroscopic crystal. An image of such a crystal is shown at the right. In the synthesis, these crystals can be capped with an epitaxial layer of ligands or by a shell of a wider bandgap semiconductor (such as ZnS in the case of CdSe), so that the inner core is effectively a quantum well. Electron-hole pairs formed by excitation of the core semiconductor are confined there and cannot reach the external surface of the particle, where they might otherwise be trapped and recombine thermally. Consequently, the quantum yield for bandgap emission of semiconductor quantum dots is typically high, giving rise to the bright emission colors shown at the right for CdSe particles of different sizes. Because of their strong and narrow emission bands, quantum dots are of interest as luminescent tags for biological imaging applications, and also as light absorbers and emitters in solar cells and LEDs.



Emission colors of CdSe nanoparticles of different sizes. Smaller particles emit blue light because the exciton energy increases as the size decreases.

The size-dependence of the emission color comes primarily from a particle-in-a-box effect. The electron and hole that are created when the quantum dot absorbs light are bound together as an **exciton** by the confines of the "box". Louis Brus used first-order perturbation theory to determine that the bandgap of a semiconductor quantum dot is given approximately by:[4]

$$E_{gap} = E_{gap,bulk} + \frac{h^2}{8\mu R^2} - \frac{1.8e^2}{4R\pi\varepsilon\varepsilon_0} + \ldots \qquad (5.12.3.1)$$

where R is the particle radius, μ is the electron-hole reduced mass ($1/\mu = 1/m_e^* + 1/m_h^*$), m_e^* and m_h^* are the electron and hole effective masses, and ε is the dielectric constant of the semiconductor. In this equation, the first term after the bulk bandgap is the kinetic energy due to confinement of the exciton, and the second term represents the electrostatic attractive energy between the

confined electron and hole. Because the energy is a function of R^2, it can be widely tuned across the visible spectrum by changing the size of the quantum dot.

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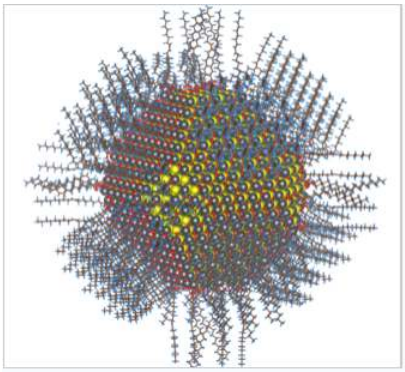
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5.12.4: Synthesis of Semiconductor Nanocrystals

Early work on the quantum size effect in semiconductor nanoparticles used simple metathesis reactions in the synthesis. For example, CdSe and PbS can be precipitated at ambient temperature by the reactions:

$$CdCl_{2\,(aq)} + H_2Se_{(g)} = CdSe_{(s)} + 2\,HCl_{(aq)}$$

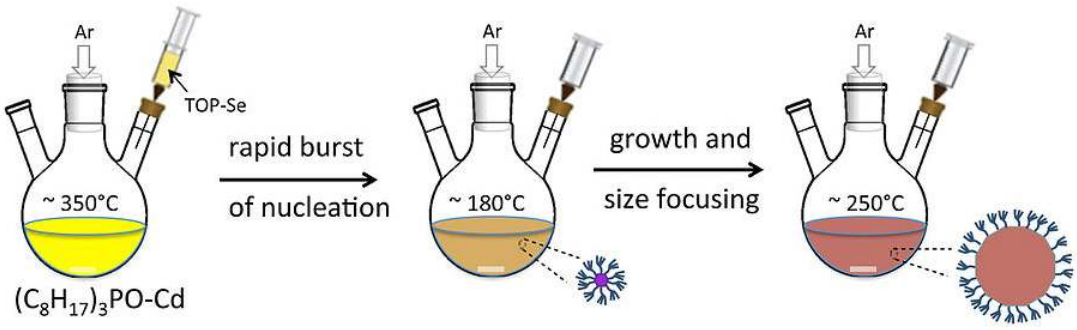
$$Pb(NO_3)_2 + H_2S_{(g)} = PbS_{(s)} + 2\,HNO_{3\,(aq)}$$



Complete atomistic model of a 5 nm diameter colloidal lead sulfide nanoparticle with surface passivation by oleic acid, oleyl and hydroxyl groups.

The growth of the particles was restricted by carrying out these reactions in different matrices, such as in polymer films or the silicate cages of zeolites, and capping ligands were also sometimes used to limit particle growth. While these reactions did produce nanoparticles, in general a broad distribution of particle sizes was obtained. The particles were also unstable to **Ostwald ripening** - in which large particles grow at the expense of smaller ones in order to minimize the total surface energy - because of the reversibility of the acid-forming synthetic reactions in aqueous media. The lack of good samples prevented detailed studies and the development of applications for semiconductor quantum dots.

A very important development in nanoparticle synthesis came in the early 1990's, when Murray, Norris, and Bawendi introduced the first non-aqueous, controlled growth process for II-VI semiconductor quantum dots.[5] The keys to this synthesis were (1) to use non-aqueous solvents and capping ligands to stabilize the products against ripening, (2) to carry out the reaction at high temperature to ensure good crystallinity, and (3) to separate the steps of particle **nucleation** and **growth**, and thereby obtain particles of uniform size. This procedure is illustrated below:

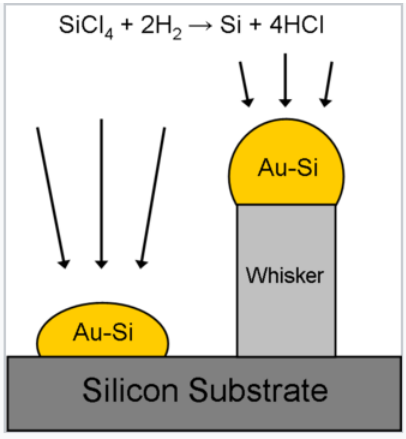


The synthesis is carried out in a coordinating, high boiling solvent that is a mixture of trioctylphosphine (**TOP**) and trioctylphosphine oxide (**TOPO**). In early experiments, organometallic cadmium compounds such as diethylcadmium were used as the metal source, but it was later found that these highly toxic and pyrophoric compounds could be replaced by CdO. At the start of the reaction, a selenium source, typically bis(trimethylsilyl)selenium, $[(CH_3)_3Si]_2Se$, dissolved in TOP is rapidly injected into the hot (350 °C) reaction mixture. The reaction causes a rapid burst of nanoparticle nucleation, but the temperature also drops as the cold solvent is injected and so the nucleation event ends quickly. The cooled solution now contains nanocrystal seeds. It is supersaturated in TOPO-Cd and TOP-Se, but particle growth proceeds slowly until the solution is heated again to the growth

temperature, ca. 250°C. Particle growth and **size-focusing** occurs because small particles require less added material to grow by an amount ΔR than larger particles. This is because the volume of an added shell around a spherical seed is $4\pi R^2\Delta R$, so for larger R, ΔR is smaller. Very narrow particle size distributions can be obtained under conditions of high supersaturation, where the rate of nanoparticle growth is fast relative to particle dissolution and Ostwald ripening.[6] The size distribution can then be narrowed further by adding a non-solvent such as hexane to the cooled reaction mixture. The largest particles precipitate first, followed by smaller particles. Because the nanoparticles are capped with a ligand shell of TOP, they can be re-suspended in organic solvents once they are size-separated.

The high temperature synthesis of semiconductor quantum dots has been applied to a broad variety of materials including II-VI, III-V, and IV-VI semiconductors. Monodisperse nanoparticles of **controlled shapes** can be made by variants of this method. For example, it is possible to adjust the conditions so that CdSe nucleates in the zincblende polymorph as tetrahedrally shaped seeds, and then grow polar wurtzite "arms" onto each triangular face, resulting in nanocrystal tetrapods. Numerous other nanocrystal shapes such as rods, arrowheads, rice (tapered rods), and polar structures such as Janus rods can be made by variants of this technique. These shape-control strategies often involve the use of ligands that adsorb specifically to certain crystal faces and inhibit their growth. For example, hexylphosphonic acid ligands adsorb selectively to Cd-rich crystal faces and thus lead to the growth of prismatic wurtzite-phase CdSe nanocrytals.

A second widely used method of semiconductor nanocrystal synthesis involves growth from molecular precursors and molten metal droplets, as shown in the figure at the right. The **vapor-liquid-solid (VLS)** and related **solution-liquid-solid (SLS)** growth processes rely on the fact that semiconductors such as Si, Ge, GaAs, InP, and others are soluble at high temperatures in liquid metals such as Au and Cu. The catalytic reduction of a molecule such as silicon tetrachloride ($SiCl_4$) at the surface of a gold nanocrystal liberates HCl gas and creates a solid solution of Si in Au. The presence of Si lowers the melting point of Au, and as more $SiCl_4$ reacts, a liquid **eutectic** droplet of the Si-Au alloy is formed. When this droplet becomes supersaturated in Si, a silicon nanocrystal nucleates and grows. This reaction can be performed on the surface of a macroscopic Si crystal, in which case nanocrystal "whiskers" grow from the surface, typically as single crystals and with an epitaxial orientation that is determined by the Si crystal face of the substrate. The diameter of the whiskers is controlled by the radius of the Au drops, which can be as small as a few nanometers and as large as several microns. Using this technique, "forests" of nanowires or microwires can be grown. Because the composition of the nanowire depends on the precursor being fed to the Au droplets, it is possible to make "totem pole" structures with varied compositions along the nanowire axis. Semiconductor shells can also be grown around the wires by **chemical vapor deposition (CVD)**. The VLS process can also be adapted to complex compositions for which no molecular precursor is available by using a laser to ablate the semiconductor from a solid target.



Epitaxial growth of silicon nanowires catalyzed by gold nanoparticles in the vapor-liquid-solid (VLS) process.

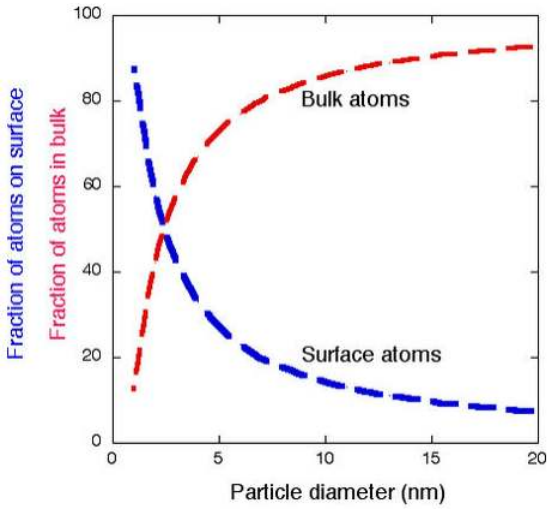
Semiconductor nanowires made by this method are the basis of extremely sensitive **biosensors**, in which a molecular binding event anywhere along the wire strongly affects its electrical conductivity.[7] Nanowire and microwire arrays are also being studied as **solar cell** and **lithium battery** materials, as well as nanoscale electronic and optoelectronic devices.

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5.12.5: Surface Energy

Nanoparticles have a substantial fraction of their atoms on the surface, as shown in the plot at the right.[8] This high surface area to volume ratio is an important factor in many of the physical properties of nanoparticles, such as their **melting point** and **vapor pressure**, and also in their **reactivity**. Heterogeneous catalysts, for example, are often based on nanoparticles because the catalytically reactive atoms are those that are on the surface of the particle.



The surface energy is always positive. A key quantity that is connected with the chemistry of all surfaces is the **surface energy**. This is the (thermodynamically unfavorable) energy of making "dangling bonds" at the surface. Atoms at the surface are under-coordinated, and because breaking bonds costs energy, surface atoms always have higher energy than atoms in the bulk. This happens regardless of whether the bonding is covalent (as in a metal), ionic (in a salt), or non-covalent (in a liquid such as water). We see this effect, for example, in water droplets that bead up on a waxy surface. The droplet contracts into a sphere (against the force of gravity that works to flatten it) in order to minimize the number of dangling hydrogen bonds at the surface.

In the case of metal or semiconductor particles, strong covalent bonds are broken at the surface. For example, a gold atom in bulk face-centered cubic Au has 12 nearest neighbors, but a gold atom on the (111) surface of the crystal (the most dense crystal plane of gold) has six nearest neighbors in-plane and three underneath, for a total of 9. We might expect the surface energy of this crystal face to be a little less (because the remaining bonds will become slightly stronger) than 3/12 = **1/4 of the bonding energy** of bulk Au, and this is in fact a fairly good rule of thumb for many materials. When translated into energy per unit area, the surface energy of metals and inorganic salts is usually in the range of 1-2 J/m^2.

Example: The sublimation energy of bulk gold is 334 kJ/mol, and the surface energy is 1.5 J/m^2. What percentage of the bulk bonding energy is lost by atoms at the (111) surface of a gold crystal?

To solve this problem, we need to know the surface area per Au atom. Gold has the face-centered cubic structure, and the unit cell edge length is 4.08 Å. From this we can determine that the Au-Au distance is 4.08/1.414 = 2.88 Å. In a hexagonal array of gold atoms with this interatomic spacing, the surface area per atom is (2.88 Å)^2 x 0.866 = 7.2 Å^2. Multiplying by Avogadro's number, we find that the area per mole of Au surface atoms on the (111) crystal face is **4.3 x 10^4 m^2.**

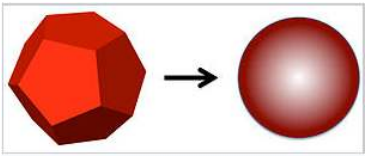
Now we multiply this area by the surface energy:

$(\mathbf{4.3 \times 10^4 \frac{m^2}{mol}}) \times (1.5 \frac{J}{mol}) \times (\frac{1kJ}{1000J}) = \mathbf{+65kJ}$ per mole of Au surface atoms.

$\frac{65kJ}{334kJ} \times 100\% = \mathbf{19\%}$ of the bulk bonding energy is lost by atoms at the surface.

It is clear from this example that the surface energy of nanoparticles can have a major effect on their physical properties, since a large fraction of the atoms in a nanoparticle are on the surface. A good example of this is the dramatic depression of the **melting point**.

Solid nanocrystals are in general faceted, whereas liquid droplets made by melting nanocrystals adopt a spherical shape to minimize the surface area.



A faceted solid nanocrystal melts into a spherical droplet in order to minimize its surface energy.

Let's consider melting a silver nanocrystal that is 2 nm in diameter, meaning that about 1/2 of the atoms are on the surface. The spherical liquid droplet has lower surface area than the faceted crystal. For example, a cube has 1.24 times the surface area of a sphere of the same volume. If the decrease in surface area is about 20% upon melting, and the surface energy is about 1/4 of the bulk bonding energy of the atoms, then for a 2 nm diameter nanocrystal we would estimate that:

$$\begin{aligned}\Delta H^o_{fusion} &\approx \Delta H^o_{fusion,\ bulk} - (\frac{1}{2})(0.25)(\frac{1}{4})\Delta H^o_{vap} \\ &= \Delta H^o_{fusion,\ bulk} - 0.025\Delta H^o_{vap,\ bulk}\end{aligned} \tag{5.12.5.1}$$

where $\Delta H°_{vap,\ bulk}$, the heat of vaporization, is the total bonding energy of atoms in a bulk crystal. For silver, $\Delta H°_{fusion,\ bulk}$ = 11.3 kJ/mol and $\Delta H°_{vap,\ bulk}$ = 250 kJ/mol. From this we can calculate the heat of fusion of a 2 nm Ag nanocrystal:

$$\Delta H^o_{fusion} \approx 11.3 - (0.025)(25) = 5.1 \frac{kJ}{mol} \tag{5.12.5.2}$$

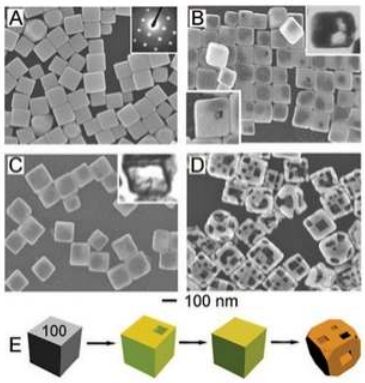
The melting point of bulk silver is 962 °C = 1235 K. Assuming that the entropy of fusion is the same in the bulk and in the nanocrystal, the melting point of the nanocrystal should be $1234K \times (\frac{5.1}{11.3}) = 557K = 284°C$, a drop of almost 700 degrees from the bulk value. Experimentally, the melting point of a 2 nm diameter silver nanocrystal drops about **800 degrees below that of the bulk,** to 127 °C.[9] This is a whopping big change in the melting point, which is in reasonable agreement with our rough estimate.

The same effect - energetic destabilization of the surface atoms relative to bulk atoms - results in the **lower boiling point**, **higher vapor pressure**, **higher solubility**, and **higher reactivity** of nanocrystals relative to microcrystals (or larger crystals) of the same material.

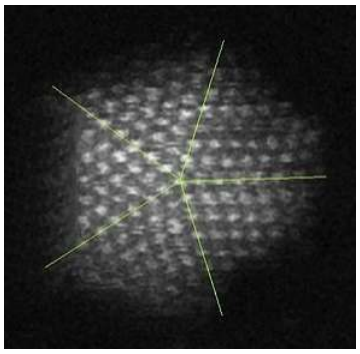
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5.12.6: Nanoscale Metal Particles



Nanoscale metal particles have been the subject of intense research over the past 20 years, especially because of their unusual **optical**, **magnetic**, and **catalytic** properties. The synthesis of metal nanocrystals in various shapes has become increasingly sophisticated and rational, like the synthesis of semiconductor nanocrystals described above. By controlling the separate phases of nucleation and growth, and by using ligands that cap specific crystal faces during growth, it is possible to make metal nanocrystals of uniform size in a variety of interesting and useful shapes including cubes, truncated cubes, octahedra, triangular prisms, and high aspect ratio rods. By exploiting displacement reactions that replace one metal with another, complex hollow shapes such as nanocages (as shown at the left) can be made starting with other shapes. In this case, solid silver nanocubes are transformed to gold nanocages.



Five-fold twinning in a gold nanoparticle

The interesting optical properties of nanocrystalline Au, Ag, Cu, and a number of other metals, derive from the collective oscillation of their valence electrons, a phenomenon known as **plasmon resonance**. Remember that in these metals, the electron mean free path is long (about 100 times larger than the size of the atoms), so the valence electrons feel only the average positive charge of the atomic cores as they zoom around the crystal. Light impinging on the metal acts as an oscillating electric field, pushing and pulling on the valence electrons at the characteristic frequency of the light wave. The situation is very much like a pendulum or a weight on a spring. The electrons, pushed away from their equilibrium positions, feel a restoring force that is proportional to their displacement. Their motion can be described by **Hooke's Law**:

$$F = kx \tag{5.12.6.1}$$

where the spring constant k determines the "stiffness" of the spring. In the case of the plasmon resonance, k is proportional to the number density of valence electrons n, and the square of the electronic charge e:

$$k = \frac{ne^2}{\varepsilon_0} \tag{5.12.6.2}$$

The **resonant frequency** of the plasma oscillation is given by:

$$\omega_p = (\frac{k}{m})^{\frac{1}{2}} = (\frac{ne^2}{m_e \varepsilon_0}^{\frac{1}{2}} \tag{5.12.6.3}$$

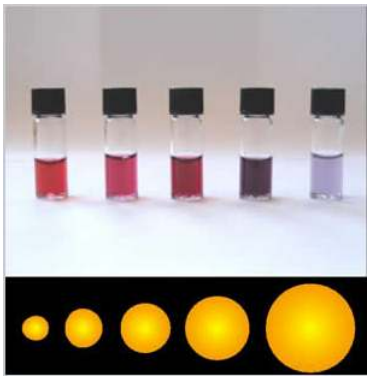
where m_e is the electron mass. For most metals, the plasmon resonance is in the ultraviolet part of the spectrum, but for a few metals like Au, Ag, and Cu it is in the visible.



The Lycurgus cup (4th century Roman glass) derives its unique coloration from noble metal nanoparticles. The cup is red in transmitted light and green in scattered (reflected) light.

For metal particles that are much smaller than the wavelength of light, this effect is called the **localized surface plasmon resonance**, or LSPR. There are three important consequences of the LSPR effect:

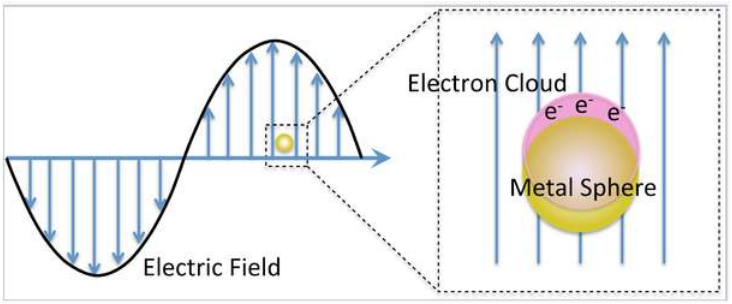
- The **local electric field** of the incoming light wave is greatly **enhanced** at the particle surface. This gives rise to huge enhancement factors in optical processes such as **Raman scattering** and **fluorescence**. Thus, certain analytical spectroscopic techniques are greatly enhanced by LSPR.
- Near the plasmon resonance frequency, metal nanocrystals **absorb** and **scatter light** very strongly. This makes them brightly reflective, and the strong light absorption can be exploited for light-induced local heating. These properties are being applied in medical diagnostics and therapy, e.g., for detection and photothermal destruction of cancer cells. By adjusting the size and shape of the gold nanoparticles, which are more stable than Ag and Cu in biological media, the plasmon frequency can be tuned to the tissue-transparent near-IR region of the spectrum between 700 and 900 nm. Small quantities of plasmonic Ag and Au particles also make brightly colored and strongly scattering pigments, e.g. in stained glass as shown above at the right.
- The plasmon frequency is sensitive to the refractive index of the particle's surroundings, i.e., its chemical environment. This makes metal nanoparticles of special interest for **sensing and biosensing** applications.



The colors of plasmonic gold nanoparticles depend on their size and shape.

Theory of light scattering and absorption by metal nanoparticles

The valence electrons in metal nanoparticles oscillate in the electric field of a light wave. While the nature of these oscillations is somewhat complex in metal particles that are non-spherical, the theory for spherical particles is relatively simple and in fact was worked out over 100 years ago by German physicist Gustav Mie.



Mie considered the interaction of a spherical particle with a **uniform electric field, E,** oscillating at angular frequency ω (= 2π f). This is a good approximation when the particle diameter is much smaller than the wavelength of light, as shown on the left. The particle is embedded in a uniform, insulating material (e.g. a solvent) that has a dielectric constant ε_{diel}. For insulators, ε_{diel} is a positive real number.

The dielectric constant ε of a metal is actually a complex number:

$$\varepsilon = \varepsilon' + i\varepsilon'' \tag{5.12.6.4}$$

Here the real part, ε', is related to the refraction of light, and the imaginary part, ε", is related to light absorption. Both ε' and ε" are dependent on the frequency of the light. For metals near the plasmon resonance frequency, ε' is typically a *negative number.*

The **cross-section for absorption** of the light wave by the particle is:

$$\sigma_{absorption} = \frac{9\omega}{c}\epsilon_{diel}^{\frac{3}{2}} V \frac{\epsilon''_{metal}}{(\epsilon'_{metal} + 2\epsilon_{diel})^2 + (\epsilon''_{metal})^2} \tag{5.12.6.5}$$

and the **cross-section for scattering** is:

$$\sigma_{scattering} = \frac{3}{2\pi}\left(\frac{\omega^4}{c}\right)\epsilon_{diel}^2 V^2 \frac{(\epsilon'_{metal} - \epsilon_{diel})^2 + (\epsilon''_{metal})^2}{(\epsilon'_{metal} + 2\epsilon_{diel})^2 + (\epsilon''_{metal})^2} \tag{5.12.6.6}$$

The sum of these two is the **cross-section for extinction**:

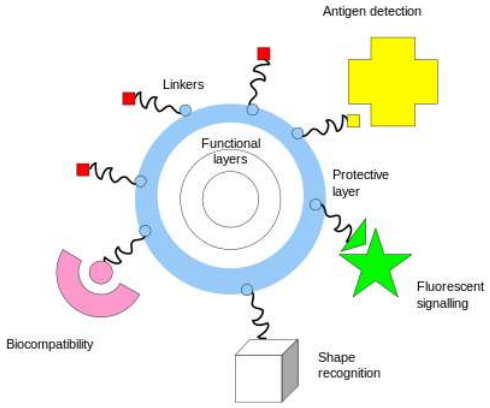
$$\sigma_{extinction} = \sigma_{absorption} + \sigma_{scattering} \tag{5.12.6.7}$$

These cross-sections become large when the (ε'_{metal} + 2ε_{diel}) term in the denominator becomes small. This occurs when

$$\epsilon'_{metal} \simeq -2\epsilon_{diel} \tag{5.12.6.8}$$

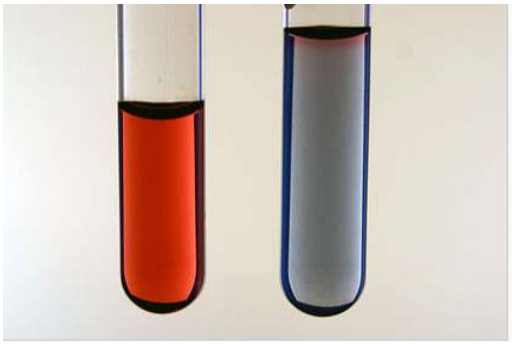
For 15 nm diameter gold nanoparticles in water, this happens at about 580 nm, resulting in the characteristic wine-red color of colloidal gold solutions. Changing the solution environment (e.g., by adsorbing a molecule onto the gold surface) changes ε_{diel} and thus alters the color slightly.

It is important to note that the cross-section for **scattering** is proportional to the **square of the volume** of the particle, V^2, whereas the absorption is proportional to V. This means that very small gold particles (< 5 nm) are strongly absorbing but not strongly scattering. Larger particles (>30 nm) scatter light very strongly. Depending on the application, therefore, we choose larger or smaller particles.



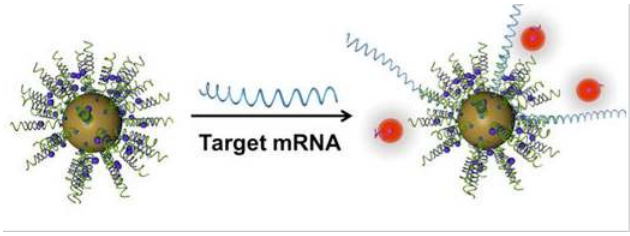
One of the key complementary properties of noble metal nanoparticles that is important to their use in biomedicine is the ease with which they can be **covalently conjugated** with polymers or small molecules, typically via thiol or amine bonds at their surface. This imparts biological recognition properties to the particles that enables them to bind to specific biomolecular targets. The figure at the left illustrates some of the functionality that can be imparted to nanoparticles through surface functionalization.

Functionalization of gold nanoparticles with thiol-terminated single-stranded DNA was the basis of one of the first nanoparticle sensors, developed by the Mirkin group at Northwestern University. **DNA-coated nanoparticles** have the characterstic wine-red plasmonic color of spherical nano-gold. However, when these particles are linked together by a complementary DNA strand, the resonance frequency shifs, resulting in a blue color. This color change, illustrated in the figure at the right, provides a "litmus test" for the presence of the target DNA sequence.[10] "Melting" of the DNA - heating it to the temperature at which double stranded DNA dissociates to make single strands - reverses the color change. The DNA hybridization/melting transition is highly **cooperative** because of the aggregation of many gold particles, so the transition temperature is very sharp. With proper temperature control, the color change can be sensitive to a **single base mismatch** in the target DNA that is detected by this method.



Aggregation of Au nanoparticles (in this case by adding salt to a colloidal solution) causes a color change from wine red (left) to blue (right). Photo credit: George Lisensky, Beloit College

Subsequent research has developed sophisticated diagnostic and therapeutic ("theranostic") applications for these **spherical nucleic acid**[11] particles. These particles easily penetrate cell membranes and can report on the chemistry happening inside living cells.



General schematic of nanoflare-based detection.

An important property of gold nanoparticles in these applications is their ability to **quench** the **fluorescence** of reporter molecules that are near their surface. Nucleic acid strands that contain a hairpin loop can position fluorescent molecules near the gold surface, where their fluorescence is turned off by nanoparticle quenching. Hybridization of these sequences to target RNA or DNA causes the fluorescence to turn on by moving the fluorescent molecule away from the nanoparticle surface. These so called "nanoflares" can thus signal the up- or down-regulation of specific genes inside cells. Nanoflares are the basis of the Verigene System, developed and commercialized by Nanosphere, Inc. to detect markers for infectious diseases and cancers.

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5.12.7: Applications of Nanomaterials

PowerPoint slides for this section

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5.12.8: Discussion Questions

- Explain how separating the nucleation and growth steps leads to nanoparticles of uniform size.
- A recent paper by Delia Milliron and coworkers (*Nature*, 2013, *500*, 323–326, doi:10.1038/nature12398) describes plasmonic indium-tin-oxide (ITO) nanoparticles that can control the infrared transparency of windows. Explain how the plasmon resonance wavelength of the nanoparticles can be tuned by electrochemical doping, and how the invention could save some of the energy used to heat and cool buildings.

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5.12.9: Problems

1. Consider a spherical gold nanoparticle that contains 500 atoms. If the diameter of an atom is approximately 3 Å, what fraction of the gold atoms in the particle are on the surface?

2. Now consider small droplets of mercury that contains 500 atoms. Mercury atoms are also about 3 Å in diameter. The heat of vaporization of bulk mercury is 64.0 kJ/mol, and the vapor pressure of mercury is 0.00185 torr = 2.43 x 10^{-6} atm. The surface tension of mercury (γ_{Hg}) is 0.518 N/m, and the surface excess energy can be calculated as $\gamma_{Hg}A$, where A is the surface area. Using this information and the Clausius-Clapyron equation ($P = const \cdot exp(-\Delta H_{vap}/RT)$), calculate the vapor pressure of these small droplets of mercury.

3. James Heath and coworkers (Phys. Rev. Lett. 1995, 75, 3466) have observed Ostwald ripening in thin films of gold nanoparticles at room temperature. Starting with an uneven distribution of particle sizes, they find that the large particles grow at the expense of smaller ones. Can you explain this observation, based on your answers to problems (1) and (2)?

4. The bandgap of bulk germanium is 0.67 eV. What bandgap would you expect for a 4 nm diameter Ge nanocrystal? Use the Brus formula,

$$\Delta E_{gap} \approx \frac{h^2}{8\mu R^2} - \frac{1.8e^2}{4R\pi\varepsilon\varepsilon_0} + \ldots \tag{5.12.9.1}$$

where R is the particle radius, ε_{Ge} = 16.2, h = 6.6 10^{-34} J s, 1 eV = 1.6 10^{-19} J, 1 J = 1 kg m^2/s^2. and $e^2/4\pi\varepsilon_0$ = 1.44 10^{-9} eV m. Assume that the electron-hole reduced mass μ is approximately 40% of the free electron mass, m_e = 9.1 10^{-31} kg.

5. Grecian Formula (a hair coloring product) until recently contained lead acetate, which reacts with the cysteine in hair to make PbS. In bulk form, PbS is a semiconductor with a band gap of 0.3 eV (1 eV = 1240 nm). The particles are initially very small but grow as more Grecian Formula is applied and reacts with cysteine. As the particles grow, they change progressively from colorless to yellow to black. Explain why the particles are initially colorless and why their color changes. (Grecian formula now uses Bi, which is less toxic than Pb, and works by the same mechanism)

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SECTION OVERVIEW

5.13: Bonding in Metals and Semicondoctors

5.13A: Electrical Conductivity and Resistivity

5.13B: Band Theory of Metals and Insulators

5.13C: The Fermi Level

5.13D: Band Theory of Semiconductors

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5.13A: Electrical Conductivity and Resistivity

Electrical resistivity and conductivity is an important property for materials. Different materials have different conductivity and resistivity. Electrical conductivity is based on electrical transport properties. These can be measured with multiple techniques by using a variety of instruments. If electricity easily flows through a material, that material has high conductivity. Some materials that have high conductivity include copper and aluminum. Electrical conductivity is the measure of how easily electricity flows through a material.

Conductivity vs Resistivity

Conductivity and resistivity are inversely proportional to each other. When conductivity is low, resistivity is high. When resistivity is low, conductivity is high. The equation is as follows:

$$\rho = \frac{1}{\sigma} \tag{5.13A.1}$$

where

- Resistivity is represented by ρ and is measured in **Ohm-meters** (Ωm),
- Conductivity is represented by σ and is measured in **Siemens** ($1/\Omega m$).

Since conductivity is the measure of how easily electricity flows, electrical resistivity measures how much a material resists the flow of electricity.

Electrical Transport Properties

Simply put, electricity is the movement of electrons through a material. As electrons move through a material, it comes into contact with atoms in the material. Collisions slow the electrons down. Each collision increases the resistivity of the material. The easier the electrons continue through a material, the fewer collisions that take place and the higher the conductivity.

When temperature increases, the conductivity of metals usually decreases, while the conductivity of semiconductors increases. This of course assumes that the material is homogenous, which is not always the case. You can calculate resistivity using the following equation

$$\frac{E}{J} = \rho \tag{5.13A.2}$$

As you already read, ρ is the symbol for resistivity. E is the electric field and has units of Volts per meter (V/m). J is the current density and has units of amps per meter squared (A/m2). The electric field is calculated by dividing the Voltage by the length, l, that voltage is applied.

$$E = \frac{V}{l} \tag{5.13A.3}$$

The current density is calculated by the equation below

$$J = \frac{I}{A} \tag{5.13A.4}$$

I is the current and is divided by the cross sectional area, A, over which the current flows.

Resistivity vs Resistance

Resistivity and resistance are two different things. Resistivity does not depend on size or shape. Resistance, however, does. You can calculate resistance with the equation below.

$$R = \frac{V}{I} \tag{5.13A.5}$$

R refers to resistance and is measured in Ω. V is the voltage and is measured in volts. I measures the current and its unit is amps (A).

References

1. Electrical Conductivity and Resistivity, Heaney, Michael, Electrical Measurement, Signal Processing, and Displays. Jul 2003
2. Levy, Peter M., and Shufeng Zhang. "Electrical Conductivity of Magnetic Multilayered Structures." *Physical Review Letters* 65.13 (1990): 1643-646. Print.

Problems

1. What is the current density of a material with a resistivity of 12.Ωm and an electric field of 64.V/m?
2. If the voltage of 6V is passed through a substance with a radius of 2m and a length of 3m, what is the electric field?
3. What is the electric field of a material when the current is equal to 25A, the resistance is measured to be 78Ω, the current density equals 24A/m2, and the length the current flows is 100m?
4. A material has a voltage of 150V and width of 24m. The material also has a current of 62A and travels a distance of 5m. What is the conductivity?
5. A metal originally has an electron colliding with every fifth atom and increases from a temperature of 6K to 100K. A semiconductor originally has an electron colliding with every fifth atom and increases from a temperature of 6K to 100K. What material will have a greater resistivity? Why?

Answers to Problems:

1. $E/J = \rho$ ---> $J=E/\rho$ = 64V/m /12Ωm = 5.33A/m^2

2. $E=V/l$ = 6V/3m = 2V/m

3. $E=V/l$

$V=IR$ ---> $E=IR/l$ = 25A x 78Ω/100m = 19.5V/m

4. $E/J = \rho$

$E=V/l$

$J=I/A$ ---> $\rho=(V/l)/(I/A)$ = (150V/5m)/(62A/(24m x 5m) = 58Ωm

$\rho = 1/\sigma$ ---> $1/\rho = \sigma$ = 1/58Ωm

5. The material that has the greatest resistivity is the metal because as temperature increases metals are more likely to increase in resistivity and semiconductors usually decrease in resistivity as temperature increase.

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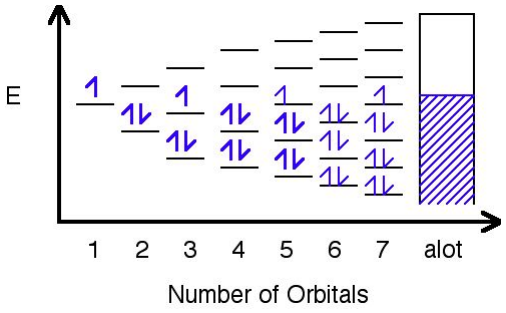
- Michael Ford (UCD) and Alexandra Christman (UCD)

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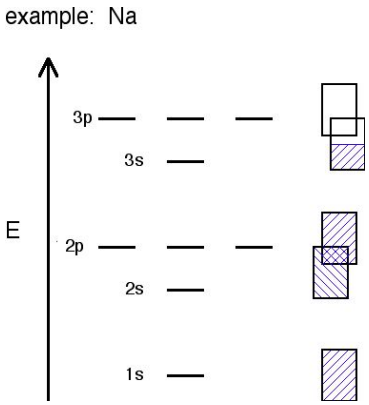
5.13B: Band Theory of Metals and Insulators

Band Theory was developed with some help from the knowledge gained during the quantum revolution in science. In 1928, Felix Bloch had the idea to take the quantum theory and apply it to solids. In 1927, Walter Heitler and Fritz London discovered bands- very closely spaced orbitals with not much difference in energy.



In this image, orbitals are represented by the black horizontal lines, and they are being filled with an increasing number of electrons as their amount increases. Eventually, as more orbitals are added, the space in between them decreases to hardly anything, and as a result, a band is formed where the orbitals have been filled.

Different metals will produce different combinations of filled and half filled bands.



Sodium's bands are shown with the rectangles. Filled bands are colored in blue. As you can see, bands may overlap each other (the bands are shown askew to be able to tell the difference between different bands). The lowest unoccupied band is called the conduction band, and the highest occupied band is called the valence band.

Bands will follow a trend as you go across a period:

- In Na, the 3s band is 1/2 full.
- In Mg, the 3s band is full.
- In Al, the 3s band is full and the 3p ban is 1/2 full... and so on.

The probability of finding an electron in the conduction band is shown by the equation:

$$P = \frac{1}{e^{\Delta E/RT} + 1} \tag{5.13B.1}$$

The ΔE in the equation stands for the change in energy or energy gap. T stands for the temperature, and R is a bonding constant. That equation and this table below show how the bigger the difference in energy is, or gap, between the valence band and the conduction band, the less likely electrons are to be found in the conduction band. This is because they cannot be excited enough to make the jump up to the conduction band.

ELEMENT	ΔE(kJ/mol) of energy gap	# of electrons/cm^3 in conduction band	insulator, or conductor?
C (diamond)	524 (big band gap)	10^{-27}	insulator
Si	117 (smaller band gap, but not a full conductor)	10^{9}	semiconductor
Ge	66 (smaller band gap, but still not a full conductor)	10^{13}	semiconductor

Conductors, Insulators and Semiconductors

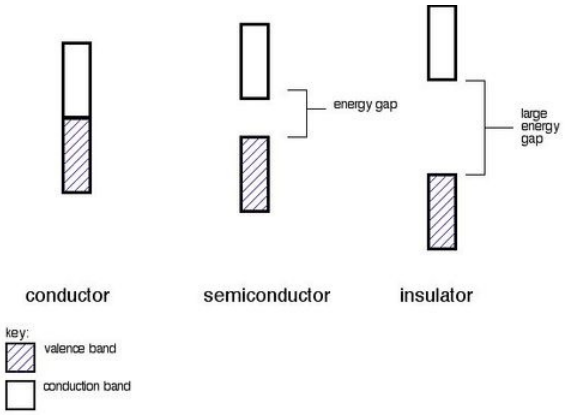


Diagram comparing conductor, semiconductor, and insulator energy bands. Conductor has overlapping bands; semiconductor has small gap; insulator has large gap. Key: valence and conduction bands.

A. Conductors

Metals are conductors. There is no band gap between their valence and conduction bands, since they overlap. There is a continuous availability of electrons in these closely spaced orbitals.

B. Insulators

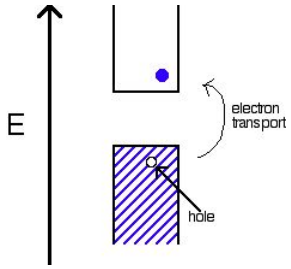
In insulators, the band gap between the valence band the the conduction band is so large that electrons cannot make the energy jump from the valence band to the conduction band.

C. Semiconductors

Semiconductors have a small energy gap between the valence band and the conduction band. Electrons can make the jump up to the conduction band, but not with the same ease as they do in conductors. There are two different kinds of semiconductors: **intrinsic** and **extrinsic**.

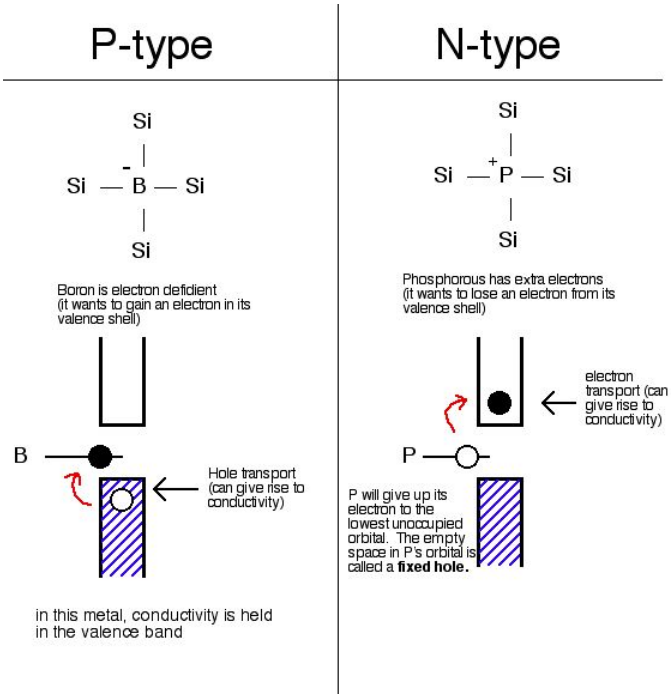
i. Intrinsic Semiconductors

An intrinsic semiconductor is a semiconductor in its pure state. For every electron that jumps into the conduction band, the missing electron will generate a hole that can move freely in the valence band. The number of holes will equal the number of electrons that have jumped.



ii. Extrinsic Semiconductors

In extrinsic semiconductors, the band gap is controlled by purposefully adding small impurities to the material. This process is called **doping**. Doping, or adding impurities to the lattice can change the electrical conductivity of the lattice and therefore vary the efficiency of the semiconductor. In extrinsic semiconductors, the number of holes will not equal the number of electrons jumped. There are two different kinds of extrinsic semiconductors, p-type (positive charge doped) and n-type (negative charge doped).



? Exercise 5.13B.1

How do you distinguish between a valence band and a conduction band?

Answer

The valence band is the highest band with electrons in it, and the conduction band is the highest band with no electrons in it.

? Exercise 5.13B.2

Is the energy gap between an insulator smaller or larger than the energy gap between a semiconductor?

Answer

Larger

Exercise 5.13B.3

What two methods bring conductivity to semiconductors?

Answer

Electron transport and hole transport

Exercise 5.13B.4

You are more likely to find electrons in a conduction band if the energy gap is smaller/larger?

Answer

Smaller

References

1. Petrucci, Harwood, Herring, Madura. GENERAL CHEMISTRY Principles and Modern Applications 9th Edition. Macmillan Publishing Co: New Jersey. 1989.
2. Moore, John T. Chemistry Made Simple. Random House Inc: New York. 2004.

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5.13C: The Fermi Level

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Fermi level

The Fermi Level is the energy level which is occupied by the electron orbital at temperature equals 0 K. The level of occupancy determines the conductivity of different materials. For solid materials such as metals, the orbital occupancy can be calculated by making an approximation based on the crystalline structure. These orbitals, combined with the energy level, determine whether the material is an insulator, semi-conductor, or conductor. The orbitals are categorized according to its energy. The lower energy orbitals combine and form a band called the valence electron band, and the higher energy orbitals combine to form a band called the conduction band. There is a gap between the valence and conduction band called the energy gap; the larger the energy gap, the more energy it is required to transfer the electron from the valence band to the conduction band.

Energy Band Diagram

The diagram below is an example of an energy band diagram. The upper box represents the conduction band, the lower box represents the valence band, and the yellow is the occupancy level of electrons. The conductivity of a material can be determined by the energy diagram. In order to conduct electricity, an electron must make a transition into another state since electrons cannot occupy the same quantum states. When the electron cannot make that transition, it will be not be able to conduct electricity. When the band is completely filled, the closest state an electron to transfer to will be the states in the conduction band, and that would require the electron to jump over the band gap, thus making it more difficult to conduct electricity. With this rule, it is easy to tell the difference between insulator, semi-conductor, and conductors. The energy band on the left side is an insulator because if an electron wants to go into a higher energy state, it will need to jump through that huge energy gap. Since it requires a large amount of energy to move the electron, the material will have a difficult time conducting electricity. The energy band in the middle is a semi-conductor because although the electrons have to jump across the energy gap, the energy gap is small. If an electron wants to make a transition, it will require very little energy since they are all int he same energy band. Thus, for the material in the middle, although it will have difficulty conducting electricity, it is not impossible. The energy

band in the right is a conductor. Although the valence band is filled just like the insulator and semi-conductor, the conduction band overlaps the valence band. If an electron wants to make a transition, it will require very little amount of energy. Which means the material on the right can conduct electricity very easily.

Fermi Level

The electrons that occupies the orbits are described by Fermi-Dirac distribution as the figure below, the distribution takes on the form of:

$$\frac{1}{1 + \exp[(E-u)/KT]} \quad (1)$$

http://upload.wikimedia.org/wikipedi...irac_distr.svg

Where E is the energy of the system, u is the fermi level, K is the Boltzmann constant, and T is the temperature. The Fermi-Dirac distribution accounts for the population level at different energies. The Fermi level is at $e/u = 1$ and $KT = u$. Whenever the system is at the Fermi level, the population n is equal to 1/2. The tail part in the exponential is very important for the conductivity of semi-conductors. If you can bring the Fermi level high enough, then part of the tail will go over to the conduction band. Thus, the electron will have an easier time making a

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transition to the conduction band and the conductivity will increase. The conductivity can also be affect by factors such as temperature and purity. From the distribution, the temperature has a direct effect on how the energy states are populated. When temperature increases the tail of the exponential gets longer and wider, thus making the conduction band level population more accessible. For Semi-conductor materials, having an access to the conduction band level means it can conduct electricity with energy, which means the conductivity of the material is increased. The purity also affects the Fermi level. Purity defects with atoms that have excess electrons would bring the Fermi level up, and making it easier for electrons to jump into the conduction band.

References

1. Kittel, Charles. Introduction to Solid State Physics. Eighth edition. New Jersey: John wiley & Sons, Inc, 2005.
2. Griffiths, Davis. Introduction to Quantum Mechanics. Second edition. New Jersey: Pearson Education, Inc, 2005.
3. Band energies.jpg

Problems

1. Besides the Fermi Level, what other factor determines the population in different energy levels?

answer: Temperature

2. What is the difference between a semi-conductor and an insulator?

answer: A semi-conductor has a smaller band gap and therefore, while more difficulty than a conductor, is able to conduct electricity if you put in enough energy.

3. What does the Fermi level determines?

answer: The Fermi level determines several factors. It determines the population at different energy levels. It also determines how easily can the material conductor electricity. As your Fermi level approaches your conduction band energy, it will be easier for the electrons from the valence band to travel to the conduction band.

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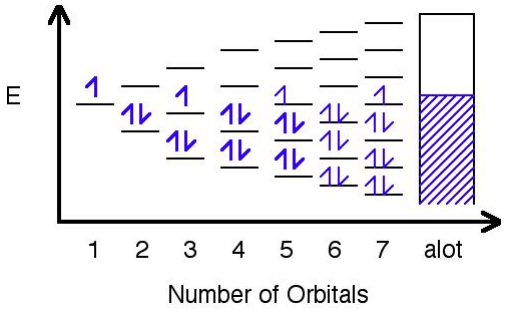
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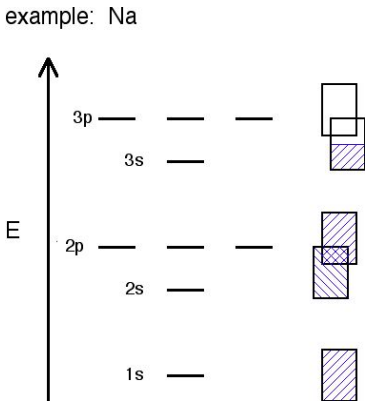
5.13D: Band Theory of Semiconductors

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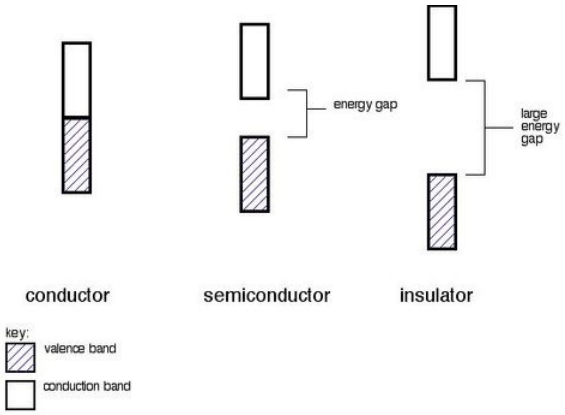


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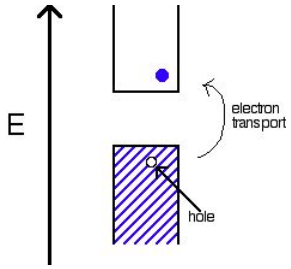
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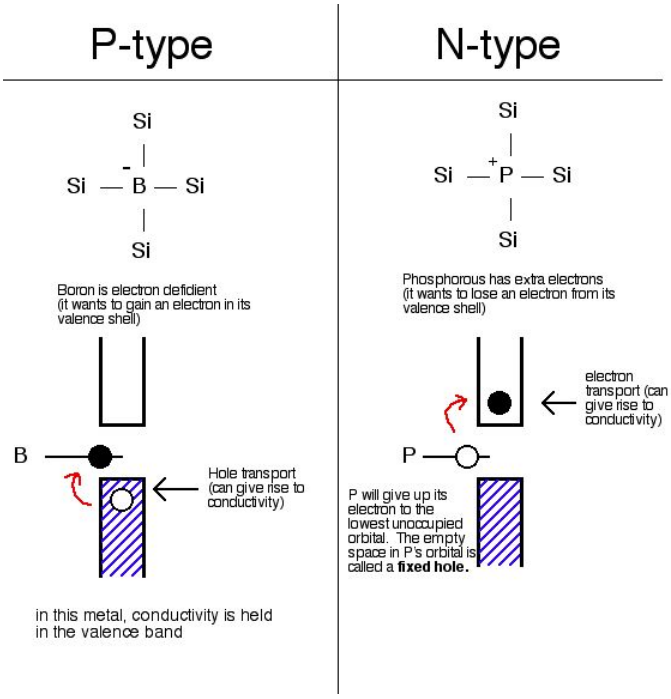
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? Exercise 5.13D.1

How do you distinguish between a valence band and a conduction band?

Answer

The valence band is the highest band with electrons in it, and the conduction band is the highest band with no electrons in it.

? Exercise 5.13D.2

Is the energy gap between an insulator smaller or larger than the energy gap between a semiconductor?

Answer

Larger

? Exercise 5.13D.3

What two methods bring conductivity to semiconductors?

Answer

Electron transport and hole transport

? Exercise 5.13D.4

You are more likely to find electrons in a conduction band if the energy gap is smaller/larger?

Answer

Smaller

References

1. Petrucci, Harwood, Herring, Madura. GENERAL CHEMISTRY Principles and Modern Applications 9th Edition. Macmillan Publishing Co: New Jersey. 1989.
2. Moore, John T. Chemistry Made Simple. Random House Inc: New York. 2004.

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5.14: Bonding in Metals

Bonding in metals and semiconductors can be described using band theory, in which a set of molecular orbitals is generated that extends throughout the solid. The primary learning objective of this Module is to describe the electrical properties of solid using band theory.

Band Theory

To explain the observed properties of metals, a more sophisticated approach is needed than the electron-sea model commonly described. The molecular orbital theory used to explain the delocalized π bonding in polyatomic ions and molecules such as NO_2^-, ozone, and 1,3-butadiene can be adapted to accommodate the much higher number of atomic orbitals that interact with one another simultaneously in metals.

In a 1 mol sample of a metal, there can be more than 10^{24} orbital interactions to consider. In our molecular orbital description of metals, however, we begin by considering a simple one-dimensional example: a linear arrangement of n metal atoms, each containing a single electron in an s orbital. We use this example to describe an approach to metallic bonding called band theory, which assumes that the valence orbitals of the atoms in a solid interact, generating a set of molecular orbitals that extend throughout the solid.

One-Dimensional Systems

If the distance between the metal atoms is short enough for the orbitals to interact, they produce bonding, antibonding, and nonbonding molecular orbitals. The left portion of Figure **5.14.1** shows the pattern of molecular orbitals that results from the interaction of ns orbitals as n increases from 2 to 5.

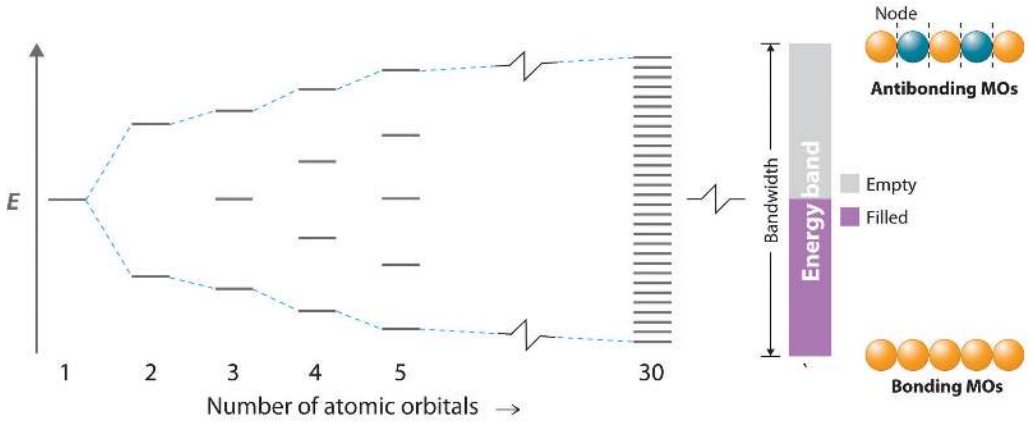


Figure **5.14.1**: The Molecular Orbital Energy-Level Diagram for a Linear Arrangement of n Atoms, Each of Which Contains a Singly Occupied s Orbital. As n becomes very large, the energy separation between adjacent levels becomes so small that a single continuous band of allowed energy levels results. The lowest-energy molecular orbital corresponds to positive overlap between all the atomic orbitals to give a totally bonding combination, whereas the highest-energy molecular orbital contains a node between each pair of atoms and is thus totally antibonding.

As we saw previously, the lowest-energy orbital is the completely bonding molecular orbital, whereas the highest-energy orbital is the completely antibonding molecular orbital. Molecular orbitals of intermediate energy have fewer nodes than the totally antibonding molecular orbital. The energy separation between adjacent orbitals decreases as the number of interacting orbitals increases. For n = 30, there are still discrete, well-resolved energy levels, but as n increases from 30 to a number close to Avogadro's number, the spacing between adjacent energy levels becomes almost infinitely small. The result is essentially a continuum of energy levels, as shown on the right in Figure **5.14.1**, each of which corresponds to a particular molecular orbital extending throughout the linear array of metal atoms. The levels that are lowest in energy correspond to mostly bonding combinations of atomic orbitals, those highest in energy correspond to mostly antibonding combinations, and those in the middle correspond to essentially nonbonding combinations.

The continuous set of allowed energy levels shown on the right in Figure **5.14.1** is called an energy band. The difference in energy between the highest and lowest energy levels is the bandwidth and is proportional to the strength of the interaction between orbitals

on adjacent atoms: the stronger the interaction, the larger the bandwidth. Because the band contains as many energy levels as molecular orbitals, and the number of molecular orbitals is the same as the number of interacting atomic orbitals, the band in Figure 5.14.1 contains n energy levels corresponding to the combining of s orbitals from n metal atoms. Each of the original s orbitals could contain a maximum of two electrons, so the band can accommodate a total of 2n electrons. Recall, however, that each of the metal atoms we started with contained only a single electron in each s orbital, so there are only n electrons to place in the band. Just as with atomic orbitals or molecular orbitals, the electrons occupy the lowest energy levels available. Consequently, only the lower half of the band is filled. This corresponds to filling all of the bonding molecular orbitals in the linear array of metal atoms and results in the strongest possible bonding.

Multidimensional Systems

The previous example was a one-dimensional array of atoms that had only s orbitals. To extrapolate to two- or three-dimensional systems and atoms with electrons in p and d orbitals is straightforward in principle, even though in practice the mathematics becomes more complex, and the resulting molecular orbitals are more difficult to visualize. The resulting energy-level diagrams are essentially the same as the diagram of the one-dimensional example in Figure 5.14.1, with the following exception: they contain as many bands as there are different types of interacting orbitals. Because different atomic orbitals interact differently, each band will have a different bandwidth and will be centered at a different energy, corresponding to the energy of the parent atomic orbital of an isolated atom.

Band Gap

Because the 1s, 2s, and 2p orbitals of a period 3 atom are filled core levels, they do not interact strongly with the corresponding orbitals on adjacent atoms. Hence they form rather narrow bands that are well separated in energy (Figure 5.14.2). These bands are completely filled (both the bonding and antibonding levels are completely populated), so they do not make a net contribution to bonding in the solid. The energy difference between the highest level of one band and the lowest level of the next is the band gap. It represents a set of forbidden energies that do not correspond to any allowed combinations of atomic orbitals.

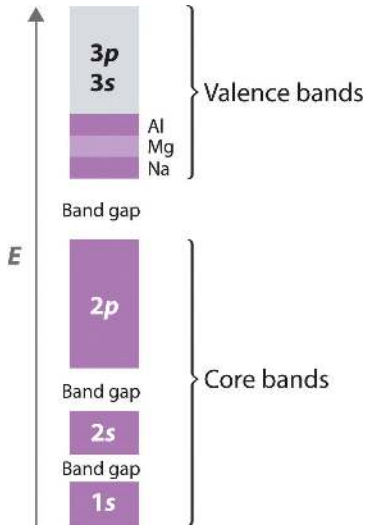


Figure 5.14.2: The Band Structures of the Period 3 Metals Na, Mg, and Al. The 3s and 3p valence bands overlap in energy to form a continuous set of energy levels that can hold a maximum of eight electrons per atom.

Because they extend farther from the nucleus, the valence orbitals of adjacent atoms (3s and 3p in Figure 5.14.2) interact much more strongly with one another than do the filled core levels; as a result, the valence bands have a larger bandwidth. In fact, the bands derived from the 3s and 3p atomic orbitals are wider than the energy gap between them, so the result is overlapping bands. These have molecular orbitals derived from two or more valence orbitals with similar energies. As the valence band is filled with one, two, or three electrons per atom for Na, Mg, and Al, respectively, the combined band that arises from the overlap of the 3s and 3p bands is also filling up; it has a total capacity of eight electrons per atom (two electrons for each 3s orbital and six electrons for each set of 3p orbitals). With Na, therefore, which has one valence electron, the combined valence band is one-eighth filled; with Mg (two valence electrons), it is one-fourth filled; and with Al, it is three-eighths filled, as indicated in Figure 5.14.2. The partially

filled valence band is absolutely crucial for explaining metallic behavior because it guarantees that there are unoccupied energy levels at an infinitesimally small energy above the highest occupied level.

Band theory can explain virtually all the properties of metals. Metals conduct electricity, for example, because only a very small amount of energy is required to excite an electron from a filled level to an empty one, where it is free to migrate rapidly throughout the crystal in response to an applied electric field. Similarly, metals have high heat capacities (as you no doubt remember from the last time a doctor or a nurse placed a stethoscope on your skin) because the electrons in the valence band can absorb thermal energy by being excited to the low-lying empty energy levels. Finally, metals are lustrous because light of various wavelengths can be absorbed, causing the valence electrons to be excited into any of the empty energy levels above the highest occupied level. When the electrons decay back to low-lying empty levels, they emit light of different wavelengths. Because electrons can be excited from many different filled levels in a metallic solid and can then decay back to any of many empty levels, light of varying wavelengths is absorbed and reemitted, which results in the characteristic shiny appearance that we associate with metals.

Requirements for Metallic Behavior

For a solid to exhibit metallic behavior,

- it must have a set of delocalized orbitals forming a band of allowed energy levels, and
- the resulting band must be partially filled (10%–90%) with electrons.

Without a set of delocalized orbitals, there is no pathway by which electrons can move through the solid.

Band theory explains the correlation between the valence electron configuration of a metal and the strength of metallic bonding. The valence electrons of transition metals occupy either their valence ns, (n − 1)d, and np orbitals (with a total capacity of 18 electrons per metal atom) or their ns and (n − 1)d orbitals (a total capacity of 12 electrons per metal atom). These atomic orbitals are close enough in energy that the derived bands overlap, so the valence electrons are not confined to a specific orbital. Metals with 6 to 9 valence electrons (which correspond to groups 6–9) are those most likely to fill the valence bands approximately halfway. Those electrons therefore occupy the highest possible number of bonding levels, while the number of antibonding levels occupied is minimal. Not coincidentally, the elements of these groups exhibit physical properties consistent with the presence of the strongest metallic bonding, such as very high melting points.

Insulators

In contrast to metals, electrical insulators are materials that conduct electricity poorly because their valence bands are full. The energy gap between the highest filled levels and the lowest empty levels is so large that the empty levels are inaccessible: thermal energy cannot excite an electron from a filled level to an empty one. The valence-band structure of diamond, for example, is shown in Figure **5.14.3*a***. Because diamond has only 4 bonded neighbors rather than the 6 to 12 typical of metals, the carbon 2s and 2p orbitals combine to form two bands in the solid, with the one at lower energy representing bonding molecular orbitals and the one at higher energy representing antibonding molecular orbitals. Each band can accommodate four electrons per atom, so only the lower band is occupied. Because the energy gap between the filled band and the empty band is very large (530 kJ/mol), at normal temperatures thermal energy cannot excite electrons from the filled level into the empty band. Thus there is no pathway by which electrons can move through the solid, so diamond has one of the lowest electrical conductivities known.

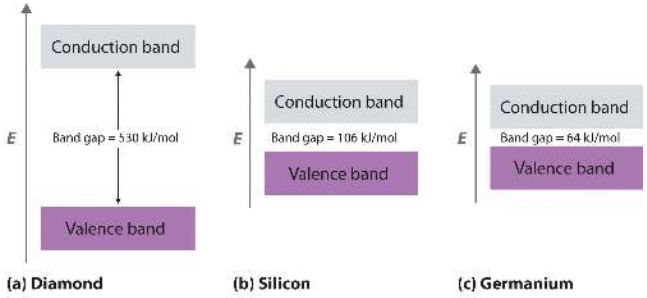


Figure **5.14.2**: Energy-Band Diagrams for Diamond, Silicon, and Germanium. The band gap gets smaller from C to Ge.

Semiconductors

What if the difference in energy between the highest occupied level and the lowest empty level is intermediate between those of electrical conductors and insulators? This is the case for silicon and germanium, which have the same structure as diamond. Because Si–Si and Ge–Ge bonds are substantially weaker than C–C bonds, the energy gap between the filled and empty bands becomes much smaller as we go down group 14 (part (b) and part (c) of Figure **5.14.2**). Consequently, thermal energy is able to excite a small number of electrons from the filled valence band of Si and Ge into the empty band above it, which is called the conduction band.

Exciting electrons from the filled valence band to the empty conduction band causes an increase in electrical conductivity for two reasons:

1. The electrons in the previously vacant conduction band are free to migrate through the crystal in response to an applied electric field.
2. Excitation of an electron from the valence band produces a "hole" in the valence band that is equivalent to a positive charge. The hole in the valence band can migrate through the crystal in the direction opposite that of the electron in the conduction band by means of a "bucket brigade" mechanism in which an adjacent electron fills the hole, thus generating a hole where the second electron had been, and so forth.

Consequently, Si is a much better electrical conductor than diamond, and Ge is even better, although both are still much poorer conductors than a typical metal (Figure **5.14.4**).

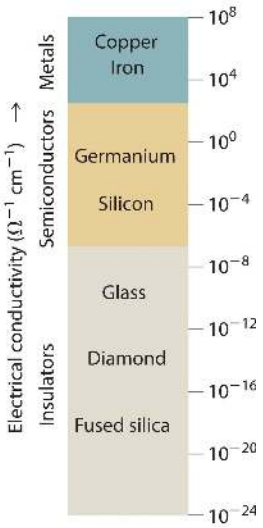


Figure **5.14.4**: A Logarithmic Scale Illustrating the Enormous Range of Electrical Conductivities of Solids

Substances such as Si and Ge that have conductivities between those of metals and insulators are called semiconductors. Many binary compounds of the main group elements exhibit semiconducting behavior similar to that of Si and Ge. For example, gallium arsenide (GaAs) is isoelectronic with Ge and has the same crystalline structure, with alternating Ga and As atoms; not surprisingly, it is also a semiconductor. The electronic structure of semiconductors is compared with the structures of metals and insulators in Figure **5.14.5**.

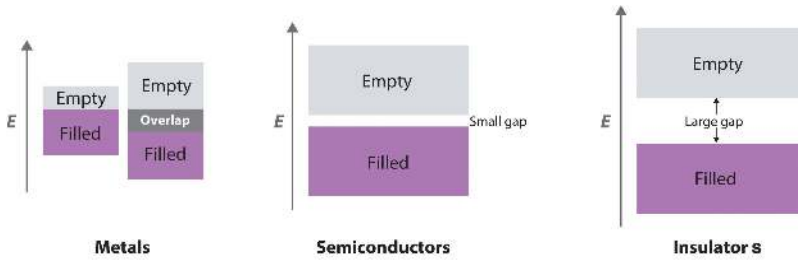


Figure **5.14.5**: A Comparison of the Key Features of the Band Structures of Metals, Semiconductors, and Insulators. Metallic behavior can arise either from the presence of a single partially filled band or from two overlapping bands (one full and one empty).

Temperature and Conductivity

Because thermal energy can excite electrons across the band gap in a semiconductor, increasing the temperature increases the number of electrons that have sufficient kinetic energy to be promoted into the conduction band. The electrical conductivity of a semiconductor therefore increases rapidly with increasing temperature, in contrast to the behavior of a purely metallic crystal. In a metal, as an electron travels through the crystal in response to an applied electrical potential, it cannot travel very far before it encounters and collides with a metal nucleus. The more often such encounters occur, the slower the net motion of the electron through the crystal, and the lower the conductivity. As the temperature of the solid increases, the metal atoms in the lattice acquire more and more kinetic energy. Because their positions are fixed in the lattice, however, the increased kinetic energy increases only the extent to which they vibrate about their fixed positions. At higher temperatures, therefore, the metal nuclei collide with the mobile electrons more frequently and with greater energy, thus decreasing the conductivity. This effect is, however, substantially smaller than the increase in conductivity with temperature exhibited by semiconductors. For example, the conductivity of a tungsten wire decreases by a factor of only about two over the temperature range 750–1500 K, whereas the conductivity of silicon increases approximately 100-fold over the same temperature range. These trends are illustrated in Figure 5.14.6.

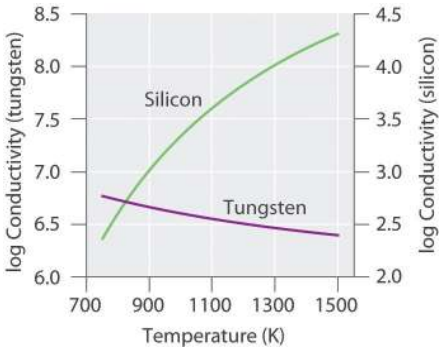


Figure 5.14.6: The Temperature Dependence of the Electrical Conductivity of a Metal versus a Semiconductor. The conductivity of the metal (tungsten) decreases relatively slowly with increasing temperature, whereas the conductivity of the semiconductor (silicon) increases much more rapidly.

n- and p-Type Semiconductors

Doping is a process used to tune the electrical properties of commercial semiconductors by deliberately introducing small amounts of impurities. If an impurity contains more valence electrons than the atoms of the host lattice (e.g., when small amounts of a group 15 atom are introduced into a crystal of a group 14 element), then the doped solid has more electrons available to conduct current than the pure host has. As shown in Figure 5.14.7*a*, adding an impurity such as phosphorus to a silicon crystal creates occasional electron-rich sites in the lattice. The electronic energy of these sites lies between those of the filled valence band and the empty conduction band but closer to the conduction band. Because the atoms that were introduced are surrounded by host atoms, and the electrons associated with the impurity are close in energy to the conduction band, those extra electrons are relatively easily excited into the empty conduction band of the host. Such a substance is called an n-type semiconductor, with the n indicating that the added charge carriers are negative (they are electrons).

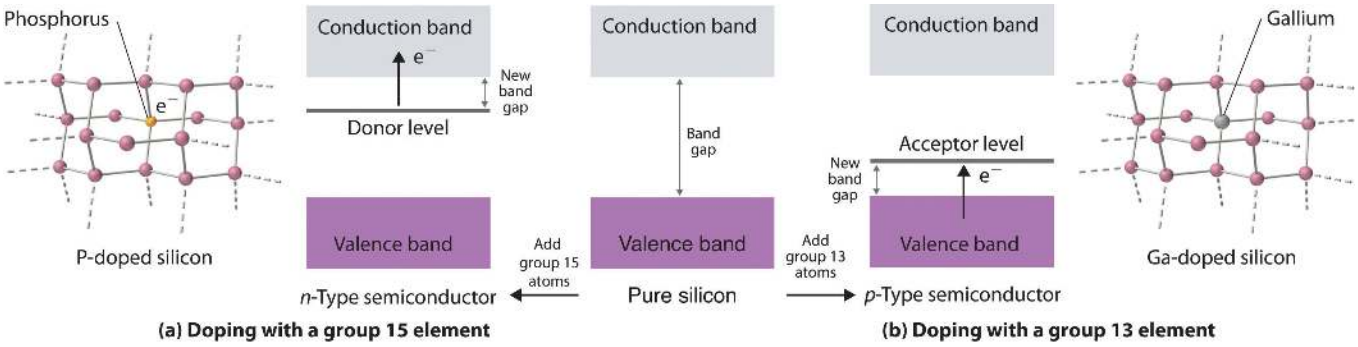


Figure 5.14.7: Structures and Band Diagrams of n-Type and p-Type Semiconductors. (a) Doping silicon with a group 15 element results in a new filled level between the valence and conduction bands of the host. (b) Doping silicon with a group 13 element results in a new empty level between the valence and conduction bands of the host. In both cases, the effective band gap is substantially decreased, and the electrical conductivity at a given temperature increases dramatically.

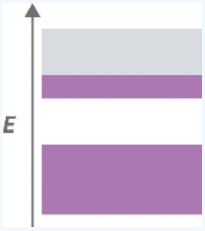
If the impurity atoms contain fewer valence electrons than the atoms of the host (e.g., when small amounts of a group 13 atom are introduced into a crystal of a group 14 element), then the doped solid has fewer electrons than the pure host. Perhaps unexpectedly, this also results in increased conductivity because the impurity atoms generate holes in the valence band. As shown in Figure **5.14.7***b*, adding an impurity such as gallium to a silicon crystal creates isolated electron-deficient sites in the host lattice. The electronic energy of these empty sites also lies between those of the filled valence band and the empty conduction band of the host but much closer to the filled valence band. It is therefore relatively easy to excite electrons from the valence band of the host to the isolated impurity atoms, thus forming holes in the valence band. This kind of substance is called a *p-type semiconductor*, with the p standing for positive charge carrier (i.e., a hole). Holes in what was a filled band are just as effective as electrons in an empty band at conducting electricity.

The electrical conductivity of a semiconductor is roughly proportional to the number of charge carriers, so doping is a precise way to adjust the conductivity of a semiconductor over a wide range. The entire semiconductor industry is built on methods for preparing samples of Si, Ge, or GaAs doped with precise amounts of desired impurities and assembling silicon chips and other complex devices with junctions between n- and p-type semiconductors in varying numbers and arrangements.

Because silicon does not stand up well to temperatures above approximately 100°C, scientists have been interested in developing semiconductors made from diamonds, a more thermally stable material. A new method has been developed based on vapor deposition, in which a gaseous mixture is heated to a high temperature to produce carbon that then condenses on a diamond kernel. This is the same method now used to create cultured diamonds, which are indistinguishable from natural diamonds. The diamonds are heated to more than 2000°C under high pressure to harden them even further. Doping the diamonds with boron has produced p-type semiconductors, whereas doping them with boron and deuterium achieves n-type behavior. Because of their thermal stability, diamond semiconductors have potential uses as microprocessors in high-voltage applications.

Example 5.14.1

A crystalline solid has the following band structure, with the purple areas representing regions occupied by electrons. The lower band is completely occupied by electrons, and the upper level is about one-third filled with electrons.



a. Predict the electrical properties of this solid.
b. What would happen to the electrical properties if all of the electrons were removed from the upper band? Would you use a chemical oxidant or reductant to effect this change?
c. What would happen to the electrical properties if enough electrons were added to completely fill the upper band? Would you use a chemical oxidant or reductant to effect this change?

Given: band structure

Asked for: variations in electrical properties with conditions

Strategy:

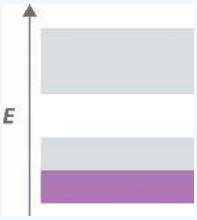
A. **B**ased on the occupancy of the lower and upper bands, predict whether the substance will be an electrical conductor. Then predict how its conductivity will change with temperature.
B. After all the electrons are removed from the upper band, predict how the band gap would affect the electrical properties of the material. Determine whether you would use a chemical oxidant or reductant to remove electrons from the upper band.
C. Predict the effect of a filled upper band on the electrical properties of the solid. Then decide whether you would use an oxidant or a reductant to fill the upper band.

Solution:

A. The material has a partially filled band, which is critical for metallic behavior. The solid will therefore behave like a metal, with high electrical conductivity that decreases slightly with increasing temperature.
B. Removing all of the electrons from the partially filled upper band would create a solid with a filled lower band and an empty upper band, separated by an energy gap. If the band gap is large, the material will be an electrical insulator. If the gap is relatively small, the substance will be a semiconductor whose electrical conductivity increases rapidly with increasing temperature. Removing the electrons would require an oxidant because oxidants accept electrons.
C. Adding enough electrons to completely fill the upper band would produce an electrical insulator. Without another empty band relatively close in energy above the filled band, semiconductor behavior would be impossible. Adding electrons to the solid would require a reductant because reductants are electron donors.

? Exercise 5.14.1

A substance has the following band structure, in which the lower band is half-filled with electrons (purple area) and the upper band is empty.



a. Predict the electrical properties of the solid.
b. What would happen to the electrical properties if all of the electrons were removed from the lower band? Would you use a chemical oxidant or reductant to effect this change?
c. What would happen to the electrical properties if enough electrons were added to completely fill the lower band? Would you use a chemical oxidant or reductant to effect this change?

Answer:

a. The solid has a partially filled band, so it has the electrical properties of a conductor.
b. Removing all of the electrons from the lower band would produce an electrical insulator with two empty bands. An oxidant is required.
c. Adding enough electrons to completely fill the lower level would result in an electrical insulator if the energy gap between the upper and lower bands is relatively large, or a semiconductor if the band gap is relatively small. A reductant is required.

- Metallic behavior requires a set of delocalized orbitals and a band of allowed energy levels that is partially occupied.
- The electrical conductivity of a semiconductor increases with increasing temperature, whereas the electrical conductivity of a metal decreases with increasing temperature.
- n-Type semiconductors are negative charge carriers; the impurity has more valence electrons than the host. p-Type semiconductors are positive charge carriers; the impurity has fewer valence electrons than the host.

Summary

Band theory assumes that the valence orbitals of the atoms in a solid interact to generate a set of molecular orbitals that extend throughout the solid; the continuous set of allowed energy levels is an energy band. The difference in energy between the highest and lowest allowed levels within a given band is the bandwidth, and the difference in energy between the highest level of one band and the lowest level of the band above it is the band gap. If the width of adjacent bands is larger than the energy gap between them, overlapping bands result, in which molecular orbitals derived from two or more kinds of valence orbitals have similar energies. Metallic properties depend on a partially occupied band corresponding to a set of molecular orbitals that extend throughout the solid to form a band of energy levels. If a solid has a filled valence band with a relatively low-lying empty band above it (a conduction band), then electrons can be excited by thermal energy from the filled band into the vacant band where they can then

migrate through the crystal, resulting in electrical conductivity. Electrical insulators are poor conductors because their valence bands are full. Semiconductors have electrical conductivities intermediate between those of insulators and metals. The electrical conductivity of semiconductors increases rapidly with increasing temperature, whereas the electrical conductivity of metals decreases slowly with increasing temperature. The properties of semiconductors can be modified by doping, or introducing impurities. Adding an element with more valence electrons than the atoms of the host populates the conduction band, resulting in an n-type semiconductor with increased electrical conductivity. Adding an element with fewer valence electrons than the atoms of the host generates holes in the valence band, resulting in a p-type semiconductor that also exhibits increased electrical conductivity.

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5.15: Bonding in Metals, Semiconductors and Insulators – Band Structure

5.15.1: INTRODUCTION

Characteristic properties of metals include: (1) electrical conductivity, (2) opaqueness and (3) malleability. A very simple model in which the metallic crystal is viewed as a lattice of positive ions surrounded by a “gas” of free electrons provides a crude understanding of the first and third properties. If the crystal has a gas of free electrons, it is easy to see why the application of an electric field will result in the motion of these electrons and thus for the high electrical conductivity. This model also allows one to explain the malleability of metals, as shown in fig. 1b. When a metallic crystal is subject to forces that displace one plane of atoms with respect to another, the environment of the charged species is left unchanged. In contrast, the displacement of neighboring planes in an ionic crystal as a result of a distorting force will lead to cleavage, largely because of changes in the interaction of the charged species (Figure 5.15.1,).

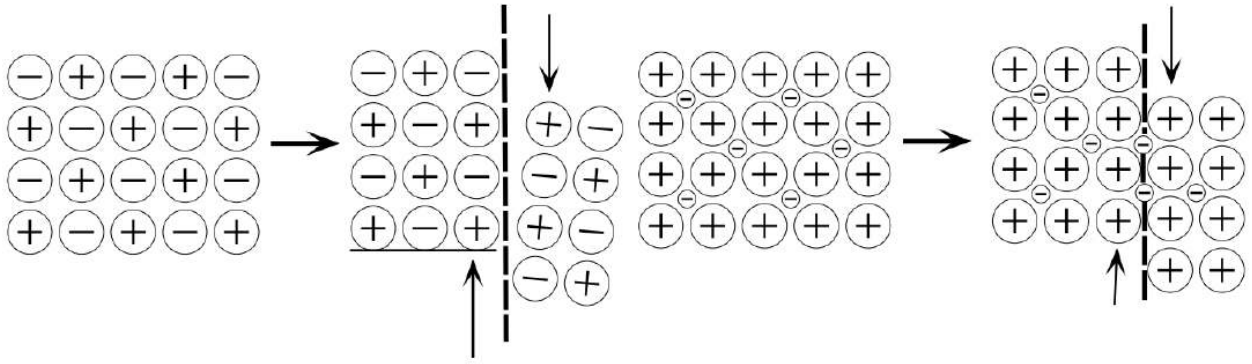


Figure 5.15.1: Mechanical properties of ionic and metallic crystals. (left) In ionic crystals the displacement of neighboring planes by shear forces frequently results in cleavage largely because of the establishment of repulsive forces in the cleavage plane. (right) In metallic crystals the displacement of neighboring planes does not lead to charge effects; slip is a common phenomenon; metals are malleable.

The **free electron gas theory or Drude–Lorentz (D-L) theory** also explains in principle the nature of the attractive bonding forces which hold the metallic ions (the metal) together: the crystal is held together by electrostatic forces of attraction between the positively charged metal ions and the non-localized, negatively charged electrons - the electron gas. The theory in its original form assumes that the classical kinetic theory of gases is applicable to the *electron gas* ; mutual repulsion between electrons was ignored and the electrons were expected to have velocities which are temperature dependent according to a Maxwell-Boltzmann distribution law.

While the Drude-Lorentz theory of metallic bonding was considered a useful model, several shortcomings soon became apparent. The most notable failure consisted of the unexplainable discrepancy between the observed and predicted specific heats of metals (energy in the form of heat, required to increase the temperature of $1\ g$ of a given metal by $1°C$). The D-L theory predicted much larger specific heats than are observed (because the Maxwell-Boltzmann energy distribution has no restrictions as to the number of species allowed to have exactly the same energy). [If there are restrictions as to the number of electrons with identical energy (Pauli exclusion principle!), we have to apply a different form of statistics (Fermi-Dirac statistics).]

5.15.2: ENERGY BAND THEORY BASED ON FORMATION OF MOLECULAR ORBITALS

A different model, and one that is more closely related to the models of the chemical bond discussed earlier, is the *band model*. This model, proposed by Bloch before the development of the molecular-orbital approach to chemical bonding, is actually a molecular-orbital model of metallic crystals. The orbitals characteristic of the whole crystal are obtained as linear combinations of the atomic orbitals of the individual atoms.

From the large electrical conductivity of metals, it appears that at least some of the electrons can move freely through the bulk of the metal. Since even lithium with only one valence electron has eight nearest neighbors (crystallizes in a body-centered cubic lattice), it is clear that the atoms can not be bonded to each other by localized electron-pair bonds (for in that case the lithium atom, which altogether has only three electrons, would have to supply eight or even fourteen valence electrons to establish bonding with

the nearest and next-to-nearest neighbor atoms). The fact that in a metal lattice one atom can simultaneously interact with a large number of others can be explained by considering that metals constitute an extreme example of *delocalized bonding*.

Conditions in metals are not as easily assessed as in organic hydrocarbon chains because metal lattices are three-dimensional structures. However, several important results from the theory of metallic bonding can be understood on a highly simplified model in which the three-dimensional lattice is replaced by a one-dimensional system. Consider the formation of a linear array of lithium atoms from individual lithium atoms:

$$\mathbf{Li} \rightarrow \mathbf{Li-Li} \rightarrow \mathbf{Li-Li-Li} \rightarrow \mathbf{Li-Li-Li-Li} \rightarrow \ldots \tag{5.15.1}$$

The first stage is the formation of a lithium molecule, $\mathbf{Li_2}$, which is comparable to the hydrogen molecule, $\mathbf{H_2}$. The two lithium atoms are bound together by a pair of valence electrons; each lithium atom supplies its 2s-electron which, through orbital overlap, forms a covalent molecular bond (fig. 2). The molecule formed occurs in lithium vapor and differs from the $\mathbf{H_2}$ molecule only by its greater interatomic distance ($\mathbf{Li-Li} = 2.67 \times 10^{-10}\ \mathbf{m}, \mathbf{H-H} = 0.75 \times 10^{-10}\ \mathbf{m}$) and smaller energy of formation. The larger separation and the consequent reduction in bond energy can be attributed to the size of the $\mathbf{Li^+}$ atomic core.

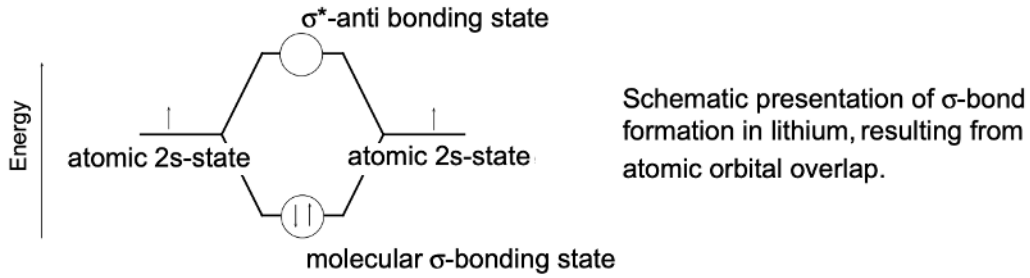


Figure 2 Formation of $\mathbf{Li_2}$ molecule

In the determination of molecular orbital states by **linear combination of atomic orbitals** (LCAO) we obtain more than one solution from the Schrödinger equation. We have so far concentrated mostly on the low energy states, leading to σ or π bonds. We have largely ignored the so-called *antibonding states* which in covalent molecules have energies higher than the original energy states of the isolated reaction partners (presently Li) and, therefore, remain unoccupied (or empty) in two-atomic molecules. In any multi-atom system (such as a piece of metal), the total number of molecular orbital states (electronic states) is always the same as the total number of original atomic states (conservation of electronic states). However, not all of these states are necessarily occupied by electrons.

Consider the hypothetical linear molecule $\mathbf{Li_3}$. Since the valence electron cloud is spherical, the central lithium atom can not give preference to either of its neighbors. The three atomic valence electron clouds overlap to form one continuous distribution and two others with nodes (antibonding states), i.e., three molecular orbitals in all (Fig. 3).

As the length of the chain is increased, the number of electronic states into which the atomic $\mathbf{2}\boldsymbol{s}$ state splits also increases, *the number of states always equaling the number of atoms*. The same occurs when lithium chains are placed side-by-side or stacked on top of each other, so that finally the space lattice of the lithium crystal is obtained. It is of great significance that these electronic states have energies which are bounded by an upper and lower limiting value (see fig. 4). Within these limits the states form an *energy band* of closely spaced values (one gram of lithium contains nearly $\mathbf{10^{23}}$ atoms). Similarly, energy bands can also result from overlapping p and d orbitals. The electronic states (orbitals) within an energy band are filled progressively by pairs of electrons in the same way that the orbitals of an atom were filled in accordance with the Pauli principle. This means that for lithium the electronic states of the 2s band will be exactly half-filled.

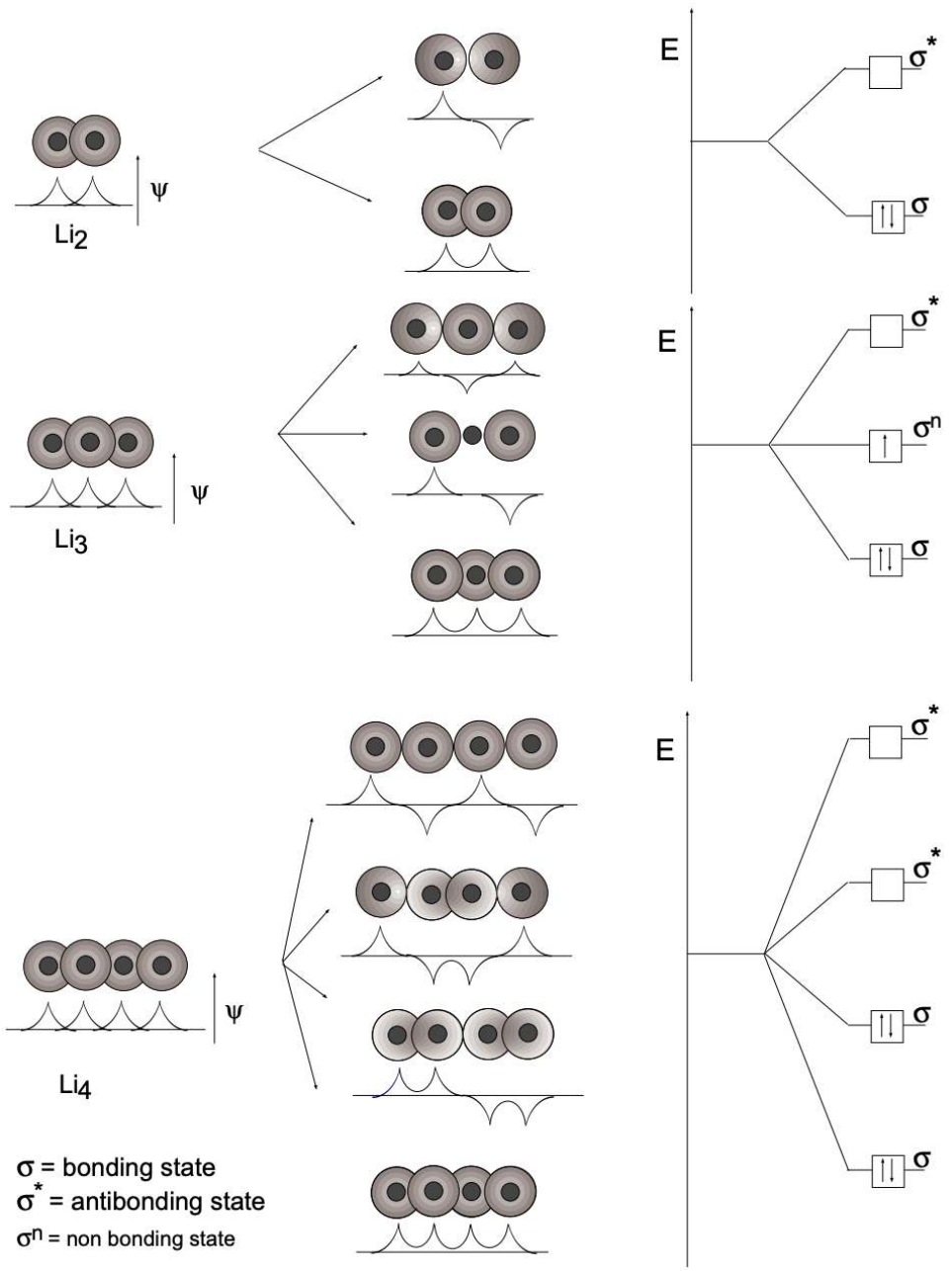


Figure 3 Formation of molecular chains of lithium atoms.

It is of interest to consider why lithium atoms or $\mathbf{Li_2}$ molecules combine to form a metal lattice. In the lithium lattice the smallest distance between neighboring atoms is $\mathbf{3.03 \times 10^{-10}\ m}$, which is larger than in the $\mathbf{Li_2}$ molecule. This reflects the fact that bonds between pairs of atoms in the metal are weaker than they are in the molecule. Nevertheless, the metallic form of lithium is more stable than the molecular form because in the metal one atom has many more neighbors than in the $\mathbf{Li_2}$ molecule. As a result, the binding energy per gram atom of lithium (i.e., per $\mathbf{6.92\ g}$ of lithium) is $\mathbf{163\ kJ}$ for the metal lattice, but only $\mathbf{56\ kJ}$ for one mole of molecule.

> The possibility of hybridization (first advanced by L. Pauling to explain metallic bonding) is also a likely factor for the formation of metallic bonds. Thus strong bonds can be formed when the valence electron clouds become concentrated along the direction in which the bonding partners are situated. According to Pauling the situation can be described by *mesomeric* limiting formulae, just as in the theory of unsaturated carbon compounds. One reason given for hydrogen not forming a metal is its inability to hybridize.

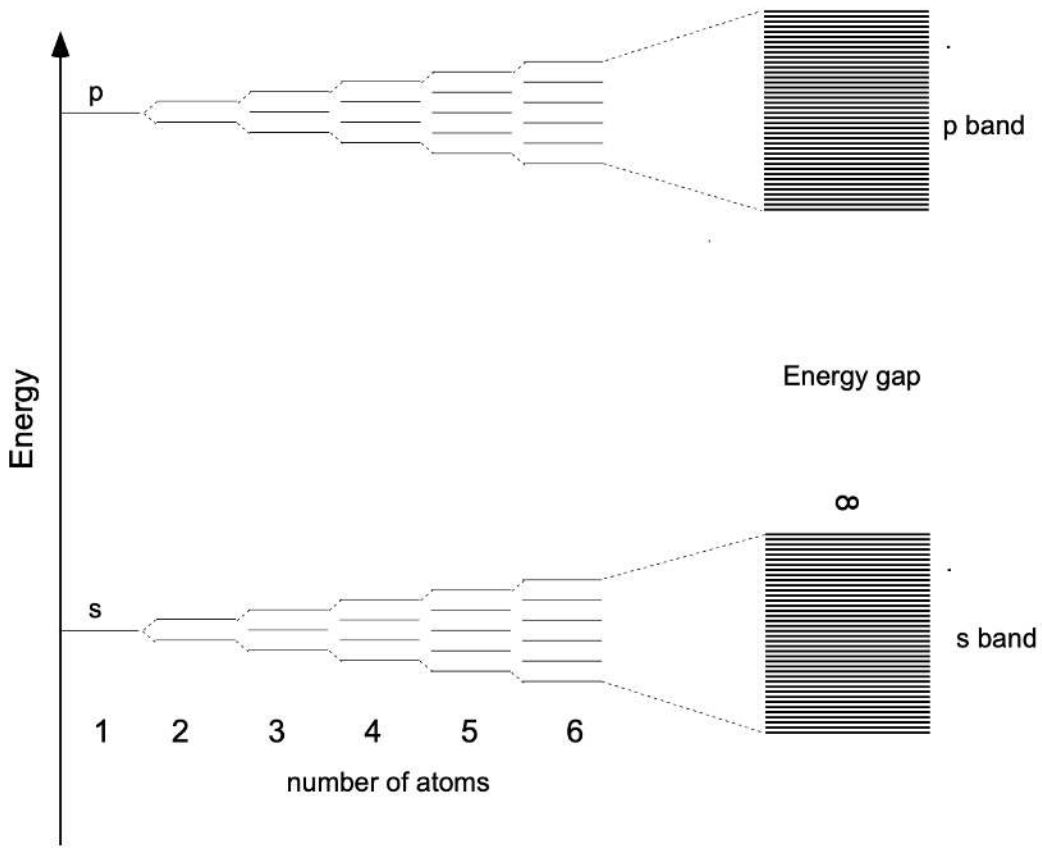


Figure 4 Formation of energy bands from energy levels of constituent atoms

The appearance of bands of allowed electron energies relates to the overlap of electron ψ functions. The width of each energy band is a function of the crystal structure because it determines the number of nearest neighbors in the crystal. Different metal atoms with the same valence, particularly elements in the same group of the periodic table, can often replace each other in arbitrary proportions without altering either the lattice type or the structure of the energy bands. This explains why such metals tend to form a complete series of *solid solutions.* Metallic alloys consist of such solid solutions or of heterogeneous mixtures of such solutions. Within certain limits, even metal atoms of different valence can be interchanged in a lattice.

5.15.2.1: Structure of Metals

According to the above considerations the band structure of Li metal can be represented as shown in fig. 5. According to previous reasoning, the $2\,s$ band has N states ($N =$ number of atoms) and accommodates $n2s$ electrons (where n is the number of electrons per atom in the $2\,s$ state times N). Thus, this band has only half of the states filled since each state can accommodate two electrons of opposite spin (Pauli exclusion principle). In accordance with the Aufbau principle, the lowest energy states of the band are filled first and the upper states remain empty - but can readily be occupied by electrons upon thermal excitation or the application of an electric field. Since the width of the energy band is of the order of a few volts, spacings of states within the band are of the order of $\sim 10^{-20}\text{eV}\,(1\text{eV} = 1.6 \times 10^{-19}\ \text{J})$, electrons can readily acquire the energy necessary to move into excited states, be accelerated, and move through the metal as *conducting electrons*. Partly filled bands thus constitute *conduction bands*.

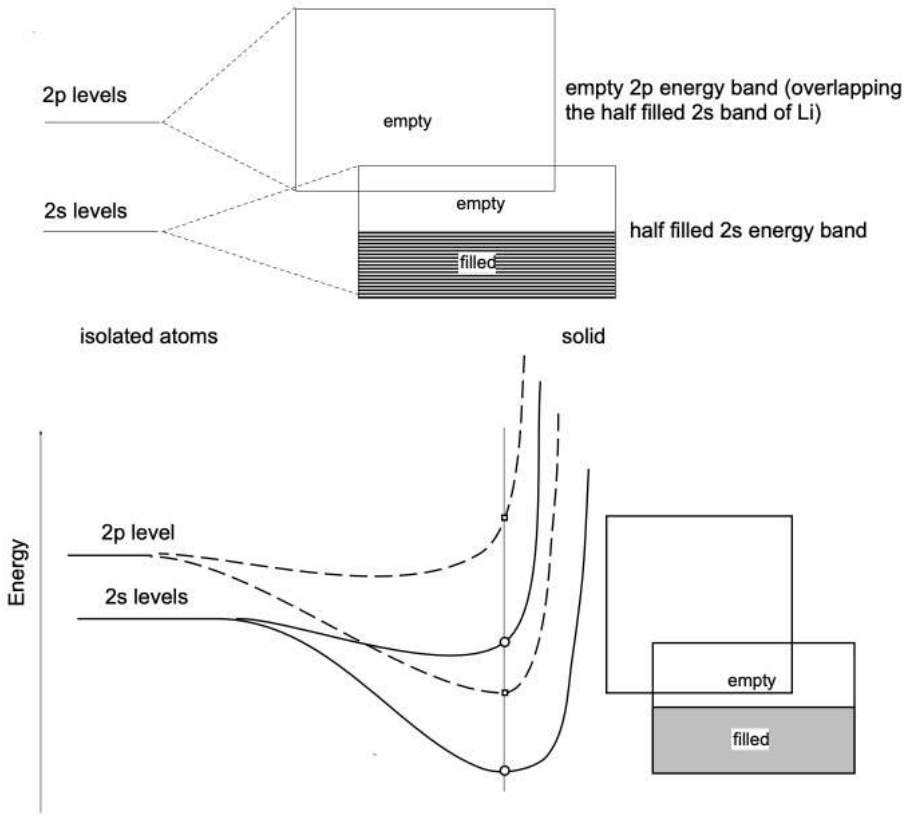


Fig. 5 Schematic energy band configuration for Li .

The conduction mechanism in Mg, for example, appears complicated by the fact that each $3s$ state of the valence shell in the atoms is doubly occupied ($3s^2$). Thus the $3s$ band must be filled completely and no electronic conduction would in principle be expected. Electronic conduction, however, is observed because of a partial overlap of the $3s$ and the empty $3p$ bands. With this overlap, electrons can be activated into empty $3p$ states and exhibit conduction, as in the partly filled s band in Li.

5.15.2.2: Structure of Insulators and Semiconductors (Molecular Crystals)

The same band model can also account for the lack of conductivity in covalent crystals, such as diamond. In the diamond crystal, with a two-electron bond between every atom and each of its neighbors, the bonding molecular orbitals form a band at much lower energies than the energy of the atomic sp^3 hybrid orbitals, and the antibonding orbitals form a band at energies much higher than the energy of the atomic orbitals. Also, since each atom contributes four orbitals and four electrons, there are just enough electrons to fill the bonding orbitals (corresponding to an electron pair bond joining every atom to each of its neighbors) and the only vacant orbitals are those in the high energy band of antibonding orbitals (see fig. 6).

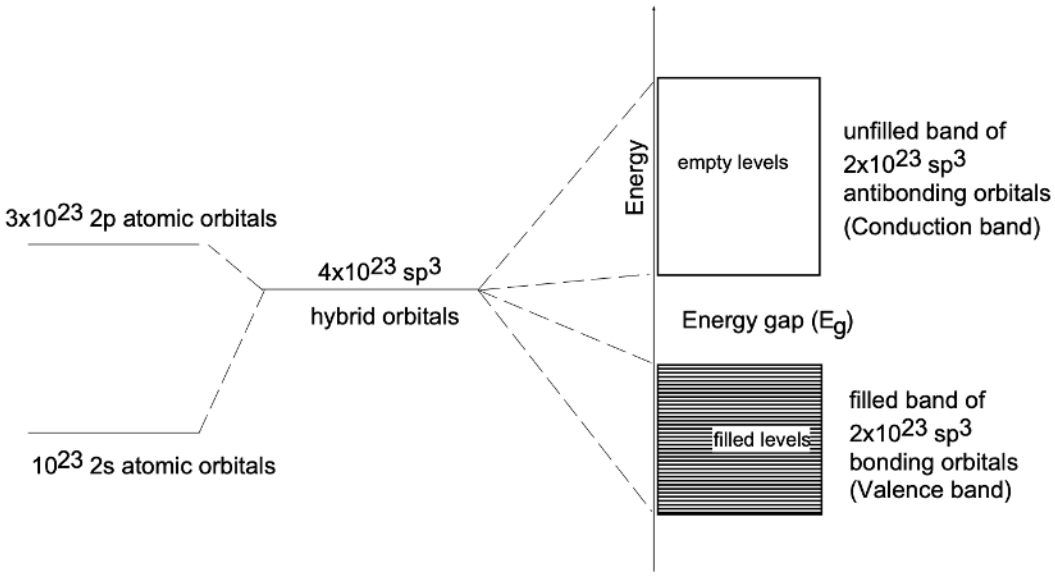


Fig. 6 Band structure of insulators and semiconductors (molecular crystals); the conditions depicted reflect a molar crystal of carbon (diamond).

Both insulators and semiconductors have the same basic band structure – the primary difference is the *width* of the forbidden energy gap ($\mathbf{E_g}$) between the valence and the conduction band.

Insulators, generically, are materials with very high resistivity (see Table I), comprising glasses, polymers, refractories, composites, liquids and gases. In the present context, an insulator is a molecular crystal, such as diamond (C) or sapphire, with a band gap (E_g) in excess of $\mathbf{4eV}$ (arbitrary value). Generally such materials will not conduct electricity since their valence band is filled and the energy required to transfer electrons from the valence band to the empty conduction band is far in excess of both the thermal energies at room temperature and the energy provided by radiation of the visible spectrum ($\mathbf{2eV}$). Therefore, insulators (in single crystal form) are normally transparent (colorless); however, if light is excessively or totally scattered at internal heterogeneities (such as grain boundaries), they may be translucent and even opaque. It should also be recognized that impurities ($\mathbf{Cr^{3+}}$ in $\mathbf{Al_2O_3}$) or particular point defects (color centers) may impart a color to the transparent insulator crystals. The color arises because of partial absorption of white light and selective transmission of the other portions of the visible spectrum.

Semiconductors: The conventional semiconductors, silicon (Si) and germanium (Ge), have a band gap ($\mathbf{E_g}$) of $\mathbf{1.1}$ and $\mathbf{0.7eV}$ respectively and therefore absorb visible radiation; they are opaque (fig. 7). Considering the statistical nature of the thermal energy distribution in the solid matrix (Maxwell-Boltzmann), a significant number of electrons in the valence band will, at room temperature, acquire sufficient energy to cross the existing energy gap and thus provide for *semiconductivity*. The conductivity will therefore increase with temperature, contrary to metallic systems, until electron scattering effects, due to increased lattice vibrations (which decrease the mobility of electrons), begin to dominate.

The value of semiconductors for solid state device fabrication lies in the fact that the number and type of conducting electric charge carriers [electrons are n-type (negative), holes are p-type (positive)] can be controlled through incorporation of appropriate *dopant elements*. Thus the substitutional incorporation of Group V elements (Sb, As, P) provides for shallow donor levels in the band gap at about $\mathbf{0.01eV}$ from the conduction band. The substitutional incorporation of Group III elements (B, Al) generates *acceptor levels* in the band gap at about $\mathbf{0.01eV}$ from the valence band. The two types of impurities are almost completely ionized at room temperature and give rise to *extrinsic* n-type and p-type conductivity – the basis for the formation of *junction devices* such as diodes and transistors (fig. 8).

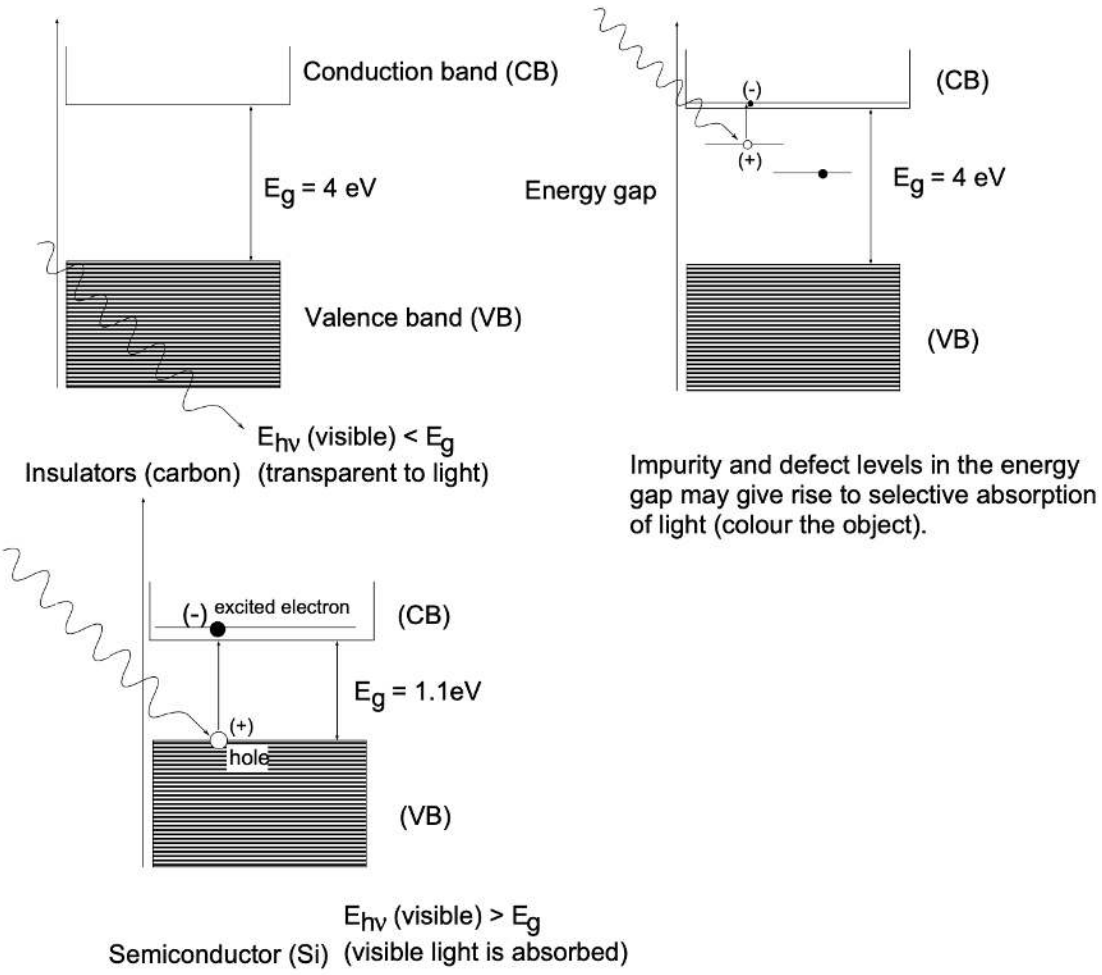


Fig. 7 Optical behavior of insulators and semiconductors

Of increasing importance are compound *III-V (adamantine) semiconductors*, such as GaAs, InSb, InP and GaP (compounds of Group III and Group V elements). Together these compounds provide eight valence electrons and, by sp^3 hybridization, are able to form a diamond-like, covalent crystal structure with semiconductor properties. These

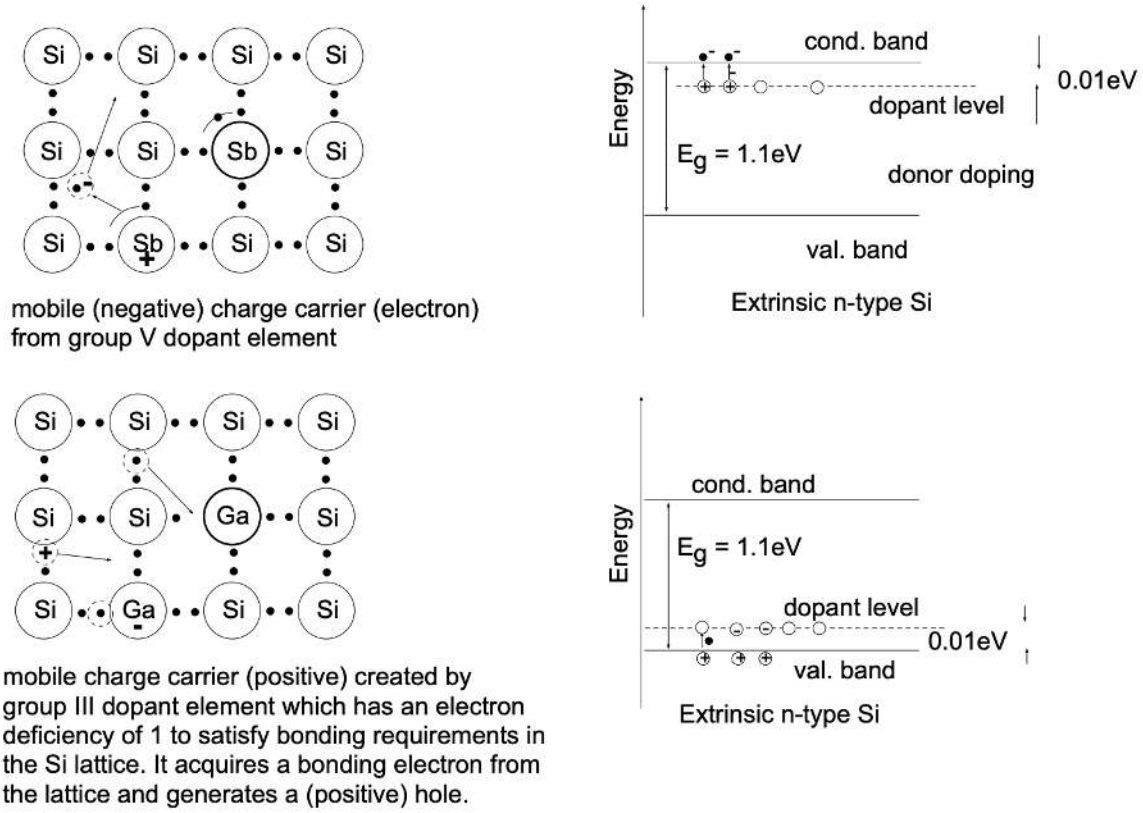


Fig. 8 Extrinsic p- and n-type semiconductors.

compounds (GaAs, for example) exhibit electron mobilities which are higher than those of silicon and, therefore, are of considerable interest for advanced device technology.

Table I. ELECTRICAL RESISTIVITIES OF METALS AND NONMETALS AT 20°C*

Metals	Resistivity, 10^{-8} ohm–m**	Nonmetals	Resistivity, ohm–m**
Silver	1.6	Semiconductors	
Copper	1.67	Silicon	1000.0
Gold	2.3	Germanium	0.09
Aluminum	2.69	Insulators	
Magnesium	4.4	Diamond	10^{10}–10^{11}
Sodium	4.61	Quartz	1.2×10^{12}
Tungsten	5.5	Ebonite	2×10^{13}
Zinc	5.92	Sulfur	4×10^{13}
Cobalt	6.24	Mica	9×10^{13}
Nickel	6.84	Selenium	2×10^{14}
Cadmium	7.4	Paraffin wax	3×10^{16}
Iron	9.71		
Tin	12.8		
Lead	20.6		
Uranium	29		
Zirconium	41		
Manganin	44		
Titanium	55		
Lanthanum	59		
96%Iron–4%Si	62		
Cerium	78		
Nichrome	100		

*From *American Institute of Physics Handbook*, Dwight E. Gray, ed. McGraw-Hill, New York (1963), pp. 4–90; 9–38.

**Note the different units in the two columns

APPENDIX

Approximate Energy Values for Some Events and Reactions

Solar Energy Emission	$\sim 10^{30}$ kJ/ day
Convertible Solar Energy on Earth	$\sim 10^{18}$ kJ/ year
Energy Consumption on Earth	$\sim 8 \times 10^{17}$ kJ/ year
Super-Nova Explosion	$\sim 10^{39}$ kJ
100 Mega-Ton H-Bomb Explosion	$\sim 10^{15}$ kJ
Atlas Blast-Off	$\sim 10^{8}$ kJ
Lethal X-Ray Dose	~ 1 kJ
25¢ Piece Falling from Pocket	$\sim 10^{-4}$ kJ
Bee's Wing Beat	$\sim 10^{-6}$ kJ
Moonlight/Face/Second	$\sim 10^{-8}$ kJ

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6.1: Introduction to Coordination Chemistry

Coordination chemistry is the study of the compounds that form between metals and **ligands**, where a ligand is any molecule or ion that binds to the metal. A metal **complex** is the unit containing the metal bound to its ligands. For example, $[PtCl_2(NH_3)_2]$ is the neutral metal complex where the Pt^{+2} metal is bound to two Cl^- ligands and two NH_3 ligands. If a complex is charged, it is called a **complex ion** (ex. $[Pt(NH_3)_4]^{+2}$ is a complex cation). A complex ion is stabilized by formation of a **coordination compound** with ions of opposite charge (ex. $[Pt(NH_3)_4]Cl_2$). It is convention to write the formula of a complex or complex ion inside of square brackets, while counterions are written outside of the brackets. In this convention, it is understood that ligands inside the brackets are bound directly to the metal ion, in the metal's *first coordination sphere* (a.k.a inner coordination sphere). Ions written outside of the brackets are assumed to be in the *second coordination sphere*, and they are not directly bound to the metal.

- Neutral Complex: $[CoCl_3(NH_3)_3]$
- Complex Cation: $[CO(NH_3)_6]^{3+}$
- Complex Anion: $[CoCl_4(NH_3)_2]^-$
- Coordination Compound: $K_4[Fe(CN)_6]$

A common metal complex is $Ag(NH_3)_2^+$, formed when Ag^+ ions are mixed with neutral ammonia molecules.

$$Ag^+ + 2NH_3 \rightarrow Ag(NH_3)_2^+$$

A complex $Ag(S_2O_3)_2^{3-}$ is formed between silver ions and negative thiosulfate ions:

$$Ag^+ + 2S_2O_3^{2-} \rightarrow Ag(S_2O_3)_2^{3-}$$

The geometry and arrangement of ligands around the metal center affect the properties of a coordination compounds. Compounds with the same molecular formula can appear as **isomers** with very different properties. Isomers are molecules that have identical chemical formulas, but have different arrangements of atoms in space. Isomers with different geometric arrangements of ligands are called **geometric isomers**. Isomers whose structures are mirror images of each other are called **optical isomers**.

How did the study of coordination compounds started?

The coordination chemistry was pioneered by Nobel Prize winner Alfred Werner (1866-1919). He received the Nobel Prize in 1913 for his coordination theory of transition metal-amine complexes. At the start of the 20th century, inorganic chemistry was not a prominant field until Werner studied the metal-amine complexes such as $[Co(NH_3)_6Cl_3]$. Werner recognized the existence of several forms of cobalt-ammonia chloride. These compounds have different color and other characteristics. The chemical formula has three chloride ions per mole, but the number of chloride ions that precipitate with Ag^+ ions per formula is not always three. He thought only **ionized chloride ions** will form precipitate with silver ion. In the following table, the number below the **Ionized Cl^-** is the number of ionized chloride ions per formula. To distinguish ionized chloride from the coordinated chloride, Werner formulated the **Complex formula** and explained structure of the cobalt complexes.

Figure 1: Proposed Structure of Cobalt Ammonia Complexes from Number of Ionized Chloride

Solid	Color	Ionized Cl^-	Complex formula
$CoCl_3 6NH_3$	Yellow	3	$[Co(NH_3)_6]Cl_3$
$CoCl_3 5NH_3$	Purple	2	$[Co(NH_3)_5Cl]Cl_2$
$CoCl_3 4NH_3$	Green	1	*trans*-$[Co(NH_3)_4Cl_2]Cl$
$CoCl_3 4NH_3$	Violet	1	*cis*-$[Co(NH_3)_4Cl_2]Cl$

The structures of the complexes were proposed based on a coordination sphere of 6. The 6 ligands can be ammonia molecules or chloride ions. Two different structures were proposed for the last two compounds, the *trans* compound has two chloride ions on opposite vertices of an octahedral, whereas the the two chloride ions are adjacent to each other in the *cis* compound. The *cis* and *trans* compounds are known as geometric isomers.

Other cobalt complexes studied by Werner are also interesting. It has been predicted that the complex $Co(NH_2CH_2CH_2NH_2)_2ClNH_3]^{2+}$ should exist in two forms, which are mirror images of each other. Werner isolated solids of the two forms, and structural studies confirmed his interpretations. The ligand $NH_2CH_2CH_2NH_2$ is ethylenediamine (en) often represented by en.

Properties of Coordination Complexes

Some methods of verifying the presence of complex ions include studying its chemical behavior. This can be achieved by observing the compounds' color, solubility, absorption spectrum, magnetic properties, etc. The properties of complex compounds are separate from the properties of the individual atoms. By forming coordination compounds, the properties of both the metal and the ligand are altered.

Metal-ligand bonds are typically thought of Lewis acid-base interactions. The metal atom acts as an electron pair acceptor (Lewis acid), while the ligands act as electron pair donors (Lewis base). The nature of the bond between metal and ligand is stronger than intermolecular forces because they form directional bonds between the metal ion and the ligand, but are weaker than covalent bonds and ionic bonds.

Common Ligands

Monodentate ligands donate one pair of electrons to the central metal atoms. An example of these ligands are the haldide ions (F^-, Cl^-, Br^-, I^-). Polydentate ligands, also called chelates or chelating agents, donate more than one pair of electrons to the metal atom forming a stronger bond and a more stable complex. A common chelating agent is ethylenediamine (en), which, as the name suggests, contains two ammines or :NH_2 sites which can bind to two sites on the central metal. An example of a tridentate ligand is bis-diethylenetriammine. An example of such a coordination complex is bis-diethylenetriamine cobalt III.

Complex compound/ion	Coordination number	Oxidation State of Metal Atom
$[Fe(CN)_6]^{4-}$	6	2+
$[Co(NH_3)_4SO_4]^-$	5	1+
$[Pt(NH_3)_4]^{2+}$	4	2+
$[Ni(NH_2CH_2CH_2NH_2)_3]^{2+}$	6	2+

Complex ions can form many compounds by binding with other complex ions in multiple ratios. This leads to many combinations of coordination compounds. The structures of certain coordination compounds can also have isomers, which can change their interactions with other chemical agents. The binding between metal and ligands is studied in metals, tetrahedral, and octahedral structures. There are many pharmaceutical and biological applications of coordination complexes and their isomers.

Contributors and Attributions

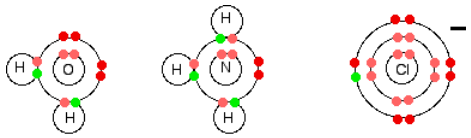
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6.2: What is a Complex Ion?

A complex ion has a metal ion at its center with a number of other molecules or ions surrounding it. These can be considered to be attached to the central ion by coordinate (dative covalent) bonds (although in some cases, the bonding is actually more complicated than that.) The molecules or ions surrounding the central metal ion are called ligands. Simple ligands include water, ammonia and chloride ions.



What all these have got in common is active lone pairs of electrons in the outer energy level. These are used to form co-ordinate bonds with the metal ion. All ligands are lone pair donors. In other words, all ligands function as Lewis bases.

Bonding in Simple Complex Ions

We are going to look in detail at the bonding in the complex ion formed when water molecules attach themselves to an aluminum ion to give $Al(H_2O)_6^{3+}$. Start by thinking about the structure of a naked aluminum ion before the water molecules bond to it.

Example 6.2.1: $Al(H_2O)_6^{3+}$

Aluminum has the electronic structure

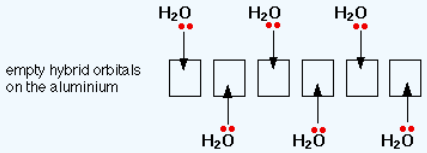
$$1s^2 2s^2 2p^6 3s^2 3p_x^1$$

When it forms an Al^{3+} ion it loses the 3-level electrons to leave

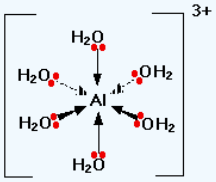
$$1s^2 2s^2 2p^6$$

That means that all the 3-level orbitals are now empty. The aluminum uses of six of these to accept lone pairs from six water molecules. It re-organizes (hybridizes) the 3s, the three 3p, and two of the 3d orbitals to produce six new orbitals all with the same energy.

You might wonder why it chooses to use six orbitals rather than four or eight or whatever. Six is the maximum number of water molecules it is possible to fit around an aluminum ion (and most other metal ions). By making the maximum number of bonds, it releases most energy and so becomes most energetically stable.



Only one lone pair is shown on each water molecule. The other lone pair is pointing away from the aluminum and so isn't involved in the bonding. The resulting ion looks like this:



Because of the movement of electrons towards the center of the ion, the 3+ charge is no longer located entirely on the aluminum, but is now spread over the whole of the ion. Because the aluminum is forming 6 bonds, the co-ordination number of the aluminum is said to be 6. The co-ordination number of a complex ion counts the number of co-ordinate bonds being formed by the metal ion at its center.

In a simple case like this, that obviously also counts the number of ligands - but that is not necessarily so, as you will see later. Some ligands can form more than one co-ordinate bond with the metal ion.

Example **6.2.2** is chosen because it is very similar to the last one - except that it involves a transition metal.

Example 6.2.2: $Fe(H_2O)_6^{3+}$

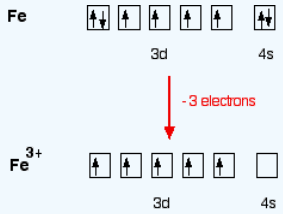
Iron has the electronic structure

$$1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$$

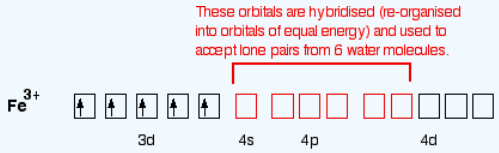
When it forms an Fe^{3+} ion it loses the 4s electrons and one of the 3d electrons to leave

$$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$$

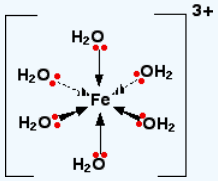
Looking at this as electrons-in-boxes, at the bonding level:



The single electrons in the 3d level are NOT involved in the bonding in any way. Instead, the ion uses 6 orbitals from the 4s, 4p and 4d levels to accept lone pairs from the water molecules. Before they are used, the orbitals are re-organized (hybridized) to produce 6 orbitals of equal energy.



Once the co-ordinate bonds have been formed, the ion looks exactly the same as the equivalent aluminum ion.



Because the iron is forming 6 bonds, the co-ordination number of the iron is 6.

Example **6.2.3** demonstrates the formation of a complex ion with a negative charge.

Example 6.2.3: $CuCl_4^{2-}$

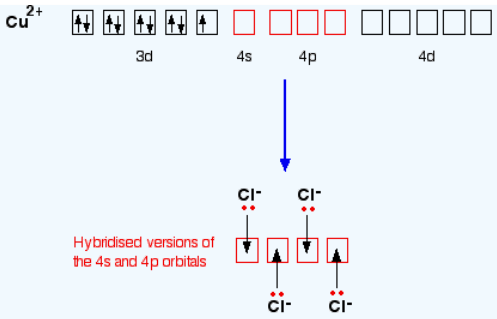
Copper has the electronic structure

$$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$$

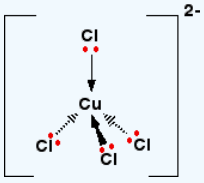
When it forms a Cu^{2+} ion it loses the 4s electron and one of the 3d electrons to leave

$$1s^2 2s^2 2p^6 3s^2 3p^6 3d^9$$

To bond the four chloride ions as ligands, the empty 4s and 4p orbitals are used (in a hybridised form) to accept a lone pair of electrons from each chloride ion. Because chloride ions are bigger than water molecules, you can't fit 6 of them around the central ion - that's why you only use 4.



Only one of the 4 lone pairs on each chloride ion is shown. The other three are pointing away from the copper ion, and aren't involved in the bonding. That gives you the complex ion:



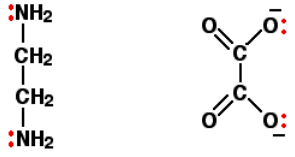
The ion carries 2 negative charges overall. That comes from a combination of the 2 positive charges on the copper ion and the 4 negative charges from the 4 chloride ions. In this case, the co-ordination number of the copper is 4.

Complex metal ions containing more complicated ligands

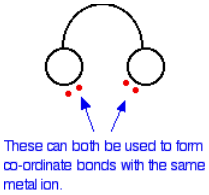
In the examples we've already looked at, each ligand only forms one bond with the central metal ion to give the complex ion. Such a ligand is said to be unidentate. That means literally that it only has one tooth! It only has one pair of electrons that it can use to bond to the metal - any other lone pairs are pointing in the wrong direction. Some ligands, however, have rather more teeth! These are known generally as multidentate or polydentate ligands, but can be broken down into a number of different types.

Bidentate ligands

Bidentate ligands have two lone pairs, both of which can bond to the central metal ion. The two commonly used examples are 1,2-diaminoethane (old name: ethylenediamine - often given the abbreviation "en"), and the ethanedioate ion (old name: oxalate).



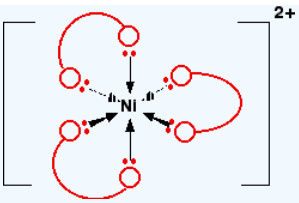
In the ethanedioate ion, there are lots more lone pairs than the two shown, but these are the only ones we are interested in. You can think of these bidentate ligands rather as if they were a pair of headphones, carrying lone pairs on each of the "ear pieces". These will then fit snuggly around a metal ion.



Example 6.2.4: $Ni(NH_2CH_2CH_2NH_2)_3^{2+}$

You might find this abbreviated to $[Ni(en)_3]^{2+}$.

The structure of the ion looks like this:



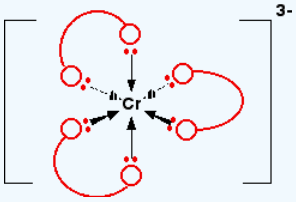
In this case, the "ear pieces" are the nitrogen atoms of the NH_2 groups - and the "bit that goes over your head " is the - CH_2CH_2- group. If you were going to draw this in an exam, you would obviously want to draw it properly - but for learning purposes, drawing all the atoms makes the diagram look unduly complicated!

Notice that the arrangement of the bonds around the central metal ion is exactly the same as it was with the ions with 6 water molecules attached. The only difference is that this time each ligand uses up two of the positions - at right angles to each other. Because the nickel is forming 6 co-ordinate bonds, the coordination number of this ion is 6, despite the fact that it is only joined to 3 ligands. Coordination number counts the **number of bonds**, not the number of ligands.

Example 6.2.5: $Cr(C_2O_4)_3^{3-}$

This is the complex ion formed by attaching 3 ethanedioate (oxalate) ions to a chromium(III) ion. The shape is exactly the same as the previous nickel complex. The only real difference is the number of charges. The original chromium ion carried 3+ charges, and each ethanedioate ion carried 2-. (3+) + (3 x 2-) = 3-.

The structure of the ion looks like this:

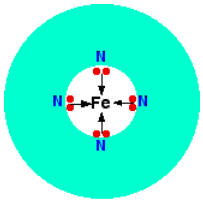


Again, if you drew this in an exam, you would want to show all the atoms properly. If you need to be able to do this, practice drawing it so that it looks clear and tidy! Refer back to the diagram of the ethanedioate ion further up the page to help you.

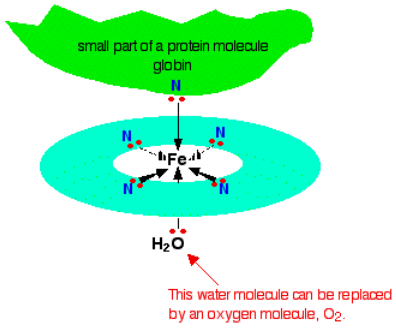
A Quadridentate Ligand

A quadridentate ligand has four lone pairs, all of which can bond to the central metal ion. An example of this occurs in haemoglobin (American: hemoglobin). The functional part of this is an iron(II) ion surrounded by a complicated molecule called heme. This is a sort of hollow ring of carbon and hydrogen atoms, at the center of which are 4 nitrogen atoms with lone pairs on them. Heme is one of a group of similar compounds called porphyrins. They all have the same sort of ring system, but with different groups attached to the outside of the ring. You aren't going to need to know the exact structure of the haem at this level.

We could simplify the heme with the trapped iron ion as:



Each of the lone pairs on the nitrogen can form a co-ordinate bond with the iron(II) ion - holding it at the center of the complicated ring of atoms. The iron forms 4 co-ordinate bonds with the haem, but still has space to form two more - one above and one below the plane of the ring. The protein globin attaches to one of these positions using a lone pair on one of the nitrogens in one of its amino acids. The interesting bit is the other position.

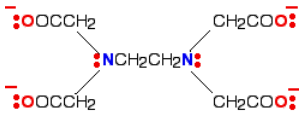


Overall, the complex ion has a co-ordination number of 6 because the central metal ion is forming 6 co-ordinate bonds. The water molecule which is bonded to the bottom position in the diagram is easily replaced by an oxygen molecule (again via a lone pair on one of the oxygens in O_2) - and this is how oxygen gets carried around the blood by the haemoglobin. When the oxygen gets to where it is needed, it breaks away from the haemoglobin which returns to the lungs to get some more.

> You probably know that carbon monoxide is poisonous because it reacts with haemoglobin. It bonds to the same site that would otherwise be used by the oxygen - but it forms a very stable complex. The carbon monoxide doesn't break away again, and that makes that haemoglobin molecule useless for any further oxygen transfer.

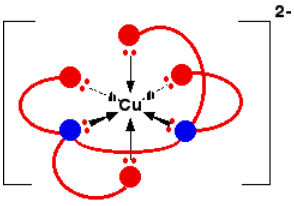
A Hexadentate Ligand

A hexadentate ligand has 6 lone pairs of electrons - all of which can form co-ordinate bonds with the same metal ion. The best example is EDTA, which is used as a negative ion - $EDTA^{4-}$. The diagram shows the structure of the ion with the important atoms and lone pairs picked out.



the $EDTA^{4-}$ ion

The EDTA ion entirely wraps up a metal ion using all 6 of the positions that we have seen before. The co-ordination number is again 6 because of the 6 co-ordinate bonds being formed by the central metal ion. The diagram below shows this happening with a copper(II) ion. Here is a simplified version. Make sure that you can see how this relates to the full structure above.



the $[Cu(EDTA)]^{2-}$ ion

The overall charge, of course, comes from the 2+ on the original copper(II) ion and the 4- on the $EDTA^{4-}$ ion.

Contributors and Attributions

- Jim Clark (Chemguide.co.uk)

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6.3: Coordination Numbers and Geometry

The total number of points of attachment to the central element is termed the **coordination number** and this can vary from 2 to as many as 16, but is usually 6. In simple terms, the coordination number of a complex is influenced by the relative sizes of the metal ion and the ligands and by electronic factors, such as charge which is dependent on the electronic configuration of the metal ion.

Introduction

Based on the radius ratio, it can be seen that the bigger the charge on the central ion, the more attraction there will be for negatively charged ligands, however at the same time, the bigger the charge the smaller the ion becomes which then limits the number of groups able to coordinate. It is important to recognize that every geometry has a specific coordination number, but every complex wish a specific coordination number will have a choice of several possible geometries (i.e., there is not a one-to-one correspondance between coordination number and geometry).

Coordination Number 2

This arrangement is not very common for first row transition metal ion complexes and some of the best known examples are for Silver(I). In this case we have a low charge and an ion at the right hand side of the d-block indicating smaller size

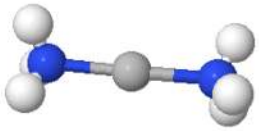


Figure 1: The linear $[Ag(NH_3)_2]^+$ ion

Coordination Number 3

Once again, this is not very common for first row transition metal ions. Examples with three different geometries have been identified:

- **Trigonal planar Geometry**: Well known for main group species like CO_3^{2-} etc., this geometry has the four atoms in a plane with the bond angles between the ligands at 120 degrees.

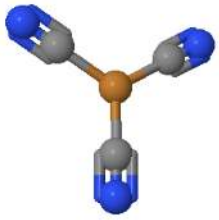


Figure 2: The Trigonal planar $[Cu(CN)_3]^{2-}$ system

- **Trigonal pyramid Geometry**: More common with main group ions.
- **T-shaped**: The first example of a rare T-shaped molecule was found in 1977.

Coordination Number 4

Two different geometries are possible. The tetrahedron is the more common while the square planar is found almost exclusively with metal ions having a d^8 electronic configuration.

- **Tetrahedral Geometry**: The chemistry of molecules centered around a tetrahedral C atom is covered in organic courses. To be politically correct, please change all occurrences of C to Co. There are large numbers of tetrahedral Cobalt(II) complexes known.

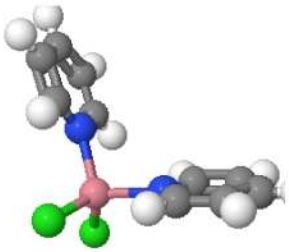


Figure 3: $CoCl_2pyr_2$

- **Square Planar Geometry:** This is fairly rare and is included only because some extremely important molecules exist with this shape.

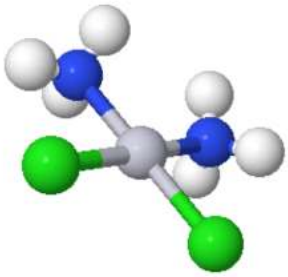


Figure 4: cisplatin - cis-$PtCl_2(NH_3)_2$

Coordination Number 5

- **Square pyramid Geometry:** Oxovanadium salts (Vanadyl, VO^{2+}) often show square pyramidal geometry, for example, $VO(acac)_2$. Note that the Vanadium(IV) can be considered coordinatively unsaturated and addition of pyridine leads to the formation of an octahedral complex.
- **Trigonal Bipyramid Geometry:** The structure of $[Cr(en)_3][Ni(CN)_5]$ 1.5 H_2O was reported in 1968 to be a remarkable example of a complex exhibiting both types of geometry in the same crystal. The reaction of cyanide ion with Ni^{2+} proceeds via several steps:

$$Ni^{2+} + 2CN^- \rightarrow Ni(CN)_2$$

$$Ni(CN)_2 + 2CN^- \rightarrow \underset{\text{orange-red}}{[Ni(CN)_4]^{2-}}$$

with $\log(\beta_4) = 30.1$

$$[Ni(CN)_4]^{2-} + CN^- \rightarrow \underset{\text{deep red}}{[Ni(CN)_5]^{3-}}$$

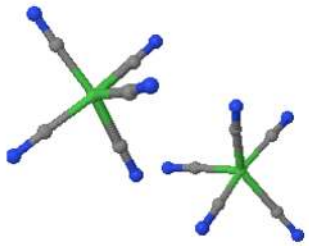


Figure 5: $[Ni(CN)_5]^{3-}$

Coordination Number 6

- **Hexagonal planar Geometry**: Unknown for first row transition metal ions, although the arrangement of six groups in a plane is found in some higher coordination number geometries.

- **Trigonal prism Geometry**: Most trigonal prismatic compounds have three bidentate ligands such as dithiolates or oxalates and few are known for first row transition metal ions.
- **Octahedral (Oh):** The most common geometry found for first row transition metal ions, including all aqua ions. In some cases distortions are observed and these can sometimes be explained in terms of the Jahn-Teller Theorem.

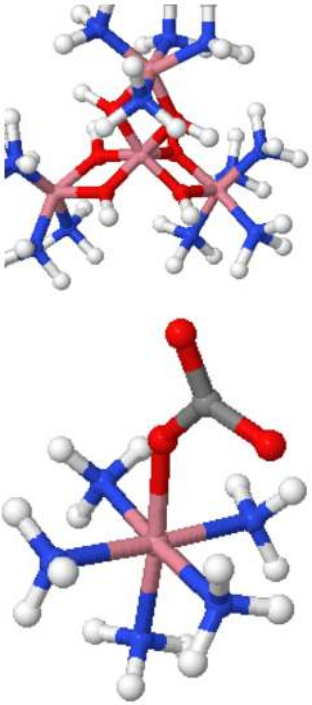


Figure 6: $[Co(en)_3]Cl_3$(left) and $[CoCO_3(NH_3)_5]^+$ (right)

Coordination Number 7

Not very common for 1st row complexes and the energy difference between the structures seems small and distortions occur so that prediction of the closest "idealized" shape is generally difficult. Three geometries are possible:

- **Capped octahedron (C_{3v}) Geometry**

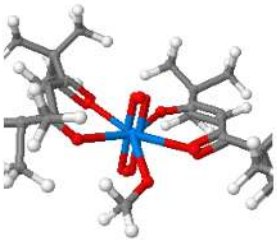


Figure 7: $K_3[NbOF_6]$

- **Capped trigonal prism (C_{2v})**
- **Pentagonal Bipyramid (D_{5h})**

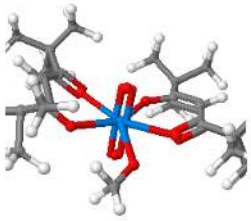


Figure 8: bis-(tert-butylacac)$_2$(DMSO)di-oxoUranium

Coordination Number 8

- **Dodecahedron (D_{2d}) Geometry**
- **Cube (O_h) Geometry**
- **Square antiprism (D_{4d}) Geometry**
- **Hexagonal bipyramid (D_{6h}) Geometry**

Coordination Number 9

- **Three-face centered trigonal prism (D_{3h}) Geometry**

Coordination Number 10

- **Bicapped square antiprism (D_{4d}) Geometry**

Coordination Number 11

- **All-faced capped trigonal prism (D_{3h}) Geometry: This is not a common stereochemistry.**

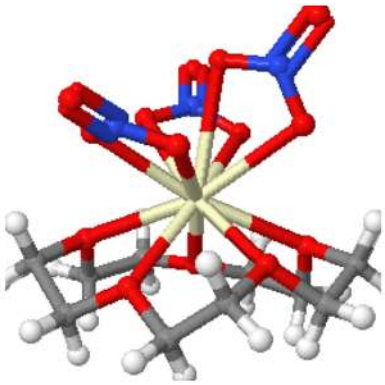


Figure 9*: aqua-(12-crown-4)-tris(nitrato-O,O')-cerium(III) (12-crown-4) solvate and (15-crown-5)-tris(nitrato-O,O')-cerium(III) the Cerium ion is 11 coordinate.*

Coordination Number 12

- **cuboctahedron (O_h) Geometry**

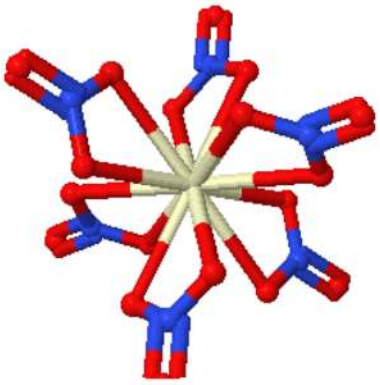


Figure 10: Ceric ammonium nitrate -$(NH_4)_2Ce(NO_3)_6$

Contributors and Attributions

- Prof. Robert J. Lancashire (The Department of Chemistry, University of the West Indies)

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SECTION OVERVIEW

6.4: Isomers

There are several types of this isomerism frequently encountered in coordination chemistry and the following represents some of them. Isomers that contain the same number of atoms of each kind but differ in which atoms are bonded to one another are called structural isomers, which differ in structure or bond type. For inorganic complexes, there are three types of structural isomers: *ionization*, *coordination*, and *linkage* and two types of stereoisomers: *geometric and optical*.

Structural isomers, as their name implies, differ in their structure or bonding, which are separate from **stereoisomers** that differ in the spatial arrangement of the ligands are attached, but still have the bonding properties. The different chemical formulas in structural isomers are caused either by a difference in what ligands are bonded to the central atoms or how the individual ligands are bonded to the central atoms. When determining a structural isomer, you look at: (1) the ligands that are bonded to the central metal, and (2) which atom of the ligands attach to the central metal. Below is a quick look at the different types of structural isomers. The highlighted ions are the ions that switch or change somehow to make the type of structural isomer it is.

6.4.1: Geometric Isomerism

6.4.1.1: Cis-platin

6.4.2: Optical Isomers in Inorganic Complexes

6.4.2.1: Optical Isomers- Enantiomers with Bidentate Ligands

6.4.3: Coordination Isomerism

6.4.4: Linkage Isomerism

6.4.5: Ionization Isomerism

6.4.6: Structural Isomerism - Hydration Isomers

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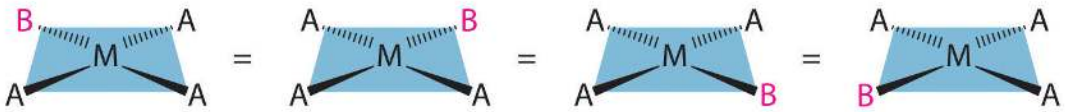
6.4.1: Geometric Isomerism

Geometric Isomers are isomers that differ in the arrangement of the ligands around the metal or the central atom. In other words, these isomers differ from each other based on where the ligands are placed in the coordinate compound. This will be much easier to understand as examples will be considered. There are 2 main types of geometric isomers:

- Cis-Trans Isomers (referencing the spatial arrangement of two species)
- Mer-Fac Isomers (referencing the spatial arrangement of three species)

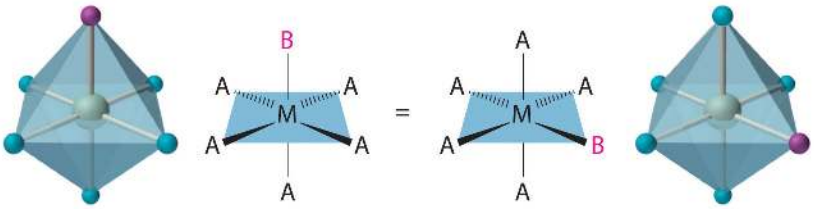
Identical Complexes

Because all vertices of a square are equivalent, it does not matter which vertex is occupied by the ligand B in a square planar MA_3B complex; hence only a single geometrical isomer is possible in this case (and in the analogous MAB_3 case). All four structures shown here are chemically identical because they can be superimposed simply by rotating the complex in space:



MA_3B square planar complex

Octahedral complexes also exhibit cis and trans isomers. Like square planar complexes, only one structure is possible for octahedral complexes in which only one ligand is different from the other five (MA_5B). Even though we usually draw an octahedron in a way that suggests that the four “in-plane” ligands are different from the two “axial” ligands, in fact all six vertices of an octahedron are equivalent. Consequently, no matter how we draw an MA_5B structure, it can be superimposed on any other representation simply by rotating the molecule in space. Two of the many possible orientations of an MA_5B structure are as follows:



MA_5B octahedral complex

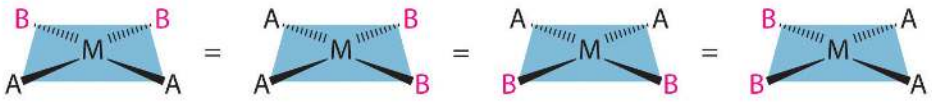
Cis-Trans Isomers

Cis-Trans Isomers are isomers that differ in the arrangement of two ligands in square planar and octahedral geometry. Cis isomers are isomers where the two ligands are 90 degrees apart from one another in relation to the central molecule. This is because Cis isomers have a bond angle of 90°, between two same atoms. Trans isomers, on the other hand, are isomers where the two ligands are on opposite sides in a molecule because trans isomers have a bond angle of 180°, between the two same atoms. When naming cis or trans isomers, the name begins either with cis or trans, whichever applies, followed by a hyphen and then the name of a molecule. For example a cis isomer of $CoCl_2F_2$ would be called cis-$CoCl_2F_2$. Finally, the last thing to keep in mind when examining cis and trans isomers is that **only square planar and octahedral** geometries can have cis or trans isomers. Examples of both isomers are provided below.

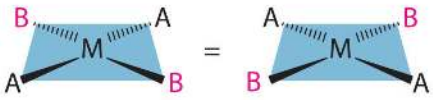
Square Planar

For an MA_2B_2 complex, there are two possible isomers: either the A ligands can be adjacent to one another (cis), in which case the B ligands must also be cis, or the A ligands can be across from one another (trans), in which case the B ligands must also be trans.

Even though it is possible to draw the cis isomer in four different ways and the trans isomer in two different ways, all members of each set are chemically equivalent. Because there is no way to convert the cis structure to the trans by rotating or flipping the molecule in space, they are fundamentally different arrangements of atoms in space.



MA_2B_2 square planar complex, *cis* isomer

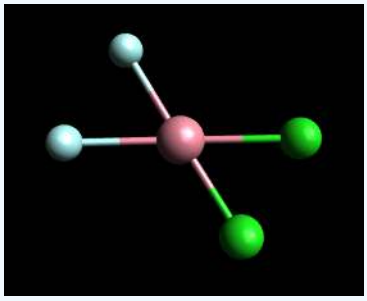


MA_2B_2 square planar complex, *trans* isomer

Example 6.4.1.1: cis Isomer

$CoCl_2F_2$:

(Color scheme: pink=cobalt, blue=fluorine, green=chlorine)



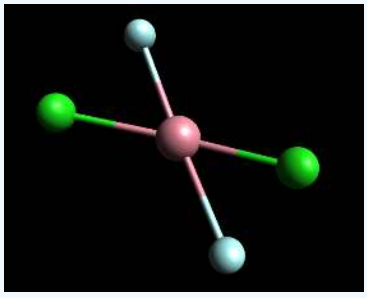
This above is an example of the molecule cis-$CoCl_2F_2$ or cis-dichlorodifluorocobalt (IV). The molecule pictured above is a cis isomer because both fluorine and chlorine ligands, respectively, are on the same side of the molecule. Additionally, one can approximate that the bond angle between each of the chlorine atoms and between each of the fluorine atoms is 90°.

Isomer

$CoCl_2F_2$:

(Color scheme: pink=cobalt, blue=fluorine, green=chlorine)

(Note, the differences in the length of the bond between the two pictures are not intentional and have nothing to do with cis-trans isomerism)

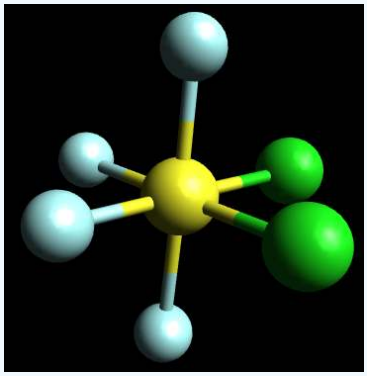


This above is an example of the molecule trans-$CoCl_2F_2$ or trans-dichlorodifluorocobalt (IV).

We know the above molecule is a trans isomer because the two same chlorine atoms and the two same fluorine atoms are opposite each other. Furthermore, the bond angle between the two chlorine atoms and between the two fluorine atoms is 180°. The above examples were all for square planar geometry but as the examples below illustrate, cis-trans isomerism can also occur in octahedral geometry. Both the molecules below are isomers of the molecule SCl_2F_4 (color scheme: yellow=sulfur, blue=fluorine, green=chlorine).

Example 6.4.1.3: Octahedral cis Isomer

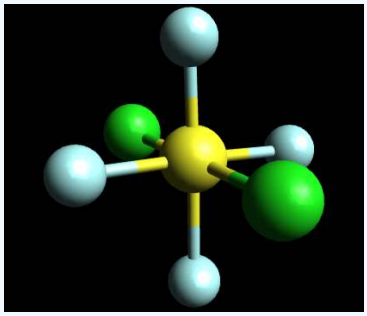
SCl_2F_4:



We know this isomer above is a cis isomer because both the chlorine ligands are on the same side and the bond angle between the chlorine atoms appears to be 90°.

Example 6.4.1.4: Octahedral trans Isomer

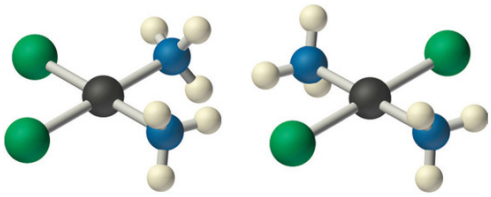
SCl_2F_4:



The isomer above is a trans isomer because the chlorine ligands are on opposite sides and the bond angle between the chlorine atoms is 180°. All other isomers are essentially just rotations of these two isomers. Once again when trying to find cis and trans isomers look at the arrangement of the ligands. If two same ligands are on the same side, it is a cis isomer and if the ligands are on opposite sides, it is a trans isomer. Another way to tell the isomers apart is the bond angles: cis isomers have a 90° bond angle whereas trans isomers have a 180° bond angle.

Cis-Platin

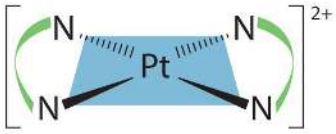
Probably the best-known examples of cis and trans isomers of an MA_2B_2 square planar complex are cis-$Pt(NH_3)_2Cl_2$, also known as cisplatin, and trans-$Pt(NH_3)_2Cl_2$, which is actually toxic rather than therapeutic.



cis-$Pt(NH_3)_2Cl_2$ *trans*-$Pt(NH_3)_2Cl_2$

The anticancer drug cisplatin and its inactive trans isomer. Cisplatin is especially effective against tumors of the reproductive organs, which primarily affect individuals in their 20s and were notoriously difficult to cure. For example, after being diagnosed with metastasized testicular cancer in 1991 and given only a 50% chance of survival, Lance Armstrong was cured by treatment with cisplatin.

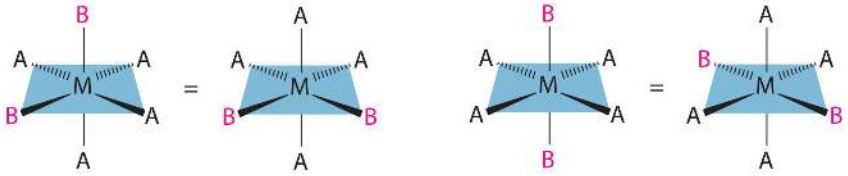
Square planar complexes that contain symmetrical bidentate ligands, such as $[Pt(en)_2]^{2+}$, have only one possible structure, in which curved lines linking the two N atoms indicate the ethylenediamine ligands:



$[Pt(en)_2]^{2+}$

Octahedral

If two ligands in an octahedral complex are different from the other four, giving an MA_4B_2 complex, two isomers are possible. The two B ligands can be cis or trans. Cis- and trans-$[Co(NH_3)_4Cl_2]Cl$ are examples of this type of system:



MA_4B_2 octahedral complex, *cis* isomer **MA_4B_2 octahedral complex, *trans* isomer**

Example 6.4.1.1

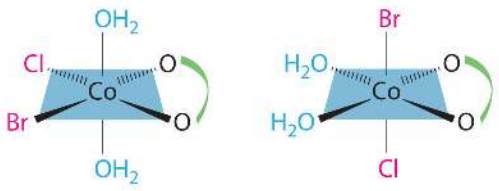
Draw all the possible geometrical isomers for the complex $[Co(H_2O)_2(ox)BrCl]^-$, where ox is $^-O_2CCO_2^-$, which stands for oxalate.

Given: formula of complex

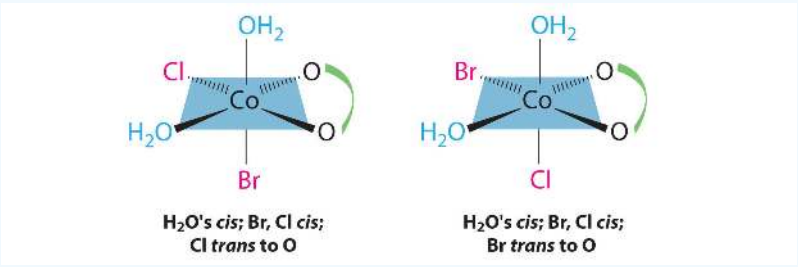
Asked for: structures of geometrical isomers

Solution

This complex contains one bidentate ligand (oxalate), which can occupy only adjacent (cis) positions, and four monodentate ligands, two of which are identical (H_2O). The easiest way to attack the problem is to go through the various combinations of ligands systematically to determine which ligands can be trans. Thus either the water ligands can be trans to one another or the two halide ligands can be trans to one another, giving the two geometrical isomers shown here:



In addition, two structures are possible in which one of the halides is trans to a water ligand. In the first, the chloride ligand is in the same plane as the oxalate ligand and trans to one of the oxalate oxygens. Exchanging the chloride and bromide ligands gives the other, in which the bromide ligand is in the same plane as the oxalate ligand and trans to one of the oxalate oxygens:

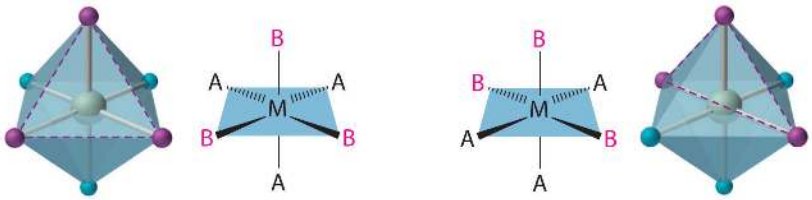


This complex can therefore exist as four different geometrical isomers.

Mer-Fac Isomers

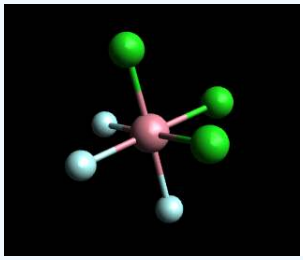
Mer-Fac isomers are easier to notice than cis-trans isomers in the sense that they only exist in octahedral geometry. Just like cis-trans isomers, mer-fac isomers are determined based on whether or not the ligands exist on the same side. Instead of dealing with 2 ligands, mer-fac isomers deal with 3 ligands. If the 3 ligands are all on the same side, the isomer is called a fac-isomer. Another way to identify fac isomers is to look at the bond angle between the ligands because fac isomers have a 90° bond angle between each of the 3 atoms. The mer isomer on the other hand is where only 2 of the 3 ligands are on the same side. In mer isomers, there exists a 90°-90°-180° bond angle between the 3 same ligands. In terms of nomenclature, mer-fac isomers follow the same rule as cis-trans isomers where you put the isomer type, followed by a hyphen, followed by the molecular formula. Examples have been provided below.

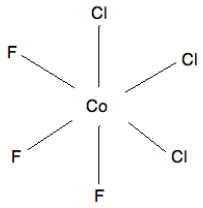
Replacing another A ligand by B gives an MA_3B_3 complex for which there are also two possible isomers. In one, the three ligands of each kind occupy opposite triangular faces of the octahedron; this is called the fac isomer (for facial). In the other, the three ligands of each kind lie on what would be the meridian if the complex were viewed as a sphere; this is called the mer isomer (for meridional):



Example 6.4.1.5: fac Isomer

Below is an example of the fac isomer, fac-$CoCl_3F_3$:



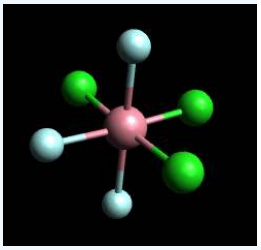


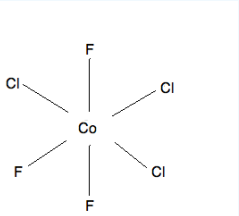
(note the color scheme: pink=cobalt, green=chlorine, blue=fluorine)

Through the 2d version, it is easier to see how the ligands are all on the same side. Nonetheless, in the 3D version, one can observe that the bond angle between the 3 same ligands is 90°, thus making this isomer a fac-isomer.

Example 6.4.1.6: mer Isomer

Below is an example of the mer isomer, mer-$CoCl_3F_3$:





(note the color scheme: pink=cobalt, green=chlorine, blue=fluorine)

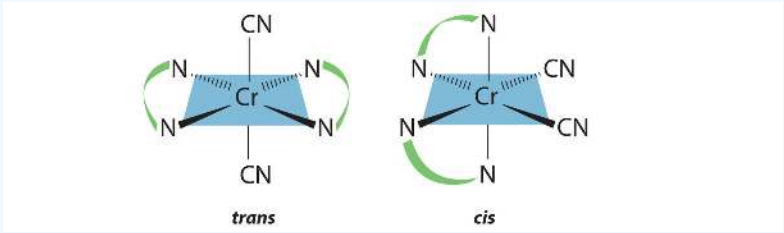
Its hard to tell in the 3D version but in the 2D version, one can easily tell how the same ligands are not on the same side. Additionally, one can approximate that the bond angle between the three chlorine atoms and between the three fluorine atoms is 90°-90°-180°, thus making the above molecule a mer isomer.

Problems

Exercise 6.4.1.1

Draw all the possible geometrical isomers for the complex $[Cr(en)_2(CN)_2]^+$.

Answer



Two geometrical isomers are possible: trans and cis.

Contributors and Attributions

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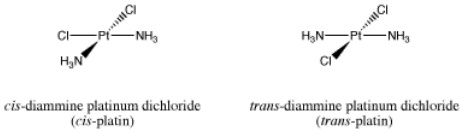
6.4.1.1: Cis-platin

Learning Objectives

- To understand that there may be more than one way to arrange the same groups around the same atom with the same geometry (stereochemistry).

Two compounds that have the same formula and the same connectivity do not always have the same shape. There are two reasons why this may happen. In one case, the molecule may be flexible, so that it can twist into different shapes via rotation around individual sigma bonds. This phenomenon is called conformation, and it is covered in a different chapter. The second case occurs when two molecules appear to be connected the same way on paper, but are connected in two different ways in three dimensional space. These two, different molecules are called **stereoisomers**.

One simple example of stereoisomers from inorganic chemistry is diammine platinum dichloride, $(NH_3)_2PtCl_2$. This important compound is sometimes called "platin" for short. As the formula implies, it contains a platinum ion that is coordinated to two ammonia ligands and two chloride ligands (remember, a ligand in inorganic chemistry is an electron donor that is attached to a metal atom, donating a pair of electrons to form a bond).



cis-diammine platinum dichloride (*cis*-platin) *trans*-diammine platinum dichloride (*trans*-platin)

Figure SC2.1. Two stereoisomers. The atoms are connected to each other in the same order, but differ in their three-dimensional relationships. (left) The cis-Platin compound is square planar at platinum and is flat when viewed from the edge, and square when viewed from the face. (right) The trans-Platin compound is connected in the same way as in cis-platin, and is still square planar, but there is a different 3-dimensional arrangement

Platin is an example of a coordination compound. The way the different pieces of coordination compounds bond together is discussed in the chapter of Lewis acids and bases. For reasons arising from molecular orbital interactions, platin has a square planar geometry at the platinum atom. That arrangement results in two possible ways the ligands could be connected. The two sets of like ligands could be connected on the same side of the square or on opposite corners.

These two arrangements result in two different compounds; they are isomers that differ only in three-dimensional space.

- The one with the two amines beside each other is called cis-platin.
- These two ligands are 90 degrees from each other.
- The one with the amines across from each other is trans-platin.
- These two ligands are 180 degrees from each other.

CIS/TRANS isomers have different physical properties

Although these two compounds are very similar, they have slightly different physical properties. Both are yellow compounds that decompose when heated to 270 degrees C, but trans-platin forms pale yellow crystals and is more soluble than cis-platin in water.

CIS/TRANS isomers have different biological properties

Cis-platin has clinical importance in the treatment of ovarian and testicular cancers. The biological mechanism of the drug's action was long suspected to involve binding of the platinum by DNA. Further details were worked out by MIT chemist Steve Lippard and graduate student Amy Rosenzweig in the 1990's. Inside the cell nucleus, the two ammines in cis-platin can be replaced by nitrogen donors from a DNA strand. To donate to the Lewis acidic platinum, the DNA molecule must bend slightly. Normally that bend is detected and repaired by proteins in the cell. However, ovarian and testicular cells happen to contain a protein that is just the right shape to fit around this slightly bent DNA strand. The DNA strand becomes lodged in the protein and can't be displaced, and so it is unable to bind with other proteins used in DNA replication. The cell becomes unable to replicate, and so cancerous growth is stopped.

Exercise SC2.1

Draw the cis and trans isomers of the following compounds:

a. $(NH_3)_2IrCl(CO)$
b. $(H_3P)_2PtHBr$
c. $(AsH_3)_2PtH(CO)$

Exercise SC2.2

Only one isomer of (tmeda)$PtCl_2$ is possible [tmeda = $(CH_3)_2NCH_2CH_2N(CH_3)_2$; both nitrogens connect to the platinum]. Draw this isomer and explain why the other isomer is not possible.

Contributors and Attributions

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6.4.2: Optical Isomers in Inorganic Complexes

Optical activity refers to whether or not a compound has optical isomers. A coordinate compound that is optically active **has** optical isomers and a coordinate compound that is not optically active does **not have** optical isomers. As we will discuss later, optical isomers have the unique property of rotating light. When light is shot through a polarimeter, optical isomers can rotate the light so it comes out in a different direction on the other end. Armed with the knowledge of symmetry and mirror images, optical isomers should not be very difficult. There are two ways optical isomers can be determined: using mirror images or using planes of symmetry.

Optical isomers do not exhibit symmetry and do not have identical mirror images. Let's go through a quick review of symmetry and mirror images. A *mirror image* of an object is that object flipped or the way the object would look in front of a mirror. For example, the mirror image of your left hand would be your right hand. Symmetry on the other hand refers to when an object looks exactly the same when sliced in a certain direction with a plane. For example imagine the shape of a square. No matter in what direction it is sliced, the two resulting images will be the same.

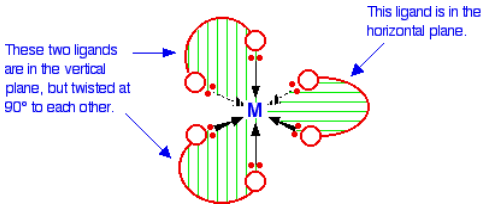
Method 1: The "Mirror Image Method"

The mirror images method uses a mirror image of the molecule to determined whether optical isomers exist or not. If the mirror image **can** be rotated in such a way that it looks identical to the original molecule, then the molecule is said to be superimposable and has no optical isomers. On the other hand, if the mirror image **cannot** be rotated in any way such that it looks identical to the original molecule, then the molecule is said to be non-superimposable and the molecule has optical isomers. Once again, if the mirror image is superimposable, then no optical isomers but if the mirror image is non-superimposable, then optical isomers exist.

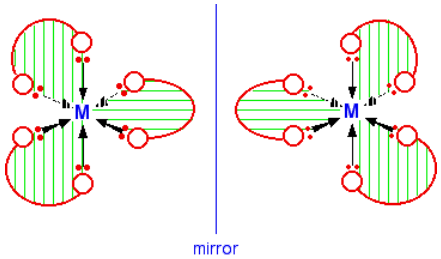
Definition: Non-superimposable

Non-superimposable means the structure cannot be rotated in a way that one can be put on top of another. This means that no matter how the structure is rotated, it cannot be put on top of another with all points matching. An example of this is your hands. Both left and right hands are identical, but they cannot be put on top of each other with all points matching.

The examples you are most likely to need occur in octahedral complexes which contain bidentate ligands - ions like $[Ni(NH_2CH_2CH_2NH_2)_3]^{2+}$ or $[Cr(C_2O_4)_3]^{3-}$. The diagram below shows a simplified view of one of these ions. Essentially, they all have the same shape - all that differs is the nature of the "headphones".



A substance with *no plane of symmetry is going to have optical isomers* - one of which is the mirror image of the other. One of the isomers will rotate the plane of polarization of plane polarised light clockwise; the other rotates it counter-clockwise. In this case, the two isomers are:



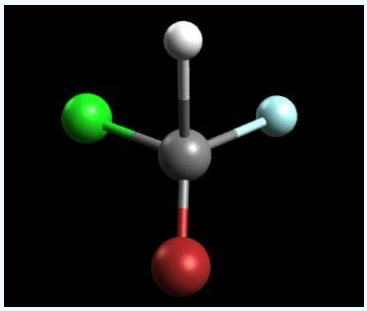
You may be able to see that there is no way of rotating the second isomer in space so that it looks exactly the same as the first one. As long as you draw the isomers carefully, with the second one a true reflection of the first, the two structures will be different.

Method 2: The "Plane of Symmetry Method"

The plane of symmetry method uses symmetry, as it's name indicates, to identify optical isomers. In this method, one tries to see if such a plane exists which when cut through the coordinate compound produces two exact images. In other words, one looks for the existence of a plane of symmetry within the coordinate compound. If a plane of symmetry exists, then no optical isomers exist. On the other hand, if there is no plane of symmetry, the coordinate compound has optical isomers. Furthermore, if a plane of symmetry exists around the central atom, then that molecule is called **achiral** but if a plane of symmetry does not exist around the central molecule, then that molecule has chiral center.

Example 6.4.2.1: CHBrClF

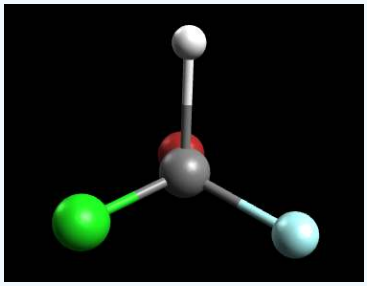
Consider the tetrahedral molecule, CHBrClF (note the color scheme: grey=carbon, white=hydrogen, green=chlorine, blue=fluorine, red=bromine)



Is this molecule optically active? In other words, does this molecule have optical isomers?

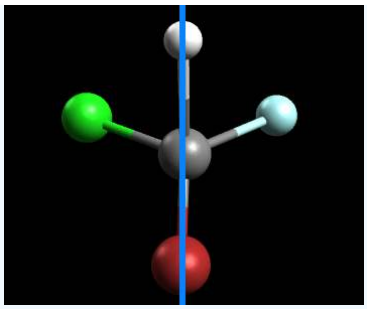
Solution

First take the Mirror-image method. The mirror image of the molecule is:



Note that this mirror image is not superimposable. In other words, the mirror image above cannot be rotated in any such way that it looks identical to the original molecule. Remember, if the mirror image is not superimposable, then optical isomers exist. Thus we know that this molecule has optical isomers.

Let's try approaching this problem using the symmetry method. If we take the original molecule and draw an axis or plane of symmetry down the middle, this is what we get:



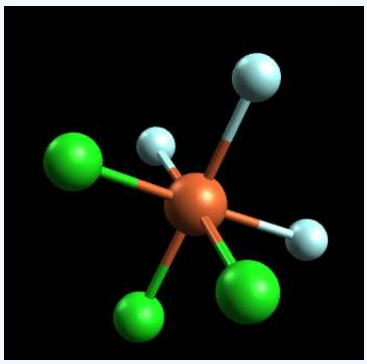
Since the left side is not identical to the right, this molecule does not have a symmetrical center and thus can be called chiral.Additionally, because it does not have a symmetrical center, we can conclude that this molecule has optical isomers. In general, when dealing with a tetrahedral molecule that has 4 different ligands, optical isomers will exist most of the time.

No matter which method you use, the answer will end up being the same.

Optical isomers because they have no plane of symmetry. In the organic case, for tetrahedral complexes, this is fairly easy to recognize the possibility of this by looking for a center atom with **four** different things attached to it. Unfortunately, this is not quite so easy with more complicated geometries!

Example 6.4.2.1: $PFeCl_3F_3$

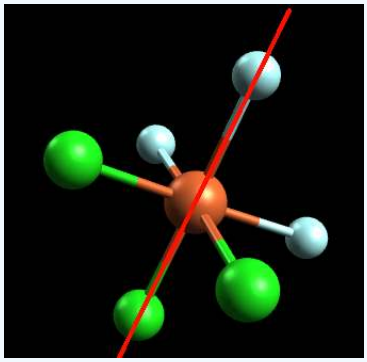
This time we will be analyzing the octahedral compound $FeCl_3F_3$. Is this molecule optically active?



(note the color scheme: orange=iron, blue=fluorine, green=chlorine):

Solution

If we try to attempt this problem using the mirror image method, we notice that the mirror image is essentially identical to the original molecule. In other words, the mirror image can be placed on top of the original molecule and is thus superimposable. Since the mirror image is superimposable, this molecule does not have any optical isomers. Let's attempt this same problem using the symmetry method. If we draw an axis or plane of symmetry, this is what we get:



> Since the left side is identical to the right side, this molecule has a symmetrical center and is an achiral molecule. Thus, it has no optical isomers.

What is a Polarimeter?

A polarimeter is a scientific instrument used to measure the angle of rotation caused by passing polarized light through an optically active substance. Some chemical substances are optically active, and polarized (uni-directional) light will rotate either to the left (counter-clockwise) or right (clockwise) when passed through these substances. The amount by which the light is rotated is known as the *angle of rotation*. The angle of rotation is basically known as observed angle.

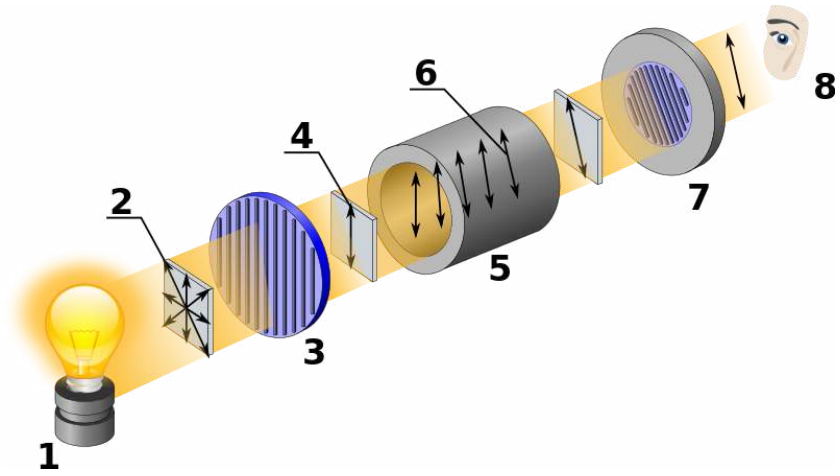


Figure **6.4.2.1**: Schematic of a polarimeter showing the principles behind it's operation. Unpolarized light is passed through a polarizing filter before traveling through a sample. The degree of rotation of polarization is determined by a second, rotatable filter. (CC AS 3.0; Kaidor).

The polarimeter is made up of a polarizer (#3 on Figure **6.4.2.1**) and an analyzer (#7 on Figure **6.4.2.1**). The polarizer allows only those light waves which move in a single plane. This causes the light to become plane polarized. When the analyzer is also placed in a similar position it allows the light waves coming from the polarizer to pass through it. When it is rotated through the right angle no waves can pass through the right angle and the field appears to be dark. If now a glass tube containing an optically active solution is placed between the polarizer and analyzer the light now rotates through the plane of polarization through a certain angle, the analyzer will have to be rotated in same angle.

Contributors and Attributions

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6.4.2.1: Optical Isomers- Enantiomers with Bidentate Ligands

Enantiomers are another kind of isomer that occur in octahedral metal complexes. Like the square planar platinum complexes seen before, these compounds consist of metal ions with other atoms or groups bound to them. More information about the binding of ligands to metals is found in the section on Lewis acids and bases. These groups that bind to metal ions are called ligands. One example of a type of octahedral compounds that can form enantiomers is bidentate complexes. In bidentate complexes (from the Greek two teeth) or chelating complexes (from the Greek crab), a ligand binds very tightly to the metal because it holds onto the metal via more than one atom. Ethylenediamine is one example of a bidentate ligand.



Figure SC18a: Ethylenediamine (sometimes abbreviated en).

Bidentate ligands bind very tightly to a metal because they form two bonds with it, rather than just one.

> *In an octahedral complex, the two donor atoms in a bidentate ligand bind **cis** to each other. They **cannot** reach all the way around the molecule to bind trans to each other.*

The spatial relationship between the metal and the two atoms connected to it from the same ligand forms a plane. If more than one bidentate ligand is connected to the metal, the relative orientation of one plane to another creates the possibility of mirror images. A complex containing three bidentate ligands can take on the shape of a left-handed propeller or a right-handed propeller.



Figure SC18b. A left-handed propeller shape (left) is seen in Λ isomers of octahedral enantiomers. A right-handed propeller (right) is seen in Δ isomers of octahedral enantiomers.

These shapes are alternatively described as a left-handed screw and a right handed screw. If you can picture turning the shape so that it screws into the page behind it, which direction would you turn the screwdriver? If you would twist the screwdriver clockwise, then you have a right handed screw. If you would twist the screwdriver counter-clockwise, then you have a left handed screw.

What do we know about enantiomers?

- enantiomers have identical physical properties, except...
- enantiomers have opposite optical rotation.

These kinds of complexes were historically important in demonstrating how small molecules and ions bound to metal cations. By showing that some metal complexes were chiral and displayed optical activity, early 20th century workers such as Alfred Werner were able to rule out some competing ideas about the structures of metal compounds. Today, we know that metal complexes play important roles in enzymes in biology, and Werner's work on metal complexes laid the groundwork for how we think about these complexes.

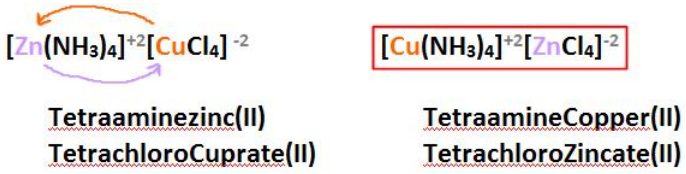
In addition, stereochemistry in metal complexes became very important in the late 20th century, especially as pharmaceutical companies looked for catalysts that could aid in the production of one enantiomer of a drug, and not the other, in order to maximize pharmaceutical effectiveness and minimize side effects.

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6.4.3: Coordination Isomerism

Coordination isomerism occurs in compounds containing complex anionic and cationic parts and can be viewed as the interchange of one or more ligands between the cationic complex ion and the anionic complex ion. For example, $[Co(NH_3)_6][Cr(CN)_6]$ is a coordination isomer with $[Cr(NH_3)_6][Co(CN)_6]$. Alternatively, coordination isomers may be formed by switching the metals between the two complex ions like $[Zn(NH_3)_4][CuCl_4]$ and $[Cu(NH_3)_4][ZnCl_4]$.



? Exercise 6.4.3.1

Are $[Cu(NH_3)_4][PtCl_4]$ and $[Pt(NH_3)_4][CuCl_4]$ coordination isomers?

Solution

Here, both the cation and anion are complex ions. In the first isomer, NH_3 is attached to the copper and the Cl^- are attached to the platinum. In the second isomer, they have swapped.

Yes, they are coordination isomers.

? Exercise 6.4.3.2

What is one coordination isomer of $[Co(NH_3)_6]$ $[Cr(C_2O_4)_3]$?

Solution

Coordination isomers involve swapping the species from the inner coordination sphere to one metal (e.g, cation) to inner coordination sphere of a different metal (e.g., the anion) in the compound. One isomer is completely swapping the ligand sphere, e.g, $[Co(C_2O_4)_3]$ $[Cr(NH_3)_6]$.

Alternative coordination isomers are $[Co(NH_3)_4(C_2O_4)]$ $[Cr(NH_3)_2(C_2O_4)_2]$ and $[Co(NH_3)_2(C_2O_4)_2]$ $[Cr(NH_3)_4(C_2O_4)]$.

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6.4.4: Linkage Isomerism

Linkage isomerism occurs with *ambidentate* ligands that are capable of coordinating in more than one way. The best known cases involve the monodentate ligands: SCN^-/NCS^- and NO_2^-/ONO^-. The only difference is what **atoms the molecular ligands bind to the central ion**. The ligand(s) must have more than one donor atom, but bind to ion in only one place. For example, the (NO_2^-) ion is a ligand can bind to the central atom through the nitrogen or the oxygen atom, but cannot bind to the central atom with both oxygen and nitrogen at once, in which case it would be called a *polydentate* rather than an *ambidentate* ligand.

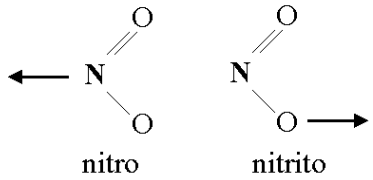
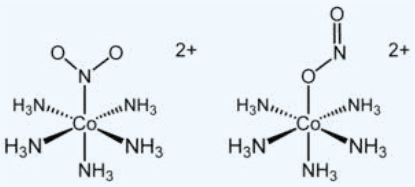


Figure 6.4.4.1: Linkage Isomerism in the NO_2 ligand. This occurs when a particular ligand is capable of coordinating to a metal in two different and distinct ways. from Angel C. de Dios.

The names used to specify the changed ligands are changed as well. For example, the (NO_2^-) ion is called *nitro* when it binds with the N atom and is called *nitrito* when it binds with the O atom.

Example 6.4.4.1: Nitro- vs. Nitrito- Linkage Isomers

The cationic cobalt complex $[Co(NH_3)_5(NO_2)]Cl_2$ exists in two separable linkage isomers of the complex ion: $(NH_3)_5(NO_2)]^{2+}$.



(left) The nitro isomer (Co-NO_2) and (right) the nitrito isomer (Co-ONO)

When donation is from nitrogen to a metal center, the complex is known as a *nitro-* complex and when donation is from one oxygen to a metal center, the complex is known as a *nitrito-* complex. An alternative formula structure to emphasize the different coordinate covalent bond for the two isomers

- $[Co(ONO)(NH_3)_5]Cl$: the *nitrito* isomer -O attached
- $[Co(NO_2)(NH_3)_5]Cl$: the *nitro* isomer - N attached.

The formula of the complex is unchanged, but the properties of the complex may differ.

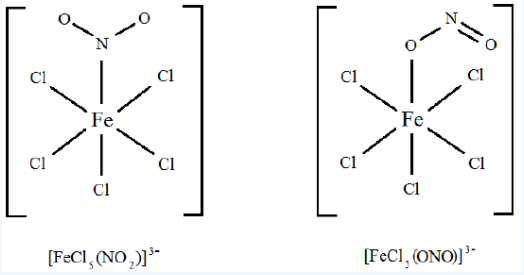
Another example of an ambidentate ligans is thiocyanate, SCN^-, which can attach at either the sulfur atom or the nitrogen atom. Such compounds give rise to linkage isomerism. Polyfunctional ligands can bond to a metal center through different ligand atoms to form various isomers. Other ligands that give rise to linkage isomers include selenocyanate, $SeCN^-$ – isoselenocyanate, $NCSe^-$ and sulfite, SO_3^{2-}.

Exercise 6.4.4.1

Are $[FeCl_5(NO_2)]^{3-}$ and $[FeCl_5(ONO)]^{3-}$ linkage isomers?

Solution

Here, the difference is in how the ligand bonds to the metal. In the first isomer, the ligand bonds to the metal through an electron pair on the nitrogen. In the second isomer, the ligand bonds to the metal through an electron pair on one of the oxygen atoms. It's easier to see it:



Contributors and Attributions

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6.4.5: Ionization Isomerism

Coordination isomerism is a form of structural isomerism in which the composition of the complex ion varies. In a coordination isomer the total ratio of ligand to metal remains the same, but the ligands attached to a specific metal ion change. Ionization isomers can be thought of as occurring because of the formation of different ions in solution.

Introduction

Ionization isomers are identical except for a ligand has exchanged places with an anion or neutral molecule that was originally outside the coordination complex. The central ion and the other ligands are identical. For example, an octahedral isomer will have five ligands that are identical, but the sixth will differ. The non-matching ligand in one compound will be outside of the coordination sphere of the other compound. Because the anion or molecule outside the coordination sphere is different, the chemical properties of these isomers is different.

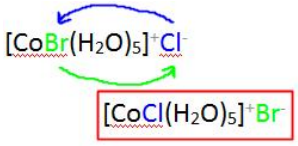


Figure **6.4.5.1**: Two Ionization isomers. The two isomers differ only which ligands are actually bound to the center metal. These two isomers are called pentaaqua**bromo**cobaltate(II) **chloride** and pentaaqua**chloro**cobaltate(II) **bromide**.

The difference between the ionization isomers can be viewed within the context of the ions generated when each are dissolved in solution.

For example, when pentaaquabromocobaltate(II)chloride is dissolved in water, Cl^- ions are generated:

$$CoBr(H_2O)_5Cl(s) \rightarrow CoBr(H_2O)_5^+(aq) + Cl^+(aq)$$

whereas when pentaaquachlorocobaltate(II)bromide is dissolved, Br^- ions are generated:

$$CoCl(H_2O)_5Br(s) \rightarrow CoCl(H_2O)_5^+(aq) + Br^+(aq).$$

Note

If one dissolved $[PtBr(NH_3)_3]NO_2$ and $[Pt(NO_2)(NH_3)_3]Br$ into solution, then two different set of ions will be general.

- Dissolving $[Pt(NO_2)(NH_3)_3]Br$ in aqueous solution would have the following reaction

$$[PtBr(NH_3)_3]NO_2(s) \rightarrow [PtBr(NH_3)_3]^+(aq) + NO_2^-(aq) \quad (6.4.5.1)$$

- Dissolving of $[Pt(NO_2)(NH_3)_3]Br$ in aqueous solution would be

$$[Pt(NO_2)(NH_3)_3]Br(s) \rightarrow [Pt(NO_2)(NH_3)_3]^+(aq) + Br^-(aq) \quad (6.4.5.2)$$

Notice that these two ionization isomers differ in that one ion is directly attached to the central metal, but the other is not.

Equations 6.4.5.1 and 6.4.5.2 are valid under the assumption that the platinum-ligand bonds of the complexes are stable (i.e., not labile). Otherwise, they may break and other ligands (e.g., water) may bind.

Example 6.4.5.1

Are $[Cr(NH_3)_5(OSO_3)]Br$ and $[Cr(NH_3)_5Br]SO_4$ coordination isomers?

Solution

First, we need confirm that each compound has the same number of atoms of the respective elements (this requires viewing both cations and anions of each compound).

Element	number of atoms in $[Cr(NH_3)_5(OSO_3)]Br$	number of atoms in $[Cr(NH_3)_5Br]SO_4$
Cr	1	1
N	5	5
H	15	15
O	4	4
S	1	1
Br	1	1

Now, let's look at what these two compounds look like (Figure **6.4.5.2**). The sulfate group is a ligand with a dative bond to the chromium atom and the bromide counter ion ($[Cr(NH_3)_5(OSO_3)]Br$). For $[Cr(NH_3)_5Br]SO_4$, this is the the reverse.

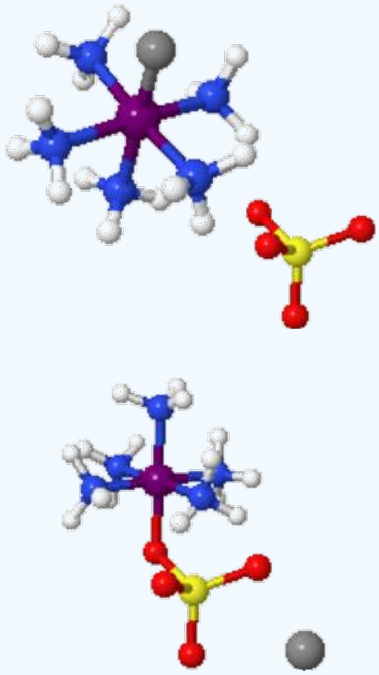


Figure **6.4.5.2**: $[Cr(NH_3)_5(OSO_3)]Br$ (left) and $[Cr(NH_3)_5Br]SO_4$ (right) are coordination isomers.

Yes, $[Cr(NH_3)_5(OSO_3)]Br$ and $[Cr(NH_3)_5Br]SO_4$ are coordination isomers.

? Exercise 6.4.5.1

Are $[Co(NH_3)_5(SO_4)]Br$ and $[Co(NH_3)_5Br]SO_4$ ionization isomers?

Solution

In the first isomer, SO_4 is attached to the Cobalt and is part of the complex ion (the cation), with Br as the anion. In the second isomer, Br is attached to the cobalt as part of the complex and SO_4 is acting as the anion.

A hydrate isomer is a specific kind of ionization isomer where a water molecule is one of the molecules that exchanges places.

Solvate or Hydrate Isomerization: A Special kind of Ionization Isomer

A very similar type of isomerism results from replacement of a coordinated group by a solvent molecule (*Solvate Isomerism*). In the case of water, this is called *Hydrate isomerism*. The best known example of this occurs for chromium chloride "$CrCl_3.6H_2O$" which may contain 4, 5, or 6 coordinated water molecules.

- $[CrCl_2(H_2O)_4]Cl \cdot 2H_2O$: bright-green colored
- $[CrCl(H_2O)_5]Cl_2 \cdot H_2O$: grey-green colored
- $[Cr(H_2O)_6]Cl_3$: violet colored

These isomers have very different chemical properties and on reaction with $AgNO_3$ to test for Cl^- ions, would find 1, 2, and 3 Cl^- ions in solution respectively.

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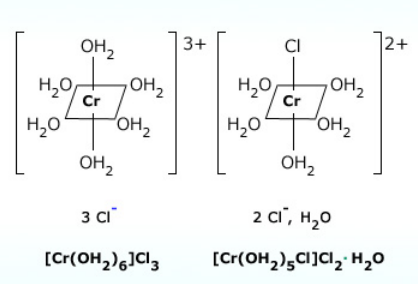
6.4.6: Structural Isomerism - Hydration Isomers

A very similar type of isomerism results from replacement of a coordinated group by a solvent molecule (*Solvate Isomerism*), which in the case of water is called *Hydrate Isomerism*. The best known example of this occurs for chromium chloride ($CrCl_3 \cdot 6H_2O$) which may contain 4, 5, or 6 coordinated water molecules (assuming a coordination number of 6). The dot here is used essentially as an expression of ignorance to indicate that, though the parts of the molecule separated by the dot are bonded to one another in some fashion, the exact structural details of that interaction are not fully expressed in the resulting formula. Using Alfred Werner's coordination theory that indicates that several of the water molecules are actually bonded directly (via coordinate covalent bonds) to the central chromium ion. In fact, there are several possible compounds that use the brackets to signify bonding in the complex and the the dots to signify "water molecules that are not bound to the central metal, but are part of the lattice:

- $[CrCl_2(H_2O)_4]Cl \cdot 2H_2O$: bright-green colored
- $[CrCl(H_2O)_5]Cl_2 \cdot H_2O$: grey-green colored
- $[Cr(H_2O)_6]Cl_3$: violet colored

These isomers have very different chemical properties and on reaction with $AgNO_3$ to test for Cl^- ions, would find 1, 2, and 3 Cl^- ions in solution, respectively.

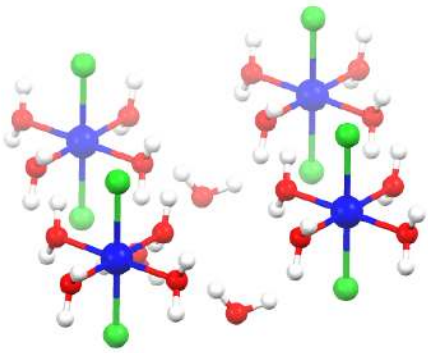
Upon crystallization from water, many compounds incorporate water molecules in their crystalline frameworks. These "waters of crystallization" refers to water that is found in the crystalline framework of a metal complex or a salt, which is **not directly bonded** to the metal cation. In the first two hydrate isomers, there are water molecules that are artifacts of the crystallization and occur inside crystals. These water of crystallization is the total weight of water in a substance at a given temperature and is mostly present in a definite (stoichiometric) ratio.



The $[Cr(H_2O)_6]Cl_3$ hydrate isomer (left) is violet colored and the $[CrCl(H_2O)_5]Cl_2 \cdot H_2O$ hydrate isomer is green-grey colored.

What are "Waters of Crystallization"?

A compound with associated water of crystallization is known as a hydrate. The structure of hydrates can be quite elaborate, because of the existence of hydrogen bonds that define polymeric structures. For example, consider the aquo complex $NiCl_2 \cdot 6H_2O$ that consists of separated *trans*-$[NiCl_2(H_2O)_4]$ molecules linked more weakly to adjacent water molecules. Only four of the six water molecules in the formula are bound to the nickel (II) cation, and the remaining two are waters of crystallization as the crystal structure resolves.



Structure of $NiCl_2 \cdot 6H_2O$ salt with chlorine atoms (green), water molecules (red), and Ni metals (blue) indicated. (CC BY-SA 4.0; Smokefoot).

Water is particularly common solvent to be found in crystals because it is small and polar. But *all* solvents can be found in some host crystals. Water is noteworthy because it is reactive, whereas other solvents such as benzene are considered to be chemically innocuous.

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6.5: Nomenclature of Coordination Complexes

Systems of nomenclature and formulae are intended as tools, to be employed insofar as they are useful

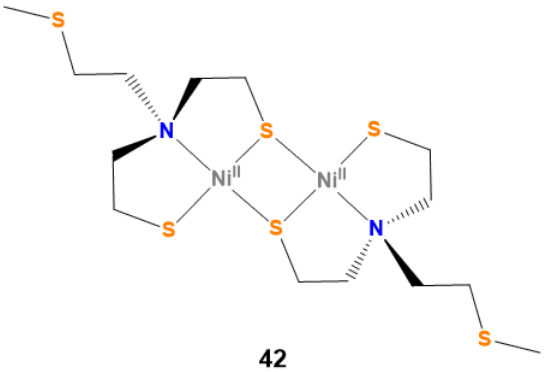
There are well-established rules for both naming and writing the formulae of coordination compounds. The purpose of these rules is to facilitate clear and precise communication among chemists. As with all such rules, some are more burdensome than others to employ, and some serve more crucial roles in the communication process while others are more peripheral - and all are poorly used in the service of pedantic tyranny, especially when used against those who are otherwise doing good work. For this reason, you are urged to approach the rules in a spirit of generosity towards others in

- naming and writing formulas as reasonably accurately as you can so that ligands and metals are where readers expect them and thus can understand what you mean more easily.
- being gracious towards the many professional inorganic chemists who adhere loosely to some of the rules you are about to learn.

recognizing that in cases when a structure is particularly complex and a picture may make be particularly useful, you should supply one (See the note below).

Note: Sometimes the most helpful name to give a compound is 42.

Even though the IUPAC nomenclature rules permit specification of even the most complex structures, it is often much easier and more effective to supply a numbered structure that can be referred to instead of the IUPAC name. Consider bis{[(μ-2-mercaptoethyl)(2-mercaptoethyl)-methylthioethylaminato (2-)]Nickel(II)}. Which is easier, to expect readers and hearers to work out the structure from that name or to just refer them to compound **42** in Figure **6.5.1**?



42

Figure **6.5.1**. Structure of bis{[(μ-2-mercaptoethyl)(2-mercaptoethyl)-methylthioethylaminato (2-)]Nickel(II)}. The authors of the synthesis of this compound in Inorganic syntheses1 may have had to figure out an IUPAC name for this compound but if you have this scheme in your paper and your instructor is OK with it you can just call it **42**

Rules for Naming Coordination Compounds

According to the Lewis base theory, ligands are Lewis bases since they can donate electrons to the central metal atom. The metals, in turn, are Lewis acids since they accept electrons. Coordination complexes consist of a ligand and a metal center cation. The overall charge can be positive, negative, or neutral. Coordination compounds are complex or contain complex ions. A ligand can be an anion or a neutral molecule that *donates an electron pair* to the complex (NH_3, H_2O, Cl^-). The number of ligands that attach to a metal depends on whether the ligand is monodentate or polydentate.

The name of a coordination compound communicates:

- information about isomerism, as appropriate
- how ligands are linked to the metal
- the identity of the metal and its oxidation state
- any counterions present

Rule 1: If ions are present, name the cation first, followed by the anion.

Example 6.5.1

Name the following transition metal complexes.

a. $K_2[PtCl_4]$
b. $[Co(NH_3)_6](NO_3)_3$
c. $[Co(NH_3)_6][Cr(C_2O_4)_3]$

Solution

a. potassium tetrachloroplatinate(II)
b. hexaamminecobalt(III) nitrate
c. hexaamminecobalt(III) tris(oxolato)chromium(III)

Rule 2: When multiple isomers are possible, designate the particular isomer in italics at the front of the name of each complex

When a complex might exist as one of two stereoisomers, prefixes are commonly used to designate which isomer is present. The most common cases are demonstrated in Figure 6.5.2.

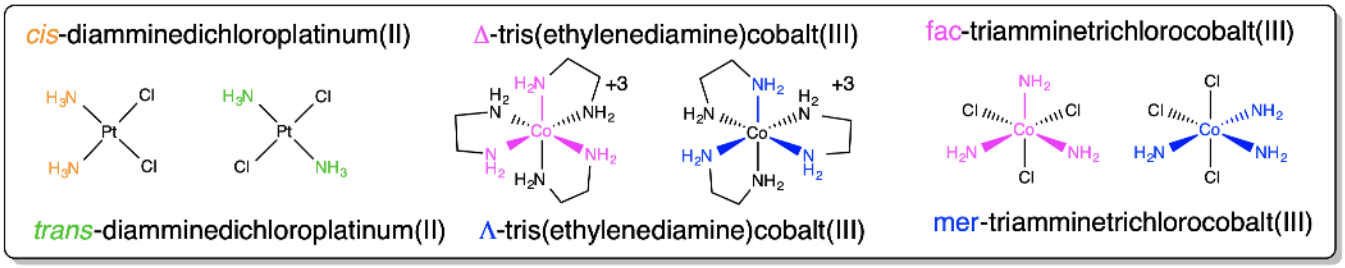


Figure 6.5.2: Application of nomenclature rules for stereosimerism about a metal. (LibreText)

Rule 3: Identity the ligands present by listing them in alphabetical order by ligand name.

The ligands are written in alphabetical order by the ligand name only; symbols are not considered and prefixes do not count in determining alphabetical order.

Example 6.5.2

Name the complex ion $[Co(NH_3)_5Cl]^{2+}$.

Solution

pentamminechlorocobalt(II)

The ammine ligand is named before the chloro ligand because the order is alphabetical by the ligand name by virtue of which ammine comes before chloro.

Rule 3a: Anionic Ligands

Ligands that act as anions which end in "-ide" are replaced with an ending "-o" (e.g., Chloride → Chloro). Anions ending with "-ite" and "-ate" are replaced with endings "-ito" and "-ato" respectively (e.g., Nitrite → Nitrito, Nitrate → Nitrato).

Table 6.5.1: Anionic Monodentate Ligands

Molecular Formula	Ligand Name	Molecular Formula	Ligand Name
F^-	Fluoro	OH^-	Hydroxo
Cl^-	Chloro	SO_4^{2-}	Sulfato
Br^-	Bromo	$S_2O_3^{2-}$	Thiosulfato
I^-	Iodo	NO_2^-	Nitrito-N-; Nitro
O^{2-}	Oxo	ONO^-	Nitrito-O-; Nitrito
CN^-	Cyano	SCN^-	Thiocyanato-S-; Thiocyanato
NC^-	Isocyano	NCS^-	Thiocyanato-N-; Isothiocyanato

Rule 3b: Neutral Ligands

Most neutral molecules that are ligands carry their normal name with a few caveats:

- Names that involve spaces should either be put in parentheses or the spaces should be eliminated (preferred)

  Example: cis-dichlorobis(**dimethyl sulfoxide**)platinum(II) or *cis*-dichlorobis(**dimethylsulfoxide**)platinum(II)

- A few ligands are named differently than their parent molecules. The few exceptions are the first four on the chart: ammine, aqua, carbonyl, and nitrosyl.

Table **6.5.2**: Select Neutral Ligands.

Molecular Formula of Ligand	Ligand Name
NH_3	Ammine
H_2O	Aqua
CO	Carbonyl
CS	Thiocarbonyl
NO	Nitrosyl
CH_3NH_2	Methylamine
C_5H_5N	Pyridine
en	Ethylenediamine
ox^{2-}	Oxalato
$EDTA^{4-}$	Ethylenediaminetetraacetato

Note: Ammine is spelled with two m's when referring to a ligand. Amines are a class of organic nitrogen-containing compounds.

Rule 4: Ligand Multiplicity

The number of ligands present in the complex is indicated with the prefixes di, tri, etc. The exceptions are polydentates that have a prefix already in their name (en and $EDTA^{4-}$ are the most common). When indicating how many of these are present in a coordination complex, put the ligand's name in parentheses and use *bis* (for two ligands), *tris* (for three ligands), and *tetrakis* (for four ligands). Prefixes always go before the ligand name; they are not taken into account when putting ligands in alphabetical order. Note that "mono" often is not used. For example, $[FeCl(CO)_2(NH_3)_3]^{2+}$ would be called triamminedicarbonylchloroiron(III) ion. Remember that ligands are always listed before the metal is listed in the name.

Table **6.5.3**. Prefixes used to specify the number of a given ligand present.

Number of Identical Ligands	Prefix for Monodentate Ligands	Prefix for Polydentate or Complex Ligands
2	di-	bis-
3	tri-	tris-
4	tetra-	tetrakis-
5	penta-	pentakis-
6	hexa-	hexakis-
7	hepta-	heptakis-
8	octa-	octakis-
9	nona-	nonakis-
10	deca-	decakis-

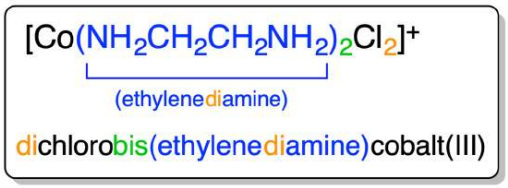


Figure 6.5.3: Example of the use of prefixes to specify the number of ligands of each type in a complex. (LibreText)

Example 6.5.3

What is the name of this complex ion: $[CrCl_2(H_2O)_4]^+$?

Solution

Let's start by identifying the ligands. The ligands here are Cl and H_2O. Therefore, we will use the monodentate ligand names of "chloro" and "aqua". Alphabetically, aqua comes before chloro, so this will be their order in the complex's name. There are 4 aqua's and 2 chloro's, so we will add the number prefixes before the names. Since both are monodentate ligands, we will say "tetra[aqua]di[chloro]".

Now that the ligands are named, we will name the metal itself. The metal is Cr, which is chromium. Therefore, this coordination complex is called tetraaquadichlorochromium(III) ion. See the next section for an explanation of the (III).

Rule 5: Specify the identity of the metal

In neutral and cationic complexes the metal's name is used directly. In anionic complexes, *-ate* replaces *-ium*, *-en*, or *–ese* or adds to the metal name.

Example 6.5.1

Name the following complexes:

a. $[Ru(NH_3)_6]^{3+}$
b. $MnCl_6^{2-}$

Solution

a. hexammineruthenium(III)
b. hexachloromanganate(IV)

Note: In anionic complexes of some metals a Latin-derived name is used instead of the element's English name. These names are given in Table 6.5.4. The rest of the metals simply have -ate added to the end (cobaltate, nickelate, zincate, osmate, cadmate,

platinate, mercurate, etc. Note that the -ate tends to replace -um or -ium, if present).

Table 6.5.4. Latin terms for select metal ions.

Transition Metal	Latin
Copper	Cuprate
Gold	Aurate
Iron	Ferrate
Lead	Plumbate
Silver	Argentate
Tin	Stannate

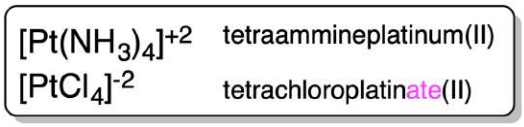


Figure 6.5.4: Example of the application of the metal specification rules to a cationic and an anionic platinum complex.(LibreText)

Rule 6: Specify the oxidation state of the metal.

When naming the metal center, you must know the formal metal name and the oxidation state. To show the oxidation state, we use Roman numerals inside parenthesis.

Example 6.5.1

Name the following complexes:

a. $[CoCl(NH_3)_5]Cl_2$
b. $[PtBr_2(bpy)]$
c. $K[Ag(SCN)_2]$

Solution

a. pentamminechlorocobalt(III) chloride
b. dibromobipyridineplatinium(II)
c. potassium di-*S*-thiocyanatoargentate(I)

Summary of rules for naming coordination complexes.

A graphical summary of the **rules for naming complexes** along with a few examples that you can use to review the nomenclature rules is given in Figure 6.5.5.

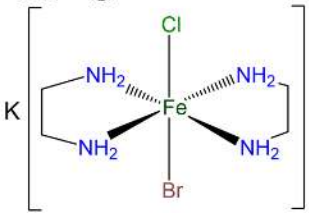
stereochemical prefix-	**Specify Ligands**	**Indicate Metal**	**Charge on the complex or metal oxidation state**
As appropriate use *cis-*, *trans-*, *fac-*, *mer-*, Λ-, Δ-, to indicate stereochemistry.	What ligands and how many? – List alphabetically by ligand name • Neutral – ligand name • Carionic – ligand name • Anionic – change last vowel to "o" – Indicate # by di-, tri-, tetra-, etc. (or bis-, tris-, tetrakis-, etc. if there is a di-, tri-, tetra, etc. in the ligand name) As appropriate, how are the ligands arranged? – Ambidentate – indicate linkage point by κ & italicized element symbol - other structure – use κ^n, η^n, μ_n, λ-, δ- For clarity, parentheses may be used to delineate ligands	Neutral, cationic: English name Anionic – change ending to "ate" - Latin names for Ag, Au, Cu, Fe, Pb, Sn; English for others	Stock system: Metal Oxidation state in capital Roman numerals Ewing-Bassett system: Complex's charge in Arabic numerals

Examples:

$[Ru(NH_3)_6](NO_3)_3$ hexammineruthenium(3+) nitrate or hexammineruthenium(III) nitrate

$K_2[PtCl_4]$ potassium tetrachloroplatinate(2-) or potassium tetrachloroplatinate(II)

$K[Ag(CN)_2]$ potassium dicyanoargentate(1-) or potassium dicyanoargentate(I)



potassium *trans*- bromochlorobis(ethylenediamine)iron(1+) (Ewing-Bassett)

-or-

potassium *trans*-bromochlorobis(ethylenediamine)iron(III) (Stock)

Figure ***PageIndex5***. Summary of nomenclature rules for coordination complexes along with a few examples of their application.

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Additional Examples

✔ Example 6.5.2

What is the name of $[Cr(OH)_4]^-$?

Solution

Immediately we know that this complex is an anion. There is only one monodentate ligand, hydroxide. There are four of them, so we will use the name "tetrahydroxo". The metal is chromium, but since the complex is an anion, we will have to use the "-ate" ending, yielding "chromate". The oxidation state of the metal is 3 (x+(-1)4=-1). Write this with Roman numerals and parentheses (III) and place it after the metal to get tetrahydroxochromate(III) ion.

✔ Example 6.5.3

What is the name of $\mathbf{[Pt(NH_3)_4][Pt(Cl)_4]}$?

Solution

NH_3 is neutral, making the first complex positively charged overall. Cl has a -1 charge, making the second complex the anion. Therefore, you will write the complex with NH_3 first, followed by the one with Cl (the same order as the formula). This coordination compound is called tetraammineplatinum(II) tetrachloroplatinate(II).

Writing Formulas of Coordination Complexes

While chemistry typically follow the nomenclature rules for naming complexes and compounds, there is disagreement with the rules for constructing formulas of inorganic complex. The order of ligand names in their formula has been ambiguous with different

conventions being used (charged vs neutral, number of each ligand, etc.). In 2005, IUPAC adopted the recommendation that all ligand names in formulas be listed **alphabetically** (in the same way as in the naming convention) irrespective of the charge or number of each ligand type.

The rules as given here are adapted from a summary by Robert Lancashire.

1. If there are multiple ions present list the cations before anions.
2. Enclose all the constituents of each complex ion in square brackets.
3. For each complex ion,
   - Give the **central metal** atom first.
   - Then **ligands** next, listed in alphabetical order, ignoring prefixes according to the first letters in the ligand's symbol as written. This is true regardless of whether the symbol is an element symbol (like C, N, O, etc.) or a symbol for the ligand name (bpy, en, MeCN, etc.). Contrary to widely-circulated myths, the ligand's charge does not matter.[4]
   - The formulae or abbreviations (*e.g.* en) for all polyatomic ligands should be enclosed in ordinary parentheses.
   - As appropriate, use italicized atom symbols to indicate linkage isomerism and prefixes such as *cis*-, *trans*-, *fac*-, *mer*-, Λ-, Δ -, κ^n, η^n , μ_n, λ-, or δ- to indicate stereochemistry.
   - When a ligand is bound to a metal through a particular atom, preferably place that atom closest to the metal - *e.g.*, $[Fe(CN)_6]^{3-}$ not $[Fe(NC)_6]^{3-}$ (Note: this rule is used primarily for ambidentate ligands; although IUPAC recommends that aqua ligands be written as OH_2 when the O would be closest to its coordinated metal, they are still usually written as H_2O).

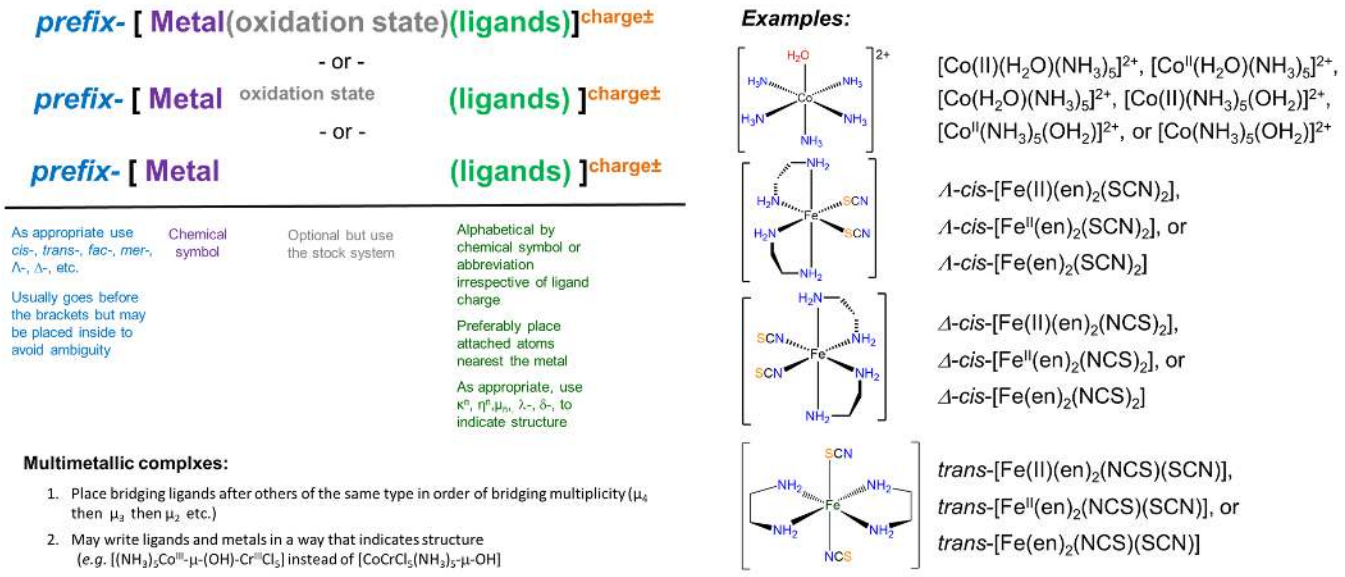


Figure **6.5.6**. Summary of the rules for writing the formula of a coordination complexes along with a few examples of their application. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

✔ Examples 6.5.4

Write the chemical formulas for:

a. Amminetetraaquachromium(II) ion
b. Amminesulfatochromium(II)

Solution

a. Amminetetraaquachromium(II) ion could be written as $[Cr(H_2O)_4(NH_3)]^{+2}$ or $[Cr(NH_3)(H_2O)_4]^{+2}$.
b. Amminesulfatochromium (II) could be written as $[Cr(SO_4)(NH_3)]$ or $[Cr(NH_3)(SO_4)]$.

Problems

Exercise 6.5.1

What is the name of this complex ion: $[CoCl_2(en)_2]^+$?

Answer

We take the same approach. There are two chloro and ethylenediamine ligands. The metal is Co, cobalt. We follow the same steps, except that *en* is a polydentate ligand with a prefix in its name (ethylene**di**amine), so "bis" is used instead of "di", and parentheses are added. Therefore, this coordination complex is called dichlorobis(ethylenediamine)cobalt(III) ion.

Exercise 6.5.2

What is the name of $[CuCl_4]^{2-}$?

Answer

tetrachlorocuprate(II) ion

Exercise 6.5.3: The Nitro/Nitrito Ambidentate Ligand

What is the name of $[CoCl(NO_2)(NH_3)_4]^+$?

Answer

This coordination complex is called tetraamminechloronitrito-N-cobalt(III). N comes before the O in the symbol for the nitrite ligand, so it is called nitrito-N. If an O came first, as in $[CoCl(ONO)(NH_3)_4]^+$, the ligand would be called nitrito-O, yielding the name tetraamminechloronitrito-O-cobalt(III).

Nitro (for NO_2) and nitrito (for ONO) can also be used to describe the nitrite ligand, yielding the names tetraamminechloronitrocobalt(III) and tetraamminechloronitritocobalt(III).

Exercise 6.5.4: The Nitro/Nitrito Ambidentate Ligand

What is the name of $[CoCl(NO_2)(NH_3)_4]^+$?

Answer

This coordination complex is called tetraamminechloronitrito-N-cobalt(III). N comes before the O in the symbol for the nitrite ligand, so it is called nitrito-N. If an O came first, as in $[CoCl(ONO)(NH_3)_4]^+$, the ligand would be called nitrito-O, yielding the name tetraamminechloronitrito-O-cobalt(III).

Nitro (for NO_2) and nitrito (for ONO) can also be used to describe the nitrite ligand, yielding the names tetraamminechloronitrocobalt(III) and tetraamminechloronitritocobalt(III).

Exercise 6.5.5

Write the chemical formulas for

a. Amminetetraaquachromium (II) sulfate
b. Potassium hexacyanoferrate (III)

Answer

a. Amminetetraaquachromium (II) sulfate can be written as $[Cr(H_2O)_4(NH_3)]SO_4$. Although $[Cr(NH_3)(H_2O)_4]SO_4$ is also acceptable.

b. Potassium hexacyanoferrate (III) is be written as $\mathbf{K_3[Fe(CN)_6]}$

Exercise 6.5.6. Assigning metal oxidation states in a complex

In order to name a complex it is necessary to assign a formal oxidation state to the metal. For this reason it is important to be able to assign the oxidation state of a metal in a complex. Fortunately, this is easy to do if you remember

1. The sum of all atoms' oxidation states will equal the overall charge on the complex
2. When determining the metal's oxidation state the ligands can be treated as having an oxidation state equal to their charge - *i.e.*, the charge they possess in the form in which they coordinate the metal, so if they need to lose a proton to bind, don't forget to account for that.

Given the above, assign the oxidation state of the metal in the following real and hypothetical complexes.

a. $K_3[Fe(CN)_6]$
b. $[CoCl(NH_3)_5](NO_3)_2$
c. $K_2[PtCl_4]$
d. [MnCl(por)]
e. $[Ru(bpy)_3]Cl_2$
f. $[PdCl_2(dppe)]$
g. $[Mn(en)_2(SCN)_2]$

Answer for $K_3[Fe(CN)_6]^{3-}$.

This contains $[Fe(CN)_6]^{3-}$; so O.S.$_{Fe}$ + 6 x (-1) (for CN^-) = -3 (the complex's charge) so O.S.$_{Fe}$ = +3 or Fe^{3+}.

Answer for $[CoCl(NH_3)_5](NO_3)_2$.

This contains $[CoCl(NH_3)_5]^{2+}$; so O.S.$_{Co}$ + 1 x (-1) (for Cl^-) + 0 x 5 (for NH_3) = +2 (the complex's charge) so O.S.$_{Co}$ = +3 or Co^{3+}.

Answer for $K_2[PtCl_4]$.

This contains $2K^+$ and $[PtCl_4]^{2-}$; so O.S.$_{Pt}$ + 4 x (-1) (for Cl^-) = -2 (the complex's charge) so O.S.$_{Pt}$ = +2 or Pt^{2+}.

Answer for [MnCl(por)].

O.S.$_{Pt}$ + 1 x (-2) (for por; see table 9.2.2) + 1 x (-1) (for Cl^-) = +0 (the complex's charge) so O.S.$_{Mn}$ = +3 or Mn^{3+}.

Answer $[Ru(bpy)_3]Cl_2$.

The complex is $[Ru(bpy)3]^{2+}$ so O.S.$_{Ru}$ + 0 x 3 (for bpy) = +2 (the complex's charge) so O.S.$_{Ru}$ = +2 or Ru^{2+}.

Answer $[PdCl_2(dppe)]$.

O.S.$_{Pd}$ + 2 x (-1) (for Cl^-) + 0 x 3 (for dppe) = +0 (the complex's charge) so O.S.$_{Pd}$ = +2 or Pd^{2+}.

Answer $[Mn(en)_2(SCN)_2]$.

O.S.$_{Mn}$ + (2 x 0) (for en) + 2 x (-1) (for SCN^-) = +0 (the complex's charge) so O.S.$_{Mn}$ = +2 or Mn^{2+}.

Exercise 6.5.7: Simple Nomenclature Problems.

Name the following compounds:

a. $[Ru(NH_3)_6](NO_3)_3$
b. $K_2[PtCl_4]$
c. $K[Ag(CN)_2]$
d. $Cs[CuBrCl_2F]$
e. $[Cu(acac)_2]$

Answer

	Complex	Name
a	$[Ru(NH_3)_6](NO_3)_3$	hexammineruthenium(III) nitrate
b	$K_2[PtCl_4]$	potassium tetrachloroplatinate(II)
c	$K[Ag(CN)_2]$	potassium dicyanoargentate(I)
d	$Cs_2[CuBrCl_2F]$	cesium bromodichlorofluorocuprate(II)
e	$[Cu(acac)_2]$	bis(acetylacetonato)copper(II)

? Exercise 6.5.8: More simple nomenclature problems.

Name the following compounds and ions.

a. $Cu(OH)_4^-$
b. $[AuXe_4]^{2+}$
c. $AuCl_4^-$
d. $Fe(CN)_6^{3-}$
e. $K_4[Fe(CN)_6]$
f. *trans*-$[Cu(en)_2(NO_2)_2]$ (the N is bound to Cu)
g. cis-$IrCl_2(CO)(PPh_3)$ (ignore stereochemistry)
h. $IrCl(PPh_3)_3$

Answer

	Compound	Name
a	$Cu(OH)_4^-$	tetrahydroxidocuprate(III) or tetrahydroxidocuprate(III)
b	$[AuXe_4]^{2+}$	tetraxenongold(II)
c	$AuCl_4^-$	tetrachloroaurate(III)
d	$Fe(CN)_6^{3-}$	hexacyanoferrate(III) or hexacyanidoferrrate(III)
e	$K_4[Fe(CN)_6]$	potassium hexacyanoferrate(II) or potassium hexacyanidoferrrate(II)
f	*trans*-$[Cu(en)_2(NO_2)_2]$ (the N is bound to Cu)	bis(ethylenediamine)bisnitrocopper(II) or bis(ethylenediamine)bis(nitrito-κ *N*)copper(II)
g	*cis*-$IrCl_2(CO)(PPh_3)$	*cis*-dichlorocarbonyltriphenylphosphineiridium(I) or *cis*-dichloro(carbonyl)(triphenylphosphine)iridium(I)
h	$IrCl(PPh_3)_3$	chlorotris(triphenylphosphine)iridium(I)

? Exercise 6.5.9: Even more simple nomenclature problems.

Name the following compounds and ions.

a. $Fe(acac)_3$

b. $K_2[CuBr_4]$
c. ReH_9
d. $[Ag(NH_3)_2]BF_4$
e. $[Ag(NH_3)_2][Ag(CN)_2]$
f. $[Ni(CN)_4]^{2-}$
g. $[Co(N_3)(NH_3)_5]SO_4$
h. $[CoBrCl(H_2O)(NH_3)]I$ (ignore stereochemistry)

Sample Answers

	Complex	Name
a	$Fe(acac)_3$	tris(acetoacetato)iron(III)
b	$Na_2[CuBr_4]$	sodium tetrabromocuprate(II)
c	$[Co(NH_3)_6][Co(ox)_3]$	hexamminecobalt(III) tris(oxalato)cobalt(III)
d	$[Ag(NH_3)_2]BF_4$	diamminesilver(I) tetrafluoroborate
e	$[Ag(NH_3)_2][Ag(CN)_2]$	diamminesilver(I) dicyanoargentate(I) or diamminesilver(I) dicyanidoargentate(I)
f	$[Ni(CN)_4]^{2-}$	tetracyanonickelate(II) or tetracyanonickelate(II) ion
g	$[Co(N_3)(NH_3)_5]SO_4$	pentammineazidocobalt(III) sulfate
h	$[CoBrCl(H_2O)(NH_3)]I$ (ignore stereochemistry)	ammineaquabromochlorocobalt(III) iodide

? Exercise 6.5.10: Nomenclature problems, some of which involve consideration of isomerism.

Name the following compounds and ions. Include the appropriate prefixes for designating isomers.

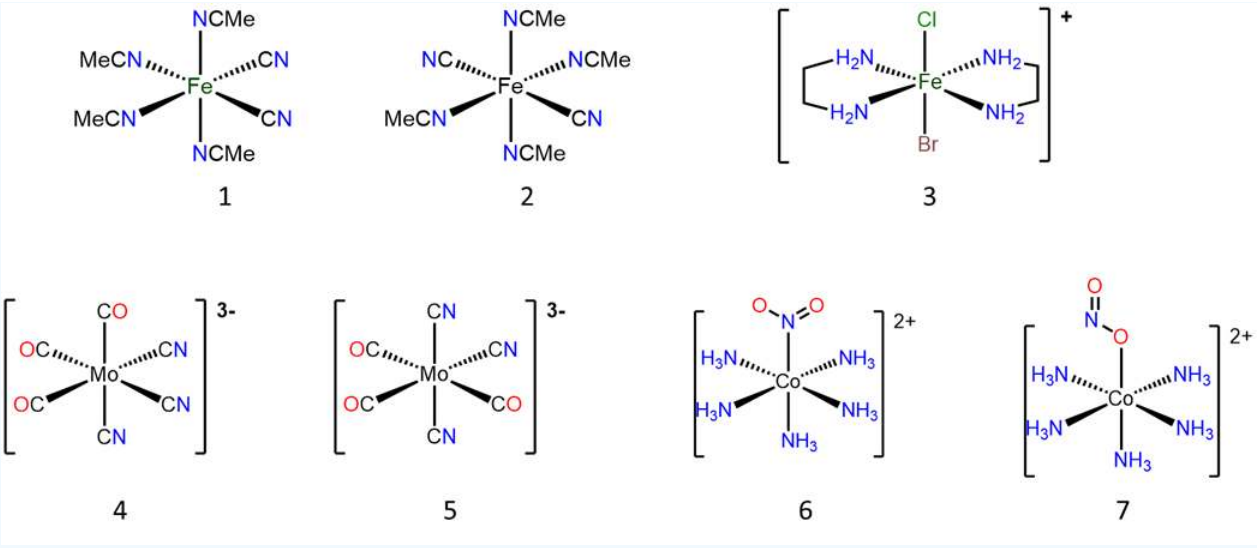
a. *trans*-$[Cu(dppe)_2(NO_2)_2]$ (the N is bound to Cu)
b. $[Pd(en)_2(SCN)_2]$, with the thiocyanates bound Pd-SCN
c. $[Mn(CO)_6]BPh_4$ (BPh_4 = tetraphenylborate)
d. $Rb[AgF_4]$
e. K_2ReH_9
f. K_3CrCl_6
g. $[Ru(H_2O)_6]Cl_2$
h. [*cis*-$Fe(CO)_4I_2$]
i. K_2[*trans*-$Fe(CN)_4(CO)_2$]
j. [*cis*-$MnCl(H_2O)_4(NH_3)$](NO_3)
k. K_3[*fac*-$RuCl_3(PMe_3)_3$]

Answer

	Complex	Name
a	*trans*-$[Cu(dppe)_2(NO_2)_2]$	*trans*-bis(diphenylphosphinoethane)bisnitrocopper(II) or *trans*-bis(diphenylphosphinoethane)bis(nitrito-κN)copper(II)
b	$[Pd(en)_2(SCN)_2]$, with the thiocyanates bound Pd-SCN	bis(ethylenediamine)bisthiocyanatopalladium(II) or bis(ethylenediamine)bis(thiocyanato-*S*)palladium(II) or bis(ethylenediamine)bis(thiocyanato-κS)palladium(II)
c	$[Mn(CO)_6]BPh_4$	hexacarbonylmanganese(I) tetraphenylborate
d	$Rb[AgF_4]$	rubidium tetrafluoroargentate(III)
e	K_2ReH_9	potassium nonahydridorhenium(VII)
f	K_3CrCl_6 or $K_3[CrCl_6]$	potassium hexachlorochromium(III) or potassium hexachloridochromium(III)
g	$[Ru(H_2O)_6]Cl_2$	hexaaquaruthenium(II) chloride
h	[*cis*-$Fe(CO)_4I_2$]	*cis*-tetracarbonyldiiodoiron(II)
i	K_2[*trans*-$Fe(CN)_4(CO)_2$]	potassium *trans*-dicarbonyltetracyanoferrate(II)
j	[*cis*-$MnCl(H_2O)_4(NH_3)](NO_3)$	*cis*-amminetetraaquachloromanganese(0) nitrate
k	K[*fac*-$RuCl_3(PMe_3)_3$]	potassium *fac*-trichlorotris(triphenylphosphine)ruthenium(II)

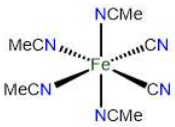
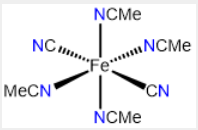
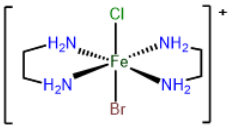
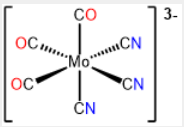
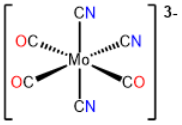
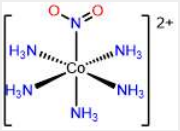
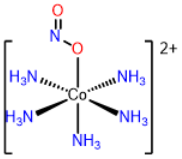
? Exercise 6.5.11

Name the compounds and ions. Include the appropriate prefixes for designating isomers.



Answer

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#	Structure	Name
1		*cis*-tetraacetonitriledicyanoiron(II) or *cis*-tetraacetonitriledicyanidoiron(II)
2		*trans*-tetraacetonitriledicyanoiron(II) or *trans*-tetraacetonitriledicyanidoiron(II)
3		*trans*-bromochlorobis(ethylenediamine)iron(III) or *trans*-bromidochloridobis(ethylenediamine)iron(III)
4		*fac*-tricarbonyltricyanomolybdate(0) or *fac*-tricarbonyltricyanidomolybdate(0)
5		*mer*-tricarbonyltricyanomolybdate(0) or *mer*-tricarbonyltricyanidomolybdate(0)
6		pentamminenitrito-*N*-cobalt(III), pentamminenitrito-κN-cobalt(III), or pentamminenitrocobalt(III)
7		pentamminenitrito-*O*-cobalt(2+), pentamminenitrito-κO-cobalt(2+), or pentamminenitritocobalt(2+)

? Exercise 6.5.12

Draw structural formulae for the following compounds and ions. You may assume that

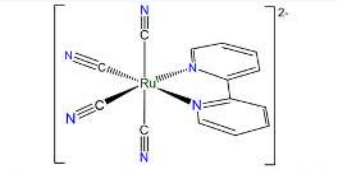
- complexes in which the metal has a coordination number of six are octahedral
- complexes in which the metal has a coordination number of five are trigonal bipyramidal
- complexes in which Pt^{II} , Pd^{II} , or Rh^{I}, or Ir^{I} have a coordination number of four are square planar
- other complexes in which the metal has a coordination number of four will be tetrahedral

a. (2,2'-bipyridine)tetracyanoruthenium(2-)
b. sodium tetrachloroaluminate (note that since Al is a main group metal with a generally fixed oxidation state no oxidation state is given)
c. pentaamminechlorocobalt(2+) sulfate
d. carbonylhydridotris(triphenylphosphine)rhodium(I) (the ligands in this complex occupy sterically preferred positions)
e. bromotrichlorocobaltate(III)
f. hexaaquacopper(2+) sulfate
g. sodium tris(oxalato)cobalt(III)

h. *fac*-(1,10-phenanthroline)tricarbonylchlororhenium(I)
i. *mer*-triaquatrichlorochromium(III)
j. *trans*-dichlorobis(ethylenediamine)platinum(IV)

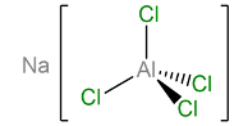
Answers

a



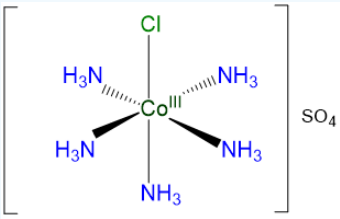
(2,2'-bipyridine)tetracyanoruthenium(2-)

b



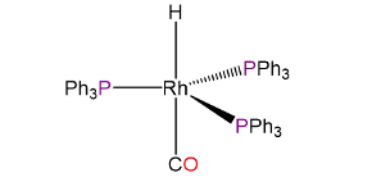
Sodium tetrachloroalumnate

c



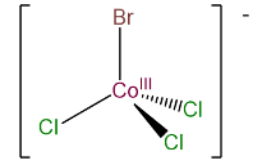
pentaamminechlorocobalt(2+) sulfate

d



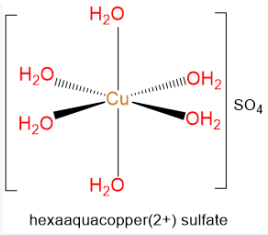
carbonylhydridotris(triphenylphosphine)rhodium(I)

e



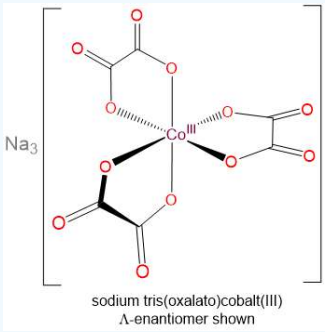
bromotrichlorocobaltate(III)

f



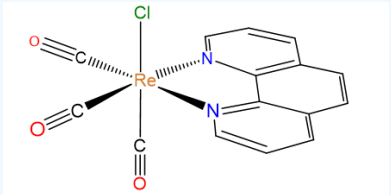
hexaaquacopper(2+) sulfate

g



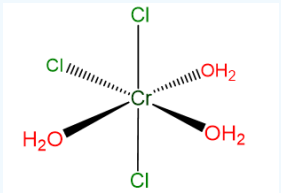
sodium tris(oxalato)cobalt(III)
Λ-enantiomer shown

h



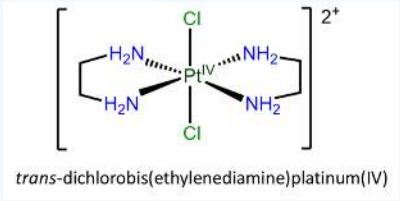
fac-(1,10-phenanthroline)tricarbonylchlororhenium(I)

i



mer-triaquatrichlorochromium(III)

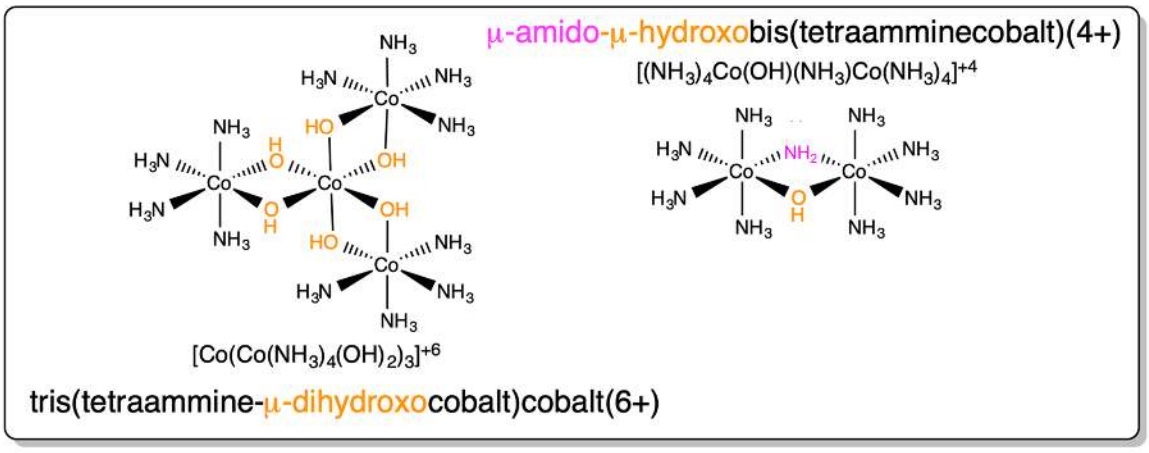
j



trans-dichlorobis(ethylenediamine)platinum(IV)

? Exercise 6.5.13.

The name of the structure named tris(tetraammine-μ-dihydroxocobalt)cobalt(6+) in the figure below is incomplete. Give the complete name of the structure.

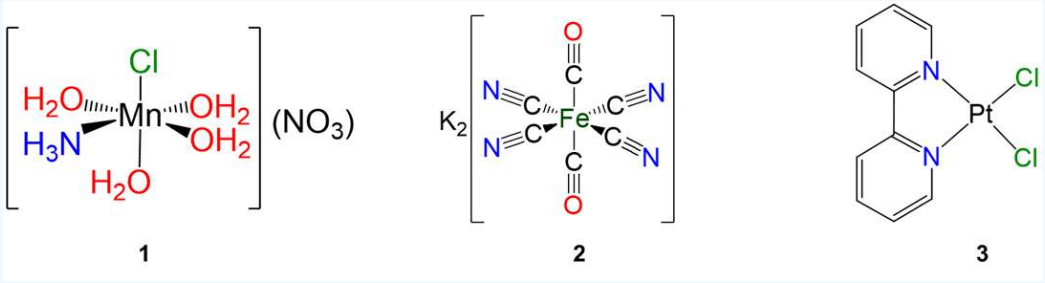


Answer

Δ-tris(tetraammine-μ-dihydroxocobalt(III)cobalt(III)

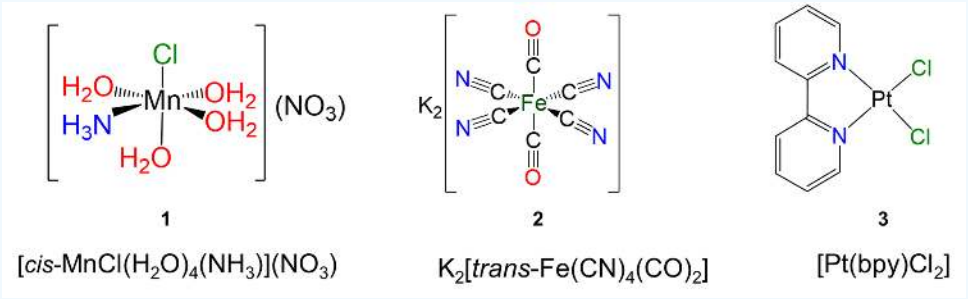
Exercise 6.5.14

Give the formulae of the following complexes.



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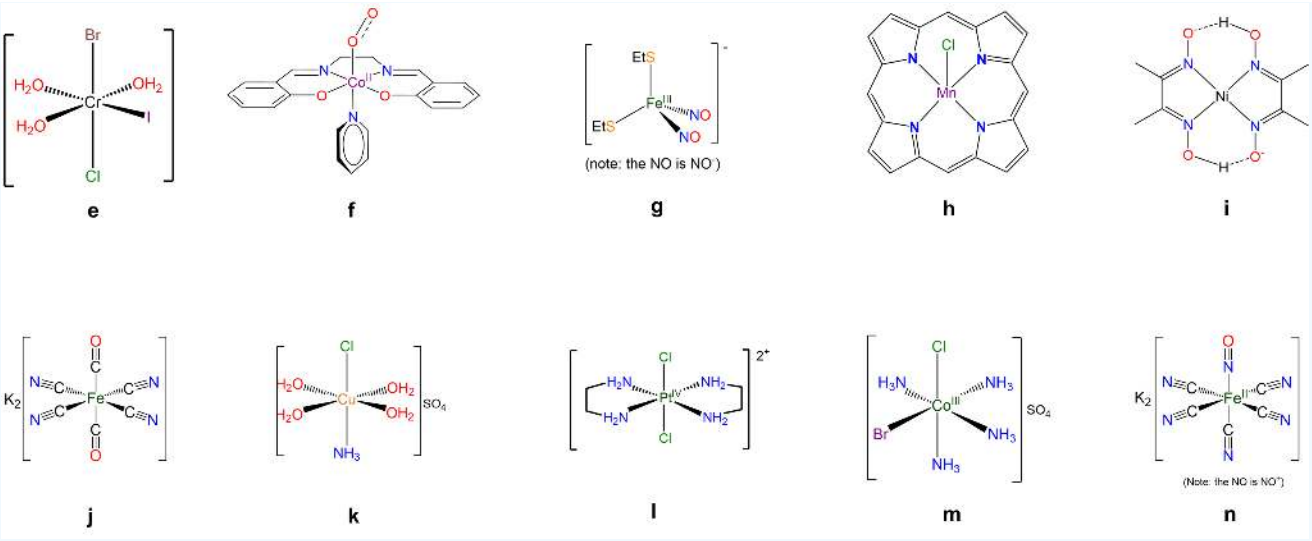
Answer



Exercise 6.5.15

Write formulae for each of the following compounds and ions. When multidentate ligands are present use suitable abbreviations.

a. pentaamminechlorocobalt(2+) sulfate
b. Δ-diamminebis(oxalato)manganate(III)
c. *trans*-tetraacetonitriledicyanoiron(II)
d. tricarbonyldichlorobis(triphenylphosphine)molybdenum



Answers

a.

$[CoCl(NH_3)_5](SO_4)$

b.

Δ-$[Mn(NH_3)_2(ox)_2]^-$

c.

trans-$[Fe(CN)_2(NCMe)_4]$

d.

$[MoCl_2(CO)_3(PPh_3)]$ or $MoCl_2(CO)_3(PPh_3)$

e.

mer-$[CrBrCl(H_2O)_3I]$

f.

$[Co(O_2)py(salen)]$

g.

$[Fe(NO)_2(SEt)_2]^-$

h.

$[MnCl(por)]^-$ or $[MnCl(porphyrin)]^-$

i.

$[Ni(DMG)_2]$ or $[Ni(Hdmg)_2]$

j.

potassium *trans*-$[Fe(CN)_2(CO)_4]$

k.

trans-$[CuCl(H_2O)_4(NH_3)]SO_4$

l.

trans-$[PtCl_2(en)_2]^{2+}$

m.

cis-$[CoBrCl(NH_3)_4]SO_4$

n.

$K_2[Fe(CN)_5NO]$

Contributors and Attributions

- Justin Hosung Lee (UCD), Sophia Muller (UCD)

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6.6: Ligands

Denticity

Ligands are classified based on whether they bind to the metal center through a single site on the ligand or whether they bind at multiple sites. Ligands that bind through only a single site are called ***monodentate*** from the Latin word for tooth; in contrast, those which bind through multiple sites are called ***chelating*** after the Greek **χαλε** for "claw". These relationships are summarized in Figure **6.6.1**.

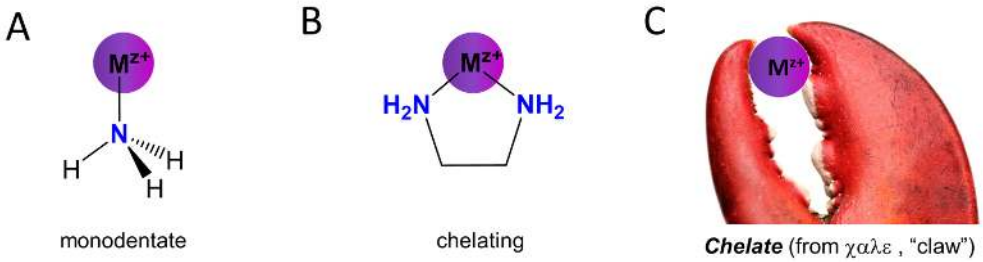


Figure **6.6.1**. (A) Ammonia is a monodentate ligand while (B) ethylene diamine is a chelating ligand owing to its capacity to bind metals via its two amine functional groups. (C) Chelating ligands act like a lobster claw in attaching to the metal via multiple sites. The lobster claw image is adapted from https://www.clipart.email/download/1127636.html. Otherwise this work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

Following naturally from the classification of non-chelating ligands as monodentate, chelating ligands are further classified according to the number of sites which they can use to bind a metal center. This number of binding sites is called the *denticity* and ligands are referred to as monodentate (non- chelating), bidentate, tridentate, etc., based on the number of sites available. Ligands with two binding sites have a denticity of two and are said to be bidentate; those with three are tridentate, four tetradentate, and so on. To illustrate this classification system examples of chelating ligands classified according to denticity are given in Figure **6.6.2**.

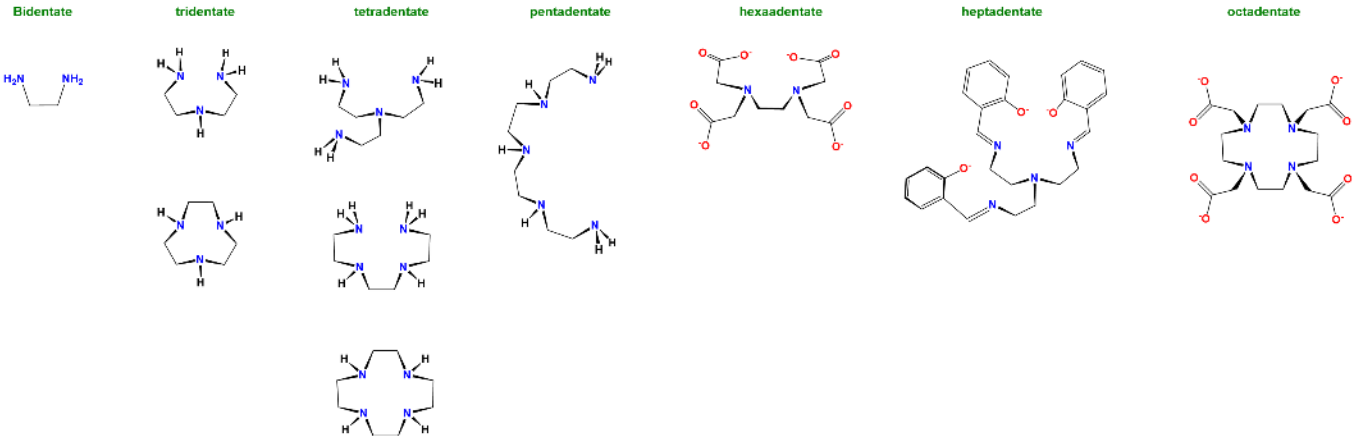


Figure **6.6.2**. Because only one oxygen per carboxylate *typically* binds, only one is counted when assigning a ligand's denticity. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

Ambidentate Ligands

A perusal of the ligands in Table **6.6.1** reveals that several can bind to a metal in multiple ways. For example, thiocyanate, SCN^- can bind metals through its S or N atoms. Such ligands are called ***ambidentate ligands***. In naming an ambidentate ligand, the atom through which it attaches to the metal is commonly specified after the ligand name using the italicized element symbol or, more formally, a **κ** followed by the italicized element symbol. An example is given in Figure **6.6.3**.[2]

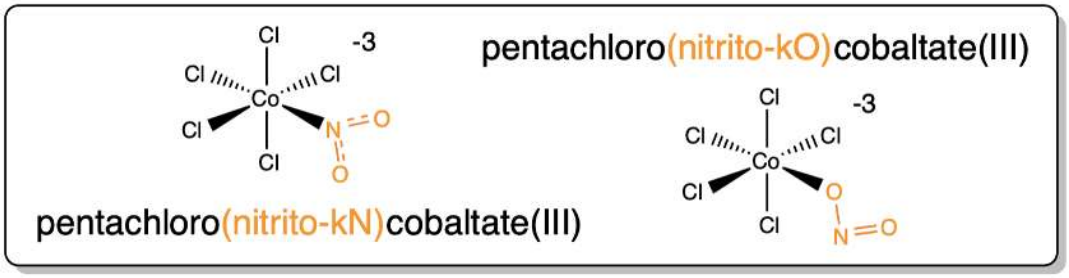
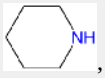
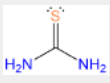


Figure **6.6.1**: Two possible binding modes of nitrite acting as a ligand.[3] This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

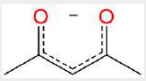
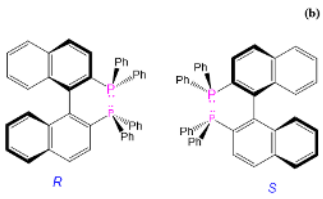
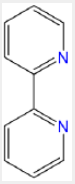
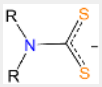
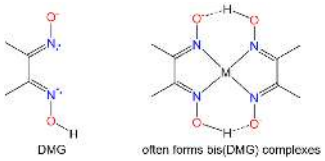
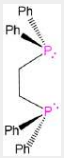
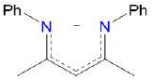
Examples of Ligands

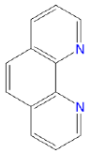
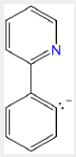
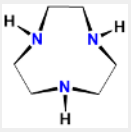
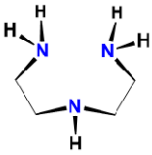
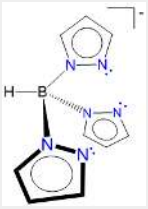
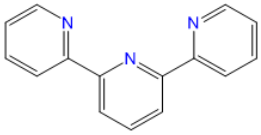
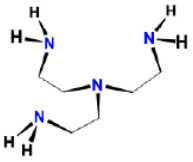
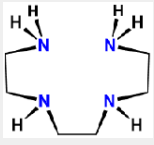
Table **6.6.1**. Common monodentate ligands. Most chemists still prefer common names over the IUPAC ones.

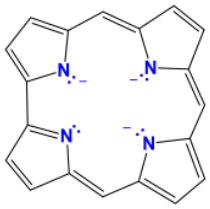
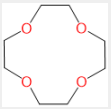
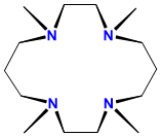
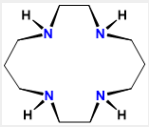
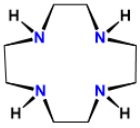
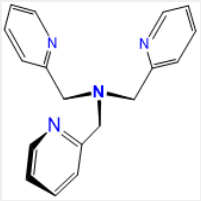
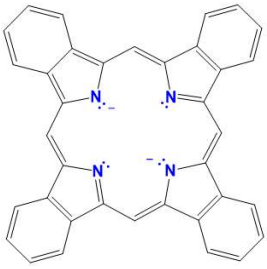
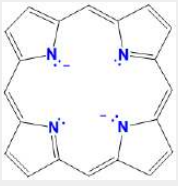
Ligand	Common name	IUPAC name
H^- (H ligands are always considered anions for naming purposes)	hydrido	hydrido
F^-	fluoro	fluorido
Cl^-	chloro	chlorido
Br^-	bromo	bromido
I^-	iodo	iodido
CN^-, as M-CN	cyano	cyanido or cyanido-κC or cyanido-*C*
CN^-, as M-NC	isocyano	isocyanido or cyanido-κN or cyanido-*N*
CH_3NC	methylisocyanide	methylisocyanide
N_3^-	azido	azido
SCN^-, *e.g.* thiocyanate as M-SCN	thiocyanato	thiocyanato-κS or thiocyanato-*S*
NCS^-, *e.g.* thiocyanate as M-NCS	isothiocyanato	thiocyanato-κN or thiocyanato-*N*
$CH_3CO_2^-$	acetato	ethanoato
N^{3-}	nitrido	nitrido
NH^{2-}	imido	azanediido
NH_2^-	amido	azanido
NH_3	ammine	ammine
RNH_2, R_2NH, R_3N	alkylamine, dialkylamine, trialkalyamine (*e.g.* methylamine for CH_3NH_2)	alkylamine, dialkylamine, trialkalyamine (*e.g.* methylamine for CH_3NH_2)
 , piperidine, abbreviated pip	piperidine	piperidine
 , pyridine, abbreviated py	pyridine	pyridine
CH_3CN, acetonitrile, abbreviated MeCN	acetonitrile	acetonitrile
P^{3-}	phosphido	phosphido
PH_3	phosphine	phosphane
PR_3	trialkylphosphine (*e.g.* trimethylphosphine for Me_3P)	trialkylphosphane (*e.g.* trimethylphosphane for Me_3P)
PAr_3	triarylphosphine (*e.g.* triphenylphosphine for Ph_3P)	triarylphosphine (*e.g.* triphenylphosphane for Ph_3P)
 , dimethylsulfoxide or DMSO or dmso	dimethylsulfoxide (sometimes called dimethylsulfoxo but this usage is rare and violates the nomenclature rules for neutral ligands)	(methanesulfinyl)methane or dimethyl(oxido)sulfur
 , thiourea or tu	thiourea	thiourea

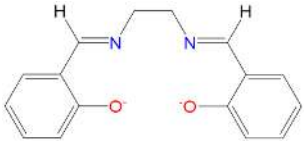
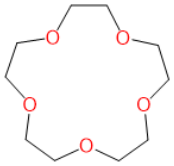
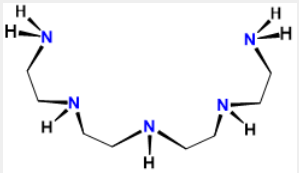
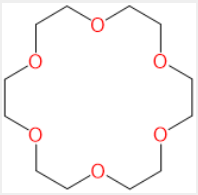
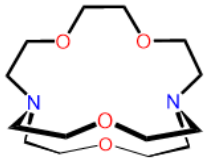
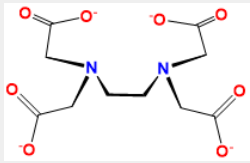
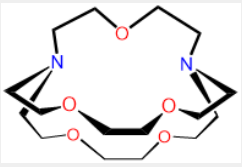
Ligand	Common name	IUPAC name
O^{2-}	oxo	oxido
OH^-	hydroxo	hydroxido
H_2O	aqua	aqua
S^{2-}	sulfo	sulfo
HS^-	hydrosulfido	hydrosulfido
RS^-	alkanethiolate (*e.g.* ethanthiolate for EtS^-)	thioalkanoate
H_2S	hydrogen sulfide	hydrogen sulfide
R_2S	alkylsulfanylalkane (*e.g.* ethylsulfanylethane for Et_2S)	dialkyl sulfide
O_2	dioxygen	dioxygen
O_2^-, superoxide	superoxido	dioxido(1-) or superoxido
O_2^{2-}, peroxide	peroxido	dioxido(2-) or peroxido
N_2	dinitrogen	dinitrogen
NO (are always considered neutral for naming purposes)	nitrosyl	nitrosyl
CO	carbonyl	carbonyl
CS	thiocarbonyl	thiocarbonyl
SO, as M-SO	sulfino	sulfur monoxide-κS or sulfur monoxide-*S*
NO_2, as M-NO_2	nitryl	nitrogen dioxide-κN or nitrogen dioxide-*N*
CO_3^{2-}	carbonato	carbonato
NO_2^-, as M-NO_2	nitro or nitrito-*N*	nitrito-κN or nitrito-*N*
NO_2^-, as M-ONO	nitrito or nitrito-*O*	nitrito-κO or nitrito-*O*
NO_3^-	nitrato	nitrato
SO_3^{2-}	sulfito	sulfito
SO_4^{2-}	sulfato	sulfato
$S_2O_3^{2-}$, as M-S-SO_2-O^-	thiosulfato-*S*	thiosulfato-κS or thiosulfato-*S*
$S_2O_3^{2-}$, as M-O-SO_2-S^-	thiosulfato-*O*	thiosulfato-κO or thiosulfato-*O*

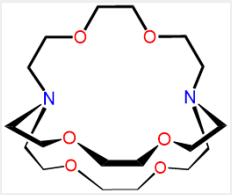
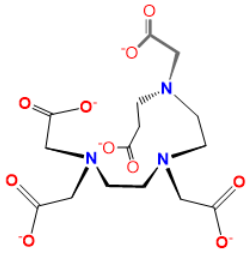
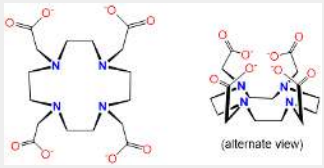
Table **6.6.2**. Common chelating ligands organized by denticity. Most chemists use the common names and abbreviations to describe these ligands.

Common Ligand name	IUPAC ligand name	abbreviation (if applicable)	structure or representative/parent structure (shown in the ionization state in which they bind to a metal)
	Bidentate Ligands		
acetylacetonato	2,4-pentanediono	acac	
R-BINAP and *S*-BINAP	*R*- or *S*-2,2'-bis(diphenylphosphino)-1,1'-binapthyl	BINAP	
2,2'-bipyridine	2,2'-bipyridine	bpy or bipy	
cyclooctadiene	1,5-cyclooctadiene	COD	 (binding to the metal occurs through the alkene π cloud)
dialkyldithiocarbamato	dialkylcarbamodithiolato	$R_2NCS_2^-$ or dtc	
dimethylgloximato	butanedienedioxime	Hdmg or DMG	
diphenylphosphinoethane or 1,2-(diphenylphosphino)ethane	Ethane-1,2-diylbis(diphenylphosphane)	dppe	
ethylenediamine	Ethane-1,2-diamine	en	
ethylenedithiolato	Ethane-1,2-dithiolato	$C_2H_2S_2^{2-}$	
nacnac	*N*,*N*'-diphenyl-2,4-pentanediiminato	nacnac	
oxalato	oxalato	ox	

Common Ligand name	IUPAC ligand name	abbreviation (if applicable)	structure or representative/parent structure (shown in the ionization state in which they bind to a metal)
1,10-phenanthroline or *o*-phenanthroline	1,10-phenanthroline	phen or *o*-phen	
phenylpyridinato	2-phenylpyridinato-C^2,*N* or 2-phenylpyridinato-κC^2,*N*	ppy	
Tridentate Ligands			
triazacyclononane	1,4,7-triazacyclononane	tacn	
diethylenetriamine	1,4,7-triazaheptane	dien	
pyrazoylborato (scorpionate)	hydrotris(pyrazo-1-yl)borato	Tp	
terpyridine or 2,2';6',2"-terpyridine	1^2,2^2:2^6,3^2-terpyridine or 2,6-bis(2-pyridyl)pyridine, tripyridyl, 2,2′:6′,2″-terpyridine	tpy or terpy	
Tetradentate Ligands			
β, *β*', *β*"-triaminotriethylamine	*β*, *β*', *β*"-tris(2-aminoethyl)amine	tren	
triethylenetetramine	1,4,7,10-tetraazadecane	trien	

Common Ligand name	IUPAC ligand name	abbreviation (if applicable)	structure or representative/parent structure (shown in the ionization state in which they bind to a metal)
corroles	variable and generally not used	cor or Cor	
12-crown-4	1,4,7,10-tetraoxacyclododecane	12-crown-4	
tetramethylcyclam	1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane	TMC or cyclam	
cyclam	1,4,8,11-tetraazacyclotetradecane	cyclam	
cyclen	1,4,7,10-tetraazacyclododecane	cyclen	
tris(2-pyridylmethyl)amine	1-pyridin-2-yl-*N*,*N*-bis(pyridin-2-ylmethyl)methanamine	tpa or TPA	
phthalocyanines	variable and generally not used	variable, usually a modified Pc	
porphyrins	variable and generally not used	variable, usually a modified por, Por, or P (e.g. TPP = tetraphenylporphyrin)	

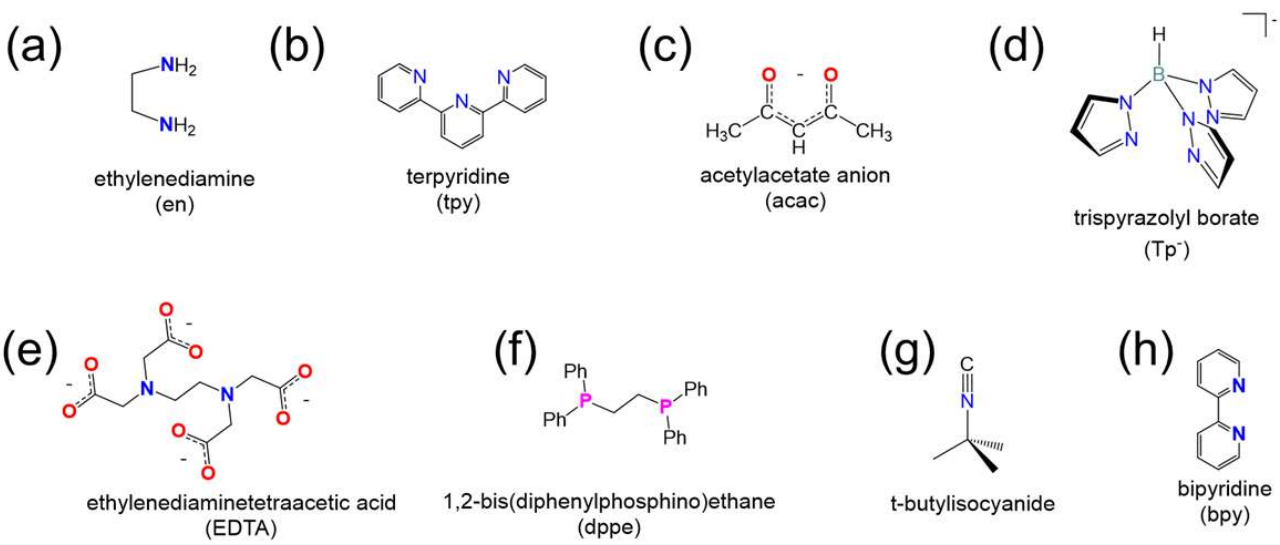
Common Ligand name	IUPAC ligand name	abbreviation (if applicable)	structure or representative/parent structure (shown in the ionization state in which they bind to a metal)
salen	2,2'-ethylenebis(nitrilomethylidene) diphenoxido	salen	
Pentadentate Ligands			
15-crown-5	1,4,7,10,13-Pentaoxacyclopentadecane	15-crown-5	
tetraethylenepentamine	1,4,7,10,13-pentaazatridecane	tepa or TEPA	
Hexadentate Ligands			
18-crown-6	1,4,7,10,13,16-hexaoxacyclooctadecane	18-crown-6	
2,1,1-cryptand	4,7,13,18-Tetraoxa-1,10-diazabicyclo[8.5.5]icosane	2,1,1-crypt or [2.1.1]-cryptand kryptofix 211 and variations thereof	
ethylenediaminetetraaceto	2,2′,2″,2‴-(Ethane-1,2-diyldinitrilo)tetraaceto	EDTA, edta, Y^{4-}	
Heptadentate Ligands			
2,2,1-cryptand	4,7,13,16,21-pentaoxa-1,10-diazabicyclo[8.8.5]icosane	2,2,1-crypt or [2.2.1]-cryptand kryptofix 221 and variations thereof	
Octadentate Ligands			

Common Ligand name	IUPAC ligand name	abbreviation (if applicable)	structure or representative/parent structure (shown in the ionization state in which they bind to a metal)
2,2,2-cryptand	4,7,13,16,21,24-Hexaoxa-1,10-diazabicyclo[8.8.8]hexacosan	2,2,2-crypt or [2.2.2]-cryptand kryptofix 222 and variations thereof	
pentetato acid or diethylenetriaminepentaacetato or DTPA	2-[bis[2-[bis(carboxylatomethyl)amino]ethyl]amino]acetato	DTPA	
DOTA or tetraxetan	1,4,7,10-Tetraazacyclododecane-1,4,7,10-tetraacetic acid	Dota, DOTA	

Problems

? Exercise 6.6.1

Determine the denticity of each ligand in the list below and classify them as monodentate, tridentate, etc.



Answer

(a) bidentate

(b) tridentate

(c) bidentate

(d) tridentate (only the lower N on each ring has a lone pair that can be used to bind the metal)

(e) hexadentate (remember that each carboxylate only counts as one point of attachment)

(f) bidentate

(g) monodentate (through the lone pair on the isocyanide C)

(h) bidentate

References

1. International Union of Pure and Applied Chemistry *Nomenclature of Inorganic Chemistry* Cambridge, UK, 2005.

2. The structure and name is taken from Choudhury, S. B.; Allan, C. B.; Maroney, M.; Wodward, A. D.; Lucas, C. R. *Inorg. Synth.* **1998**, *32*, 98-107.

3. Haas, K. Naming Transition Metal Complexes. https://chem.libretexts.org/Courses/Saint_Mary's_College%2C_Notre_Dame%2C_IN/CHEM_342%3A_Bio-inorganic_Chemistry/Readings/Week_2%3A_Introduction_to_Metal-Ligand_Interactions_and_Biomolecules/2.1_Transition_metal_complexes/2.1.6%3A_Naming_Transition_Metal_Complexes

Contributors and Attributions

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with some examples taken from Naming Transition Metal Complexes by Kathryn Haas.

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6.7: Electronic Configurations



To be able to use Crystal Field Theory (CFT) successfully, it is essential that you can determine the **electronic configuration** of the central metal ion in any complex.

This requires being able to recognize all the entities making up the complex and knowing whether the ligands are neutral or anionic, so that you can determine the **oxidation number** of the metal ion. The oxidation number is then used to determine the electron configuration and the number of electrons in d-orbitals for a metal ion.

Example 6.7.1

What is the electronic configuration of Fe(III)?

Solution

Start with the electron configuration of the neutral atom. It is sufficient to use the noble gas configuration.

Fe: [Ar] $4s^2$ $3d^6$

Then, remove (or add) electrons to reflect the oxidation state of the metal. Remember to remove electrons from the orbital with the highest principal quantum number first!

Fe(III) has lost 3 electrons relative to Fe(0). Fe^{3+}: [Ar] $3d^5$

From the electron configuration, we see that Fe^{3+} has 5 electrons in its outermost d-orbitals.

Oxidation Numbers and their Relative Stabilities

The IUPAC definition of the oxidation number in a coordination compound is:

> *the charge a central atom in a coordination entity would bear if all the ligands were removed along with the electron pairs that were shared with the central atom. It is represented by a Roman numeral.*

The transition metals show a wide range of oxidation numbers. The Table **6.7.1** summarizes the known oxidation numbers of the first row transition elements.

Table **6.7.1**: Known Oxidation Numbers of First Row Transition Elements*. The most prevalent oxidation numbers are shown in **bold.**

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
	I	I	I	I	I	I	I	**I**	
	II	**II**	**II**	**II**	**II**	**II**	**II**	**II**	**II**
III	**III**	**III**	**III**	**III**	**III**	**III**	III	III	
	IV	**IV**	IV	**IV**	IV	IV	IV		
		V	V	V	V	V			
			VI	**VI**	VI				
				VII					

* The oxidation number zero usually assigned to the elemental state has been omitted from the Table. The elements Cr to Co form several metal carbonyl compounds where the metals are considered to have an oxidation number of zero.

A number of important conclusions can be drawn from Table **6.7.1**.

1. There is an increase in the number of oxidation numbers from Sc to Mn. All seven oxidation numbers are exhibited by Mn. The oxidation number of VII represents the formal loss of all seven electrons from 3d and 4s orbitals. In fact all of the elements in the series can utilize all the electrons in their 3d and 4s orbitals.
2. There is a decrease in the number of oxidation states from Mn to Zn. This is because the pairing of d-electrons occurs after Mn (Hund's rule) which in turn decreases the number of available unpaired electrons and hence, the number of oxidation states.
3. The stability of higher oxidation states decreases in moving from Sc to Zn. Mn(VII) and Fe(VI) are powerful oxidizing agents and the higher oxidation states of Co, Ni and Zn are unknown.
4. The relative stability of the +2 state with respect to higher oxidation states, particularly the +3 state increases in moving from left to right. This is justifiable since it will be increasingly difficult to remove the third electron from the d orbitals.
5. There is a tendency of intermediate oxidation states to disproportionate. For example, Mn(VI) → Mn(IV) + Mn(VII) and Cu(I) → Cu(0) + Cu(II).
6. The lower oxidation numbers are usually found in ionic compounds and higher oxidation numbers tend to be involved in covalent compounds.

The relative stability of oxidation numbers is an extremely important topic in transition metal chemistry and is usually discussed in terms of the standard reduction potential (E°) values. Thermodynamically E° values are equated to ΔG° values by the relationship: $\Delta G^\circ = -nFE^\circ$ where n = number of electrons involved and F = Faraday of electricity. Hence, the E° values indicate the possibility of spontaneous change from one oxidation state to the other. This value however, does not give any information about the reaction rate. Predictions regarding the stability of a particular oxidation state of an element can be made from the Tables of Redox values found in any standard text book or online.

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6.8: Bonding Theories

Coordination complexes caused great fascination among chemists during the nineteenth century, although it wasn't until the century's end that Alfred Werner determined the fundamental principles of their structure. A fuller understanding of their structures was developed over the first half of the twentieth century. This understanding developed in stages, with newer theories and models building on previous ones rather than replacing them completely.

Crystal Field Theory

In the early 1930's, American physicists John Hasbrouck van Vleck and Hans Bethe developed a theoretical treatment of crystalline transition metal compounds that explained their magnetic and optical properties. This treatment did not consider bonding in any way, but it did concern itself with the geometry of ligands, or counterions, around a central metal ion. Electrostatic considerations formed the basis of the theory, with attention to repulsive forces between ligand electrons and ***d*** electrons on the metal ion. The model gave good predictions about the effect of ligand geometry on the electronic structure of the metal ion. Crystal field theory will be the basis of our discussion of transition metal complexes for the remainder of this unit.

Ligand Field Theory

During the 1950's, British chemists John Stanley Griffith and Leslie Orgel combined some aspects of crystal field theory with molecular orbital theory to produce a bonding model for coordination complexes. Rather than just considering electrostatic interactions between metal and ligand, this approach used orbital interactions to model the role of covalency in determining the electronic structure of the complex.

Angular Overlap Model

This model is a specific approach to considering how ligand and metal orbitals combine to produce molecular orbitals in a coordination complex. It uses the symmetry and orientation of atomic orbitals to determine what combinations of these orbitals should be considered.

Computational Chemistry

The three "pencil-and-paper models" described above for bonding in coordination complexes have been greatly augmented by the power of modern computational chemistry. Although based on the same principles, computational methods offer a much higher level of quantitative information about electronic energy and allow relatively easy assessment of possible structural features such as coordination geometry. Pioneering methods included extended Hückel theory, originally developed by Roald Hoffman and Robert Burns Woodward to study pericyclic reactions. The method was later adapted by Hoffman and others to investigate inorganic and organometallic complexes. More recently, developments such as density functional theory have greatly facilitated computational work on transition metal systems because of their simplified treatment of many-electron systems. These approaches and others like them allow for the prediction of coordination complex properties through a computer interface.

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6.9: Crystal Field Theory

Crystal field theory (CFT) is a bonding model that explains many important properties of transition-metal complexes, including their colors, magnetism, structures, stability, and reactivity. The central assumption of CFT is that metal–ligand interactions are purely electrostatic in nature. CFT qualitatively describes the strength of the metal-ligand interactions; based on the strength of the metal-ligand interactions, the energy of the system is altered and the degeneracy of the d-orbitals in transition metal complexes breaks. Even though the initial assumption is not strictly valid for many complexes, such as those that contain neutral ligands like CO, CFT enables chemists to explain many of the properties of transition-metal complexes with a reasonable degree of accuracy. T

Crystal Field Theory was developed by Hans Bethe and John Hasbrouck van Vleck. As the name implies, crystal field theory was developed as a way of explaining observed colors and magnetic properties of ionic crystalline solids. The colors of transition metel complexes results from the wavelength of light absorbed, which reveals something about differences in electronic energy levels in the ions of the crystalline solid. The magnetic properties depend on the presence of unpaired electrons and, thus, also depend on electronic energy levels.

Basic Concept

Consider a transition metal ion in an octahedral hole in a crystalline lattice (Figure **6.9.1**). In Crystal Field Theory, it is assumed that the ions are *simple point charges* (a simplification). The blue metal ion is a positive point charge that has six nearest neighbors, and the red ligands/counterions are negative point charges. The ions are held together by electrostatics: the negative charges of the (red) counterions are attracted to the positive charge of the (blue) metal ion. The attractive and repulsive interactions between the ions can be described by Coulomb's Law:

$$E \propto \frac{q_1 q_2}{r}$$

with

- E the bond energy between the charges and
- q_1 and q_2 are the charges of the interacting ions and
- r is the distance separating them.

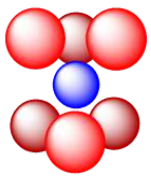


Figure **6.9.1**: A positively charged metal ion (blue) surrounded by six near neighbors with negative charges (red). (CC-BY-NC; Chris Schaller)

The attractive and repulsive forces between the positively charged metal ion and the surrounding ligands affect the energy of the electrons on the metal ion. To understand these interactions, we first consider a single transition metal ion; its five *d*-orbitals have the same energy (they are *degenerate*) (Figure **6.9.2**). When the metal ion is placed in a field of evenly distributed negative charge, there are repulsive forces between the metal ion's electrons and the surrounding negative charge. The result is the electrons on the metal increase in energy, and they all increase in energy by the same amount.

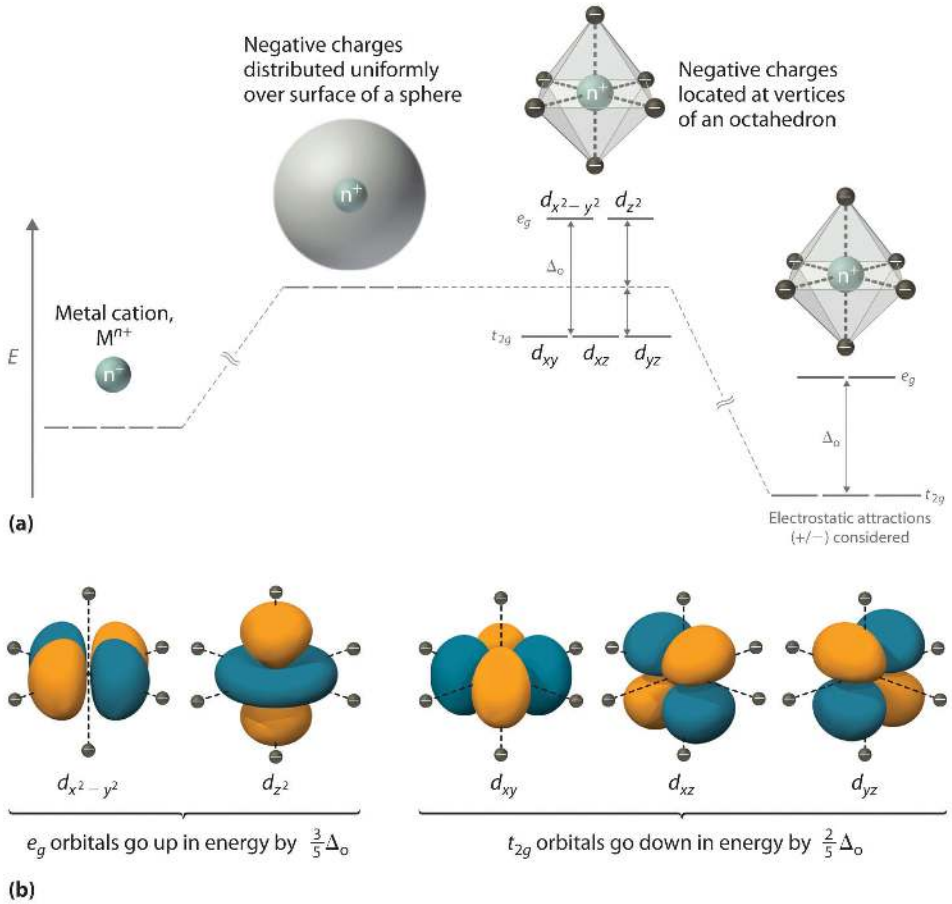


Figure **6.9.2**: An Octahedral Arrangement of Six Negative Charges around a Metal Ion Causes the Five d Orbitals to Split into Two Sets with Different Energies. (a) Distributing a charge of −6 uniformly over a spherical surface surrounding a metal ion causes the energy of all five d orbitals to increase due to electrostatic repulsions, but the five d orbitals remain degenerate. Placing a charge of −1 at each vertex of an octahedron causes the d orbitals to split into two groups with different energies: the $d_{x^2-y^2}$ and d_{z^2} orbitals increase in energy, while the d_{xy}, d_{xz}, and d_{yz} orbitals decrease in energy. The average energy of the five d orbitals is the same as for a spherical distribution of a −6 charge, however. Attractive electrostatic interactions between the negatively charged ligands and the positively charged metal ion (far right) cause all five d orbitals to decrease in energy but does not affect the splittings of the orbitals. (b) The two e_g orbitals (left) point directly at the six negatively charged ligands, which increases their energy compared with a spherical distribution of negative charge. In contrast, the three t_{2g} orbitals (right) point between the negatively charged ligands, which decreases their energy compared with a spherical distribution of charge. (CC BY-SA-NC; anonymous by request)

In reality, the negative charges in a transition metal complex are not uniformly distributed around the positive metal ion. When the ligand point charges approach the metal ion, some experience more repulsion from the d-orbital electrons than others based on the geometric structure of the molecule. Due to the variation in shape and orientation of the d-orbitals, some ligands will interact more directly with d-orbitals and others will have less direct interactions. For an octahedral complex, the ligands approach the metal ion along the x, y, and z axes. Therefore, the electrons in the d_{z^2} and $d_{x^2-y^2}$ orbitals, which lie along these axes, experience greater repulsion (Figure **6.9.2**). It requires more energy to have an electron in these orbitals than it would to put an electron in one of the other orbitals due to the electron-electron repulsions. The energies of the d_{z^2} and $d_{x^2-y^2}$ orbitals increase due to greater interactions with the ligands. By the same logic, the d_{xy}, d_{xz}, and d_{yz} orbitals have less-direct interactions and decrease in energy. This causes a splitting in the energy levels of the *d*-orbitals. This is known as **crystal field splitting**.

For an octahedral complex, the energy difference between the two sets of orbitals is called the *octahedral field splitting*, Δ_o. Because the total amount of repulsion is the same in the octahedral field and the spherical field (it is just distributed differently) the average energy level of the orbitals should be the same in the two fields. This average energy of the orbitals is called the **barycenter**, a term borrowed from astronomy. Because two of the orbitals are raised above the barycenter in the octahedral field and three are lowered below the barycenter, then the e_g set must be $\frac{3}{5}\Delta_o$ $(= 0.6\Delta_o)$ above the barycenter and the t_{2g} set must be $\frac{2}{5}\Delta_o$ $(= 0.4\Delta_o)$ below the barycenter. That means the average energy lies at the barycenter.

Thus far, we have considered only the effect of repulsive electrostatic interactions between electrons in the d orbitals and the six negatively charged ligands, which increases the total energy of the system and splits the d orbitals. Interactions between the positively charged metal ion and the ligands results in a net stabilization of the system, which decreases the energy of all five d orbitals without affecting their splitting (as shown at the far right in Figure **6.9.2**).

Three Complexes Explained

Description of *d*-Orbitals

To understand CFT, one must understand the description of the lobes:

- d_{xy}: lobes lie in-between the x and the y axes.
- d_{xz}: lobes lie in-between the x and the z axes.
- d_{yz}: lobes lie in-between the y and the z axes.
- $d_{x^2-y^2}$: lobes lie on the x and y axes.
- d_{z^2}: there are two lobes on the z axes and there is a donut shape ring that lies on the xy plane around the other two lobes.

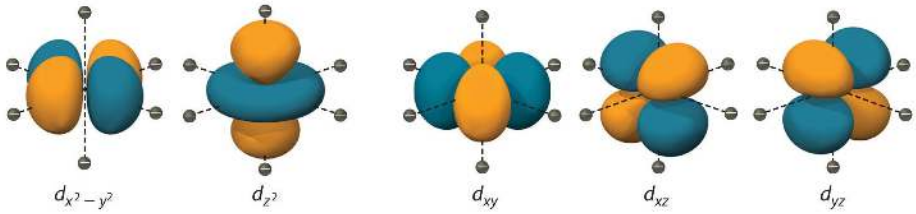


Figure **6.9.3**: Spatial arrangement of ligands in the an octahedral ligand field with respect to the five d-orbitals. (**LibreText**)

Octahedral Complexes

In an octahedral complex, there are six ligands attached to the central transition metal. The d-orbital splits into two different levels (Figure **6.9.4**). The bottom three energy levels are named d_{xy}, d_{xz}, and d_{yz} (collectively referred to as t_{2g}). The two upper energy levels are named $d_{x^2-y^2}$, and d_{z^2} (collectively referred to as e_g).

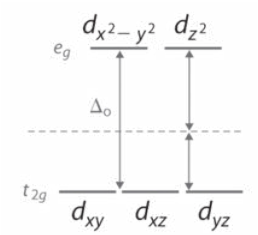


Figure **6.9.4**: Spllitting of degenerate d-orbitalsdue to an on octahedral ligand field. (**LibreText**)

The reason they split is because of the electrostatic interactions between the electrons of the ligand and the lobes of the d-orbital. In an octahedral, the electrons are attracted to the axes. Any orbital that has a lobe on the axes moves to a higher energy level. This means that in an octahedral, the energy levels of e_g are higher ($0.6\Delta_o$) while t_{2g} is lower ($0.4\Delta_o$). The distance that the electrons have to move from t_{2g} from e_g and it dictates the energy that the complex will absorb from white light, which will determine the color. Whether the complex is paramagnetic or diamagnetic will be determined by the spin state. If there are unpaired electrons, the complex is paramagnetic; if all electrons are paired, the complex is diamagnetic.

Tetrahedral Complexes

In a tetrahedral complex, there are four ligands attached to the central metal. The d orbitals also split into two different energy levels. The top three consist of the d_{xy}, d_{xz}, and d_{yz} orbitals. The bottom two consist of the $d_{x^2-y^2}$ and d_{z^2} orbitals. The reason for this is due to poor orbital overlap between the metal and the ligand orbitals. The orbitals are directed on the axes, while the ligands are not.

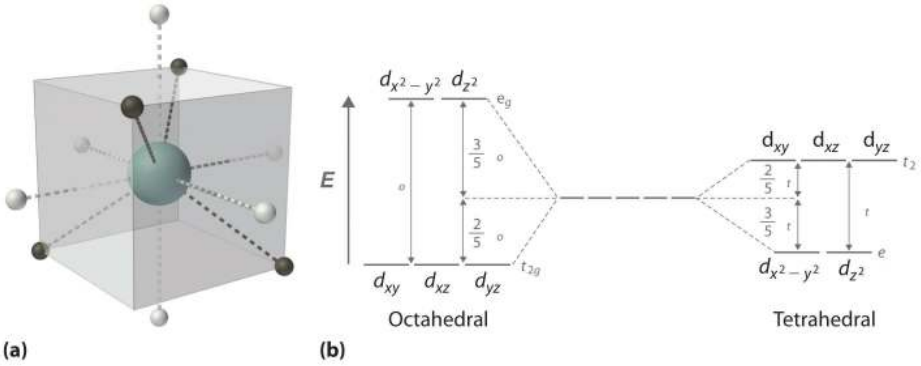


Figure **6.9.5**: (a) Tetraheral ligand field surrounding a central transition metal (blue sphere). (b) Splitting of the degenerate d-orbitals (without a ligand field) due to an octahedral ligand field (left diagram) and the tetrahedral field (right diagram). (**LibreText**)

The difference in the splitting energy is tetrahedral splitting constant (Δ_t), which less than (Δ_o) for the same ligands:

$$\Delta_t = 0.44\,\Delta_o \tag{6.9.1}$$

Consequentially, Δ_t is typically smaller than the spin pairing energy, so tetrahedral complexes are usually **high spin**.

Square Planar Complexes

In a square planar, there are four ligands as well. However, the difference is that the electrons of the ligands are only attracted to the xy plane. Any orbital in the xy plane has a higher energy level (Figure **6.9.6**). There are four different energy levels for the square planar (from the highest energy level to the lowest energy level): $d_{x^2-y^2}$, d_{xy}, d_{z^2}, and both d_{xz} and d_{yz}.

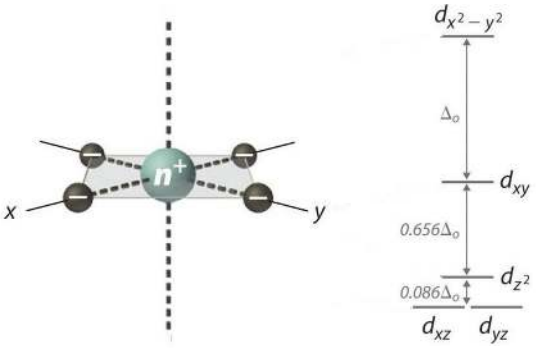


Figure **6.9.6**: Splitting of the degenerate d-orbitals (without a ligand field) due to an square planar ligand field. (**LibreText**)

The splitting energy (from highest orbital to lowest orbital) is Δ_{sp} and tends to be larger then Δ_o

$$\Delta_{sp} = 1.74\,\Delta_o \tag{6.9.2}$$

Moreover, Δ_{sp} is also larger than the pairing energy, so the square planar complexes are usually **low spin** complexes.

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6.10: Factors Affecting Electronic Structure

Electronic Structures of Metal Complexes

According to the Aufbau principle, electrons are filled from lower to higher energy orbitals. For the octahedral case, this corresponds to filling the d_{xy}, d_{xz}, and d_{yz} orbitals first. Following Hund's rule, electrons are distributed into orbitals to give the highest number of unpaired electrons. For example, if one had a d^3 complex, there would be three unpaired electrons.

Consider several examples of electronic configurations for octahedral complexes shown in Figure **6.10.1**. The Ti^{3+} ion contains a single d electron, and additional configurations can be obtained as we proceed across the first row of the transition metals by adding a single electron at a time. Additional electrons are placed in the lowest-energy orbital available, while keeping their spins parallel as required by Hund's rule. As shown in Figure **6.10.1**, for d^1–d^3 systems—such as $[Ti(H_2O)_6]^{3+}$, $[V(H_2O)_6]^{3+}$, and $[Cr(H_2O)_6]^{3+}$, respectively—the electrons successively occupy the three degenerate t_{2g} orbitals with their spins parallel, giving one, two, and three unpaired electrons, respectively. We can summarize this for the complex $[Cr(H_2O)_6]^{3+}$, for example, by saying that the chromium ion has a d^3 electron configuration or, more succinctly, Cr^{3+} is a d^3 ion.

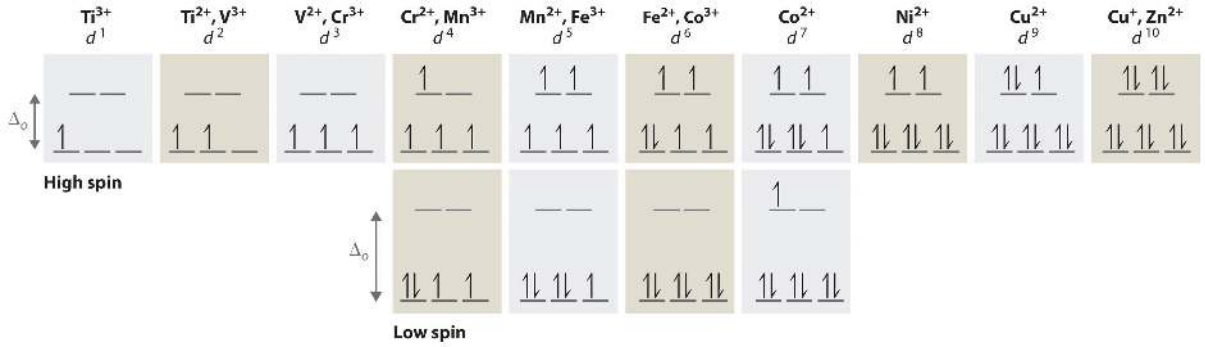


Figure **6.10.1**: The Possible Electron Configurations for Octahedral d^n Transition-Metal Complexes (n = 1–10). Two different configurations are possible for octahedral complexes of metals with d^4, d^5, d^6, and d^7 configurations; the magnitude of Δ_o determines which configuration is observed. (CC BY-SA-NC; anonymous by request)

When we reach the d^4 configuration, there are two possible choices for the fourth electron: it can occupy one of the empty, higher-energy e_g orbitals (d_{z^2} or $d_{x^2-y^2}$) or it can occupy one of the lower-energy, singly-occupied t_{2g} orbitals (d_{xy}, d_{xz}, or d_{yz}). Recall that placing an electron in an already occupied orbital results in electrostatic repulsions that increase the energy of the system; this increase in energy is called the spin-pairing energy (P). If Δ_o is less than P, then the lowest-energy arrangement places the fourth electron in one of the empty e_g orbitals. This configuration maximizes the spin multiplicity. Because this arrangement results in four unpaired electrons, it is called a **high-spin** configuration, and a complex with this electron configuration, such as the $[Cr(H_2O)_6]^{2+}$ ion, is called a high-spin complex. Conversely, if Δ_o is greater than P, then the lowest-energy arrangement places the fourth electron in one of the occupied t_{2g} orbitals. Because this arrangement results in only two unpaired electrons, it is called a **low-spin** configuration, and a complex with this electron configuration, such as the $[Mn(CN)_6]^{3-}$ ion, is called a low-spin complex. Similarly, metal ions with the d^5, d^6, or d^7 electron configurations can be either high spin or low spin, depending on the magnitude of Δ_o.

In contrast, only one arrangement of d electrons is possible for metal ions with d^8–d^{10} electron configurations. For example, the $[Ni(H_2O)_6]^{2+}$ ion is d^8 with two unpaired electrons, the $[Cu(H_2O)_6]^{2+}$ ion is d^9 with one unpaired electron, and the $[Zn(H_2O)_6]^{2+}$ ion is d^{10} with no unpaired electrons.

> *If Δ_o is less than the spin-pairing energy, a high-spin configuration results. Conversely, if Δ_o is greater, a low-spin configuration forms.*

A Note on units

The crystal field splitting energy, Δ_o, may be reported in units of J/mol or wave numbers (cm^{-1}). Typically, energies obtained by spectroscopic measurements are often given wave numbers; the wave number is the reciprocal of the wavelength of the corresponding electromagnetic radiation expressed in centimeters: 1 cm^{-1} = 11.96 J/mol.

Factors That Affect the Magnitude of Δ_o

The magnitude of the crystal field splitting energy, Δ_o, dictates whether a complex with four, five, six, or seven d electrons is high spin or low spin, which affects its magnetic properties, structure, and reactivity. Large values of Δ_o (i.e., Δ_o > P) yield a low-spin complex, whereas small values of Δ_o (i.e., Δ_o < P) produce a high-spin complex. As we noted, the magnitude of Δ_o depends on three factors: the charge on the metal ion, the principal quantum number of the metal (and thus its location in the periodic table), and the nature of the ligand. Values of Δ_o for some representative transition-metal complexes are given in Table **6.10.1**.

Table **6.10.1**: Crystal Field Splitting Energies for Some Octahedral (Δ_o) and Tetrahedral (Δ_t) Transition-Metal Complexes

Octahedral Complexes	Δ_o (cm^{-1})	Octahedral Complexes	Δ_o (cm^{-1})	Tetrahedral Complexes	Δ_t (cm^{-1})
$[Ti(H_2O)_6]^{3+}$	20,300	$[Fe(CN)_6]^{4-}$	32,800	VCl_4	9010
$[V(H_2O)_6]^{2+}$	12,600	$[Fe(CN)_6]^{3-}$	35,000	$[CoCl_4]^{2-}$	3300
$[V(H_2O)_6]^{3+}$	18,900	$[CoF_6]^{3-}$	13,000	$[CoBr_4]^{2-}$	2900
$[CrCl_6]^{3-}$	13,000	$[Co(H_2O)_6]^{2+}$	9300	$[CoI_4]^{2-}$	2700
$[Cr(H_2O)_6]^{2+}$	13,900	$[Co(H_2O)_6]^{3+}$	27,000		
$[Cr(H_2O)_6]^{3+}$	17,400	$[Co(NH_3)_6]^{3+}$	22,900		
$[Cr(NH_3)_6]^{3+}$	21,500	$[Co(CN)_6]^{3-}$	34,800		
$[Cr(CN)_6]^{3-}$	26,600	$[Ni(H_2O)_6]^{2+}$	8500		
$Cr(CO)_6$	34,150	$[Ni(NH_3)_6]^{2+}$	10,800		
$[MnCl_6]^{4-}$	7500	$[RhCl_6]^{3-}$	20,400		
$[Mn(H_2O)_6]^{2+}$	8500	$[Rh(H_2O)_6]^{3+}$	27,000		
$[MnCl_6]^{3-}$	20,000	$[Rh(NH_3)_6]^{3+}$	34,000		
$[Mn(H_2O)_6]^{3+}$	21,000	$[Rh(CN)_6]^{3-}$	45,500		
$[Fe(H_2O)_6]^{2+}$	10,400	$[IrCl_6]^{3-}$	25,000		
$[Fe(H_2O)_6]^{3+}$	14,300	$[Ir(NH_3)_6]^{3+}$	41,000		

Source of data: Duward F. Shriver, Peter W. Atkins, and Cooper H. Langford, Inorganic Chemistry, 2nd ed. (New York: W. H. Freeman and Company, 1994).

Factor 1: Charge on the Metal Ion

Increasing the charge on a metal ion has two effects: the radius of the metal ion decreases, and negatively charged ligands are more strongly attracted to it. Both effects decrease the metal–ligand distance, which in turn causes the negatively charged ligands to interact more strongly with the d-orbitals. Consequently, the magnitude of Δ_o increases as the charge on the metal ion increases. Typically, Δ_o for a +3 ion is about 50% greater than for the +2 ion of the same metal; for example, for $[V(H_2O)_6]^{2+}$, Δ_o = 11,800 cm^{-1}; for $[V(H_2O)_6]^{3+}$, Δ_o = 17,850 cm^{-1}.

Factor 2: Principal Quantum Number of the Metal

For a series of complexes of metals from the same group in the periodic table with the same charge and the same ligands, the magnitude of Δ_o increases with increasing principal quantum number: Δ_o (3d) < Δ_o (4d) < Δ_o (5d). The data for hexaammine complexes of the trivalent Group 9 metals illustrate this point:

$$[Co(NH_3)_6]^{3+}: \Delta_o = 22{,}900\ cm^{-1}$$

$$[Rh(NH_3)_6]^{3+}: \Delta_o = 34{,}100\ cm^{-1}$$

$$[Ir(NH_3)_6]^{3+}: \Delta_o = 40{,}000\ cm^{-1}$$

The increase in Δ_o with increasing principal quantum number is due to the larger radius of valence orbitals down a column. In addition, repulsive ligand–ligand interactions are most important for smaller metal ions. Relatively speaking, this results in shorter M–L distances and stronger d orbital–ligand interactions.

Factor 3: The Nature of the Ligands

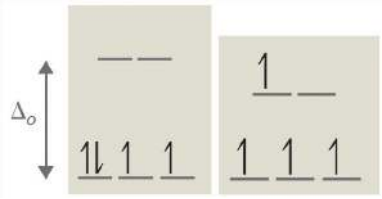


Figure **6.10.2**: Low Spin, Strong Field ($\Delta_o > P$) High Spin, Weak Field ($\Delta_o < P$)Splitting for a d^4 complex under a strong field (left) and a weak field (right). The strong field is a low spin complex, while the weak field is a high spin complex.

Experimentally, it is found that the Δ_o observed for a series of complexes of the same metal ion depends strongly on the nature of the ligands. Ligands that cause a transition metal to have a small crystal field splitting, which leads to a high-spin configuration, are called **weak-field**

ligands. Ligands that produce a large crystal field splitting, which leads to a low-spin configuration, are called **strong field ligands** (Figure **6.10.2**).

For a series of chemically similar ligands, the magnitude of Δ_o decreases as the size of the donor atom increases. For example, Δ_o values for halide complexes generally decrease in the order $F^- > Cl^- > Br^- > I-$ because smaller, more localized charges, such as we see for F^-, interact more strongly with the d orbitals of the metal ion.

In addition, a small neutral ligand with a highly localized lone pair, such as NH_3, results in significantly larger Δ_o values than might be expected. Because the lone pair points directly at the metal ion, the electron density along the M–L axis is greater than for a spherical anion such as F^-.

The experimentally observed order of the crystal field splitting energies produced by different ligands is called the spectrochemical series. It is shown here in order of increasing Δ_o:

$$\underset{\text{weak-field ligands}}{I^- < Br^- < Cl^- < \underline{S}CN^- < CH_3COO^- < F^- < OH^- < ox^{2-}} < \underset{\text{intermediate-field ligands}}{ONO^- < H_2O < SC\underline{N}^-} < EDTA^{4-} < NH_3 < en < NO_2^- < \underset{\text{strong-field ligands}}{CN^- \approx CO}$$

Note that SCN^- and NO_2- ligands are represented twice in the above spectrochemical series since there are two different Lewis base sites (e.g., free electron pairs to share) on each ligand (e.g., for the SCN^- ligand, the electron pair on the sulfur or the nitrogen can form the coordinate covalent bond to a metal). The specific atom that binds in such ligands is underlined.

> *The largest Δ_o splittings are found in complexes of metal ions from the third row of the transition metals with charges of at least +3 and ligands with localized lone pairs of electrons.*

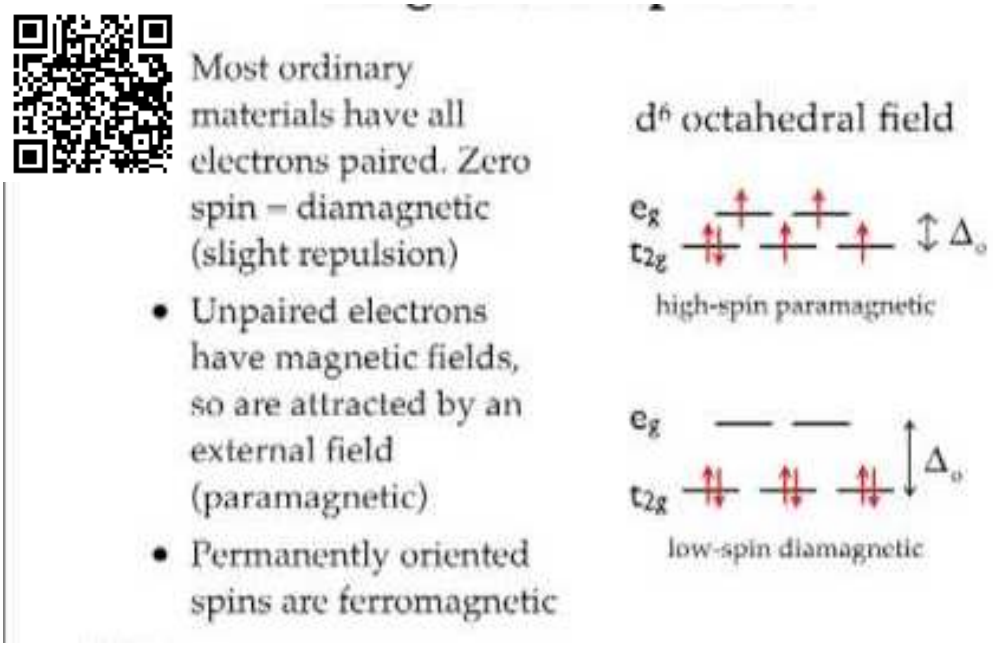
Factor 4: Molecular Geometry

In addition to octahedral complexes, two common geometries observed are that of tetrahedral and square planar. These complexes differ from the octahedral complexes in that the orbital levels are raised in energy due to the interference with electrons from ligands. For the tetrahedral complex, the d_{xy}, d_{xz}, and d_{yz} orbitals are raised in energy while the d_{z^2}, $d_{x^2-y^2}$ orbitals are lowered. For the square planar complexes, there is greatest interaction with the $d_{x^2-y^2}$ orbital and therefore it has higher energy. The next orbital with the greatest interaction is d_{xy}, followed below by d_{z^2}. The orbitals with the lowest energy are the d_{xz} and d_{yz} orbitals. There is a large energy separation between the d_{z^2} orbital and the d_{xz} and d_{yz} orbitals, meaning that the crystal field splitting energy is large. We find that the square planar complexes have the greatest crystal field splitting energy compared to all the other complexes. This means that most square planar complexes are low spin, strong field ligands.

The splitting energy (from highest orbital to lowest orbital) is Δ_{sp} and tends to be larger then Δ_o

$$\Delta_{sp} = 1.74\,\Delta_o \tag{6.10.1}$$

Moreover, Δ_{sp} is also larger than the pairing energy, so the square planar complexes are usually **low spin** complexes.



Example 6.10.1

For the complex, predict its structure, whether it is high spin or low spin, and the number of unpaired electrons present:

$[CoF_6]^{3-}$

Solution

With six ligands, we expect this complex to be octahedral.

The fluoride ion is a small anion with a concentrated negative charge, but compared with ligands with localized lone pairs of electrons, it is weak field. The charge on the metal ion is +3, giving a d^6 electron configuration.

Because of the weak-field ligands, we expect a relatively small Δ_o, making the compound high spin.

In a high-spin octahedral d^6 complex, the first five electrons are placed individually in each of the d orbitals with their spins parallel, and the sixth electron is paired in one of the t_{2g} orbitals, giving four unpaired electrons.

Example 6.10.2

For the complex, predict its structure, whether it is high spin or low spin, and the number of unpaired electrons present:

$[Rh(CO)_2Cl_2]^-$

Solution

This complex has four ligands, so it is either square planar or tetrahedral.

Because rhodium is a second-row transition metal ion with a d^8 electron configuration and CO is a strong-field ligand, the complex is likely to be square planar with a large Δ_o, making it low spin. Because the strongest d-orbital interactions are along the x and y axes, the orbital energies increase in the order $d_{z^2}d_{yz}$, and d_{xz} (these are degenerate); d_{xy}; and $d_{x^2-y^2}$.

The eight electrons occupy the first four of these orbitals, leaving the $d_{x^2-y^2}$. orbital empty. Thus there are no unpaired electrons.

Problems

Exercise 6.10.1

For the complex, predict its structure, whether it is high spin or low spin, and the number of unpaired electrons present.

$[Mn(H_2O)_6]^{2+}$

Answer

octahedral; high spin; five

Exercise 6.10.2

For the complex, predict its structure, whether it is high spin or low spin, and the number of unpaired electrons present.

$[PtCl_4]^{2-}$

Answer

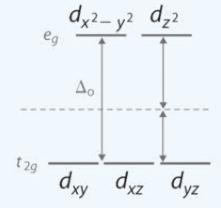
square planar; low spin; no unpaired electrons

Exercise 6.10.3

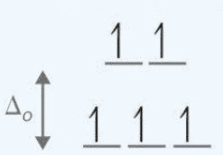
For the complex ion $[Fe(Cl)_6]^{3-}$ determine the number of d electrons for Fe, sketch the d-orbital energy levels and the distribution of d electrons among them, list the number of lone electrons, and label whether the complex is paramagnetic or diamagnetic.

Answer

Step 1: Determine the oxidation state of Fe. Here it is Fe^{3+}. Based on its electron configuration, Fe^{3+} has **5 d-electrons**. Step 2: Determine the geometry of the ion. Here it is an octahedral which means the energy splitting should look like:



Step 3: Determine whether the ligand induces is a strong or weak field spin by looking at the spectrochemical series. Cl^- is a weak field ligand (i.e., it induces high spin complexes). Therefore, electrons fill all orbitals before being paired.



Step four: Count the number of lone electrons. Here, there are **5 electrons**. Step five: The five unpaired electrons means this complex ion is **paramagnetic** (and strongly so).

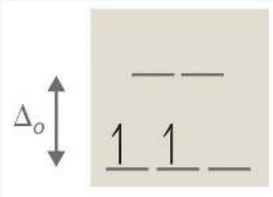
Exercise 6.10.4

For each of the following, sketch the d-orbital energy levels and the distribution of d electrons among them, state the geometry, list the number of d-electrons, list the number of lone electrons, and label whether they are paramagnetic or dimagnetic:

a. $[Ti(H_2O)_6]^{2+}$
b. $[NiCl_4]^{2-}$
c. $[CoF_6]^{3-}$ (also state whether this is low or high spin)
d. $[Co(NH_3)_6]^{3+}$ (also state whether this is low or high spin)
e. True or False: Square Planer complex compounds are usually low spin.

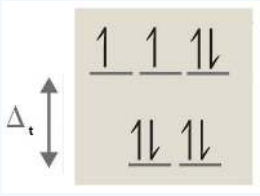
Answer a

octahedral, 2, 2, paramagnetic



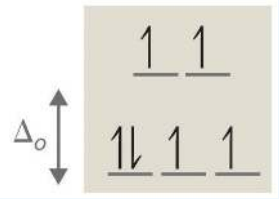
Answer b

tetrahedral, 8, 2, paramagnetic (see Octahedral vs. Tetrahedral Geometries)



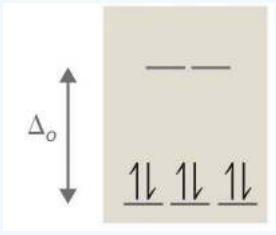
Answer c

octahedral, 6, 4, paramagnetic, high spin



Answer d

octahedral, 6, 0, diamagnetic, low spin



Answer e

True

Summary

Crystal field theory, which assumes that metal–ligand interactions are only electrostatic in nature, explains many important properties of transition-metal complexes, including their colors, magnetism, structures, stability, and reactivity. Crystal field theory (CFT) is a bonding model that explains many properties of transition metals that cannot be explained using valence bond theory. In CFT, complex formation is assumed to be due to electrostatic interactions between a central metal ion and a set of negatively charged ligands or ligand dipoles arranged around the metal ion. Depending on the arrangement of the ligands, the d orbitals split into sets of orbitals with different energies. The difference between the energy levels in an octahedral complex is called the crystal field splitting energy (Δ_o), whose magnitude depends on the charge on the metal ion, the position of the metal in the periodic table, and the nature of the ligands. The spin-pairing energy (P) is the increase in energy that occurs when an electron is added to an already occupied orbital. A high-spin configuration occurs when the Δ_o is less than P, which produces complexes with the maximum number of unpaired electrons possible. Conversely, a low-spin configuration occurs when the Δ_o is greater than P, which produces complexes with the minimum number of unpaired electrons possible. Strong-field ligands interact strongly with the d orbitals of the metal ions and give a large Δ_o, whereas weak-field ligands interact more weakly and give a smaller Δ_o. The colors of transition-metal complexes depend on the environment of the metal ion and can be explained by CFT.

Contributors and Attributions

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6.11: Crystal Field Stabilization Energy

The difference in energy between the two sets of d orbitals is called the crystal field splitting energy (Δ_o), where the subscript o stands for octahedral. The magnitude of the splitting depends on the charge on the metal ion, the position of the metal in the periodic table, and the nature of the ligands. Crystal field splitting energy also applies to tetrahedral complexes (Δ_t), where the subscript t standands for tetrahedral. It is important to note that the splitting of the d orbitals in a crystal field does not change the total energy of the five d orbitals. In an octahedral complex, the two e_g orbitals increase in energy by $0.6\Delta_o$, and the three t_{2g} orbitals decrease in energy by $0.4\Delta_o$ (Figure **6.11.1**). Thus the total change in energy is

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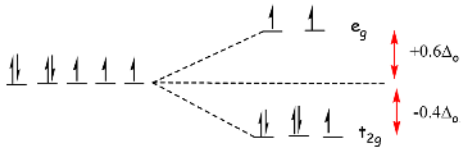


Figure **6.11.1**: Crystal field diagram of an octahedral complex showing the increased energy of the e_g and decreased energy of the t_{2g} orbitals. (LibreText)

> *Crystal field splitting does not change the total energy of the d orbitals.*

Quantifying Crystal Field Stabilization Energy

Recall that stable molecules contain more electrons in the lower-energy (bonding) molecular orbitals in a molecular orbital diagram than in the higher-energy (antibonding) molecular orbitals. If the lower-energy set of d orbitals (the t_{2g} orbitals) is selectively populated by electrons, then the stability of the complex increases relative to the d-orbitals on the free metal ion. For example, the single d electron in a d^1 complex such as $[Ti(H_2O)_6]^{3+}$ is located in one of the t_{2g} orbitals. Consequently, this complex will be more stable than expected on purely electrostatic grounds by $0.4\Delta_o$. The additional stabilization of a metal complex by selective population of the lower-energy d orbitals is called its **crystal field stabilization energy** (CFSE).

The CFSE of a complex can be calculated by multiplying the number of electrons in t_{2g} orbitals by the energy of those orbitals ($-0.4\Delta_o$), multiplying the number of electrons in e_g orbitals by the energy of those orbitals ($+0.6\Delta_o$), and summing the two. Using the high-spin d^7 configuration shown in Figure **6.11.1** as an example:

$$\mathbf{CFSE} = (5 \times -0.4\Delta_o) + (2 \times 0.6\Delta_o) = -0.8\Delta_o \tag{6.11.1}$$

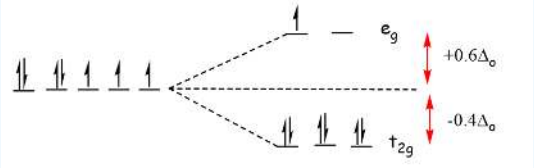
CFSEs are important for two reasons. First, the existence of CFSE nicely accounts for the difference between experimentally measured values for bond energies in metal complexes and values calculated based solely on electrostatic interactions. Second, CFSE represents relatively large amounts of energy (up to several hundred kilojoules per mole), which has important chemical consequences.

Example 6.11.1

What is the Crystal Field Stabilization Energy for a low spin d^7 octahedral complex?

Solution

The splitting pattern and electron configuration for both isotropic and octahedral ligand fields are compared below.



$$\mathbf{CFSE} = (6 \times -0.4\Delta_O) + (1 \times 0.6\Delta_O) = -1.8\Delta_O \tag{6.11.2}$$

Table **6.11.1** gives CFSE values for octahedral complexes with different d electron configurations. The CFSE is highest for low-spin d^6 complexes, which accounts in part for the extraordinarily large number of Co(III) complexes known. The other low-spin configurations also have high CFSEs, as does the d^3 configuration.

Table **6.11.1**: CFSEs for Octahedral Complexes with Different Electron Configurations (in Units of Δo)

	High Spin		CFSE (Δ_o)	Low Spin		CFSE (Δ_o)
	t_{2g}	e_g		t_{2g}	e_g	
d^0			0			
d^1	↑		0.4			
d^2	↑ ↑		0.8			
d^3	↑ ↑ ↑		1.2			
d^4	↑ ↑ ↑	↑	0.6	↑↓ ↑ ↑		1.6
d^5	↑ ↑ ↑	↑ ↑	0.0	↑↓ ↑↓ ↑		2.0
d^6	↑↓ ↑ ↑	↑ ↑	0.4	↑↓ ↑↓ ↑↓		2.4
d^7	↑↓ ↑↓ ↑	↑ ↑	0.8	↑↓ ↑↓ ↑↓	↑	1.8
d^8	↑↓ ↑↓ ↑↓	↑ ↑	1.2			
d^9	↑↓ ↑↓ ↑↓	↑↓ ↑	0.6			
d^{10}	↑↓ ↑↓ ↑↓	↑↓ ↑↓	0.0			

> *Octahedral d^3 and d^8 complexes and low-spin d^6, d^5, d^7, and d^4 complexes exhibit large CFSEs.*

Octahedral Preference

Similar CFSE values can be constructed for non-octahedral ligand field geometries. In an octahedral complex, the two e_g orbitals decrease in energy by $0.6\Delta_t$, and the three t_{2g} orbitals increase in energy by $0.4\Delta_t$ (Figure **6.11.2**). As for octahedral complexes, the total energy of the d-orbitals in a tetrahedral complex does not change; the total change in energy is

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Note: Δ_o and Δ_t represent different units of energy. The tetrahedral crystal field is smaller in energy than the octahedral crystal field, which contributes to the tetrahedral preference for high-spin complexes (Figure **6.11.2**). The following conversion may be used for comparing octahedral and tetrahedral complexes that involve same ligands only:

$$\Delta_t \approx \frac{4}{9}\Delta_o \tag{6.11.3}$$

The CFSE for a tetrahedral complex is calculated in Table **6.11.2**. These energies can then be compared to the octahedral CFSE to calculate a thermodynamic preference (Enthalpy-wise) for a metal-ligand combination to favor the octahedral geometry. This is quantified via a **Octahedral Site Preference Energy**:

$$OSPE = CFSE_{(oct)} - CFSE_{(tet)}$$

The OSPE quantifies the preference of a complex to exhibit an octahedral geometry vs. a tetrahedral geometry. Figure **6.11.3** compares the CFSE for tetrahedral and octahedral high-spin complexes for each d-electron configuration. From a simple inspection of Figure **6.11.3**, the following observations can be made:

- The OSPE is *small* in d^1, d^2, d^5, d^6, d^7 complexes and other factors influence the stability of the complexes including steric factors.

- The OSPE is *large* in d^3 and d^8 complexes which strongly favor octahedral geometries.

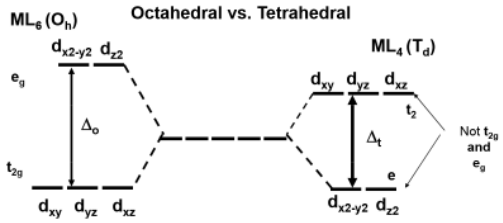


Figure **6.11.2**: A comparison of octahedral and tetrahedral crystal fields. (LibreText)

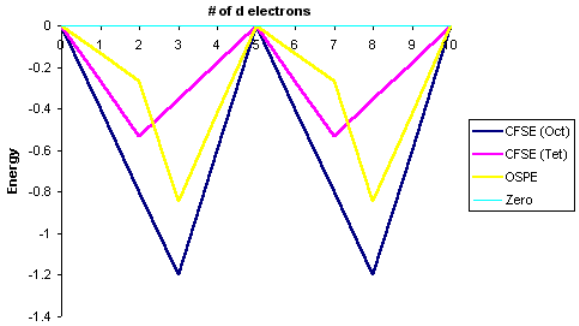


Figure **6.11.1**: Crystal Field Stabilization Energies for both octahedral fields ($CFSE_{oct}$) and tetrahedral fields ($CFSE_{tet}$). Octahedral Site Preference Energies (OSPE) are in yellow. This is for high spin complexes. (LibreText)

Table **6.11.2**: Octahedral Site Preference Energies (OSPE)

Total d-electrons	**CFSE(Octahedral)**		**CFSE(Tetrahedral)**		**OSPE (for high spin complexes)****
	High Spin	Low Spin	Configuration	**Always High Spin***	
d^0	0 Δ_o	0 Δ_o	e^0	0 Δ_t	0 Δ_o
d^1	-2/5 Δ_o	-2/5 Δ_o	e^1	-3/5 Δ_t	-6/45 Δ_o
d^2	-4/5 Δ_o	-4/5 Δ_o	e^2	-6/5 Δ_t	-12/45 Δ_o
d^3	-6/5 Δ_o	-6/5 Δ_o	$e^2t_2^1$	-4/5 Δ_t	-38/45 Δ_o
d^4	-3/5 Δ_o	-8/5 Δ_o + P	$e^2t_2^2$	-2/5 Δ_t	-19/45 Δ_o
d^5	0 Δ_o	-10/5 Δ_o + 2P	$e^2t_2^3$	0 Δ_t	0 Δ_o
d^6	-2/5 Δ_o	-12/5 Δ_o + P	$e^3t_2^3$	-3/5 Δ_t	-6/45 Δ_o
d^7	-4/5 Δ_o	-9/5 Δ_o + P	$e^4t_2^3$	-6/5 Δ_t	-12/45 Δ_o
d^8	-6/5 Δ_o	-6/5 Δ_o	$e^4t_2^4$	-4/5 Δ_t	-38/45 Δ_o
d^9	-3/5 Δ_o	-3/5 Δ_o	$e^4t_2^5$	-2/5 Δ_t	-19/45 Δ_o
d^{10}	0	0	$e^4t_2^6$	0 Δ_t	0 Δ_o

Example 6.11.2

For each complex, predict its structure, whether it is high spin or low spin, and the number of unpaired electrons present.

1. $[Cu(NH_3)_4]^{2+}$
2. $[Ni(CN)_4]^{2-}$

Solution

Because Δ_o is so large for the second- and third-row transition metals, all four-coordinate complexes of these metals are square planar due to the much higher crystal field stabilization energy (CFSE) for square planar versus tetrahedral structures. The only exception is for d^{10} metal ions such as Cd^{2+}, which have zero CFSE and are therefore tetrahedral as predicted by the VSEPR model. Four-coordinate complexes of the first-row transition metals can be either square planar or tetrahedral; the former is favored by strong-field ligands, whereas the latter is favored by weak-field ligands. For example, the $[Ni(CN)_4]^{2-}$ ion is square planar, while the $[NiCl_4]^{2-}$ ion is tetrahedral.

1.

The copper in this complex is a d^9 ion and it has a coordination number of 4. So it is probably either square planar or tetrahedral. To estimate which, we need to fill in the CFT splitting diagrams for each with 9 electrons and ask which has a lower energy. Comparing the square planer (Figure **6.11.1**) splitting diagram with tetrahedral (Figure **6.11.2**), suggests that 9 electrons will have a net lower total energy for square planar (since the $d_{x^2-y^2}$ orbital is high in energy, the others are lower).

For the square planar structure, neither high nor low spin states are possible (only one state) with a single unpaired electron.

2.

The nickle in this complex is a d^8 ion and it has a coordination number of 4. So it is probably either square planar or tetrahedral. To estimate which, we need to fill in the CFT splitting diagrams for each with 8 electrons and ask which has a lower energy. Comparing the square planer (Figure **6.11.1**) splitting diagram with tetrahedral (Figure **6.11.2**), suggests that 8 electrons will have a net lower total energy for square planar (since the $d_{x^2-y^2}$ orbital is high in energy, the others are lower).

For the square planar structure, it is a low spin complex since a high spin requires a lot of energy to promote to the $d_{x^2-y^2}$ orbital. Hence, there are no unpaired electrons.

Example 6.11.3

Which is the preferred configuration for a d^3 metal: tetrahedral or octahedral?

Solution

To answer this, the *Crystal Field Stabilization Energy* has to be calculated for a (d^3 metal in both configurations. The geometry with the greater stabilization will be the preferred geometry.

- For a d^3 *octahedral* configuration, the *Crystal Field Stabilization Energy* is

$$3 \times -0.4\Delta_o = -1.2\Delta_o$$

- For a d^3 *tetrahedral* configuration (assuming high spin), the *Crystal Field Stabilization Energy* is

$$-0.8\Delta_{tet}$$

Remember that because Δ_{tet} is less than half the size of Δ_o, tetrahedral complexes are often high spin. We can now put this in terms of Δ_o (we can make this comparison because we're considering the same metal ion and the same ligand: all that's changing is the geometry)

So for tetrahedral d^3, the Crystal Field Stabilization Energy is:

$$\text{CFSE} = -0.8 \text{ x } 4/9\ \Delta_o = -0.355\ \Delta_o.$$

And the difference in Crystal Field Stabilization Energy between the two geometries will be:

$$1.2 - 0.355 = 0.845\ \Delta_{o.}$$

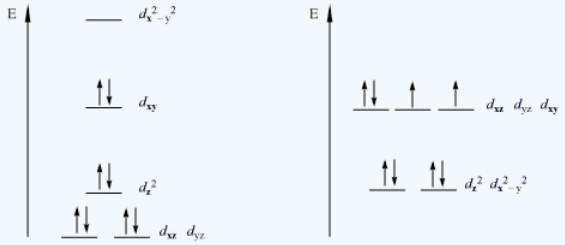
Example 6.11.4

The molecule $[PdCl_4]^{2-}$ is diamagnetic, which indicates a square planar geometry as all eight d-electrons are paired in the lower-energy orbitals. However, $[NiCl_4]^{2-}$ is also d^8 but has two unpaired electrons, indicating a tetrahedral geometry. Why is $[PdCl_4]^{2-}$ square planar if Cl^- is not a strong-field ligand?

Solution

The geometry of the complex changes going from $[NiCl_4]^{2-}$ to $[PdCl_4]^{2-}$. Clearly this cannot be due to any change in the ligand since it is the same in both cases. It is the other factor, the metal, that leads to the difference.

Consider the splitting of the d-orbitals in a generic d^8 complex. If it were to adopt a square planar geometry, the electrons will be stabilized (with respect to a tetrahedral complex) as they are placed in orbitals of lower energy. However, this comes at a cost: two of the electrons, which were originally unpaired in the tetrahedral structure, are now paired in the square-planer structure:



We can label these two factors as ΔE (stabilization derived from occupation of lower-energy orbitals) and P (spin pairing energy) respectively. One can see that:

- If $\Delta E > P$, then the complex will be square planar
- If $\Delta E < P$, then the complex will be tetrahedral.

This is analogous to deciding whether an octahedral complex adopts a high- or low-spin configuration; where the crystal field splitting parameter Δ_o ΔE does above. Unfortunately, unlike Δ_o in octahedral complexes, there is no simple graphical way to represent ΔE on the diagram above since multiple orbitals are changed in energy between the two geometries.

Interpreting the origin of metal-dependent stabilization energies can be tricky. However, we know experimentally that Pd^{2+} has a larger splitting of the d-orbitals and hence a larger ΔE than Ni^{2+} (moreover P is also smaller).

Practically all 4d and 5d d^8 ML_4 complexes adopt a square planar geometry, irrespective if the ligands are strong-field ligand or not. Other examples of such square planar complexes are $[PtCl_4]^{2-}$ and $[AuCl_4]^-$.

Problems

? Exercise 6.11.1

Determine the crystal field stabilization energy (CFSE) in the following octahedral ions:

a. V^{3+}
b. Ni^{2+}
c. Cr^{3+}
d. Zn^{2+}

Answer a

V^{3+} is d^2, with two electrons in the t_{2g} and zero electrons in e_g.

CFSE = $[2(-0.4) + 0(0.6)] \times \Delta_o = -0.8\Delta_o$

Answer b

Ni^{2+} is d^8, with six electrons in t_{2g} and two electrons in e_g.

CFSE = $[6(-0.4) + 2(0.6)] \times \Delta_o = -1.2\Delta_o$

Answer c

Cr^{3+} is d^3, with three electrons in t_{2g} and zero electrons in e_g.

CFSE = $[3(-0.4) + 0(0.6)] \times \Delta_o = -1.2\Delta_o$

Answer d

Zn^{2+} is d^{10}, with six electrons in t_{2g} and four electrons in e_g.

CFSE = $[6(-0.4) + 4(0.6)] \times \Delta_o = 0\Delta_o$.

? Exercise 6.11.2

What are the geometries of the following two complexes?

1. $[AlCl_4]^-$
2. $[Ag(NH_3)_2]^+$

Answer 1

tetrahedral

Answer 2

linear

Contributors and Attributions

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6.12: Colors of Coordination Complexes

The color for a coordination complex can be predicted using the Crystal Field Theory (CFT). The tendency for coordination complexes to display such a wide array of colors is merely coincidental; the d-orbital splitting in coordination complexes results in a gap (**Δ**) that happens to be just the right magnitude to absorb visible light. Because metal complexes can absorb visible light, they display an array of colors. Not only is the color attractive to the eye, it is an indication of the chemical and physical properties of the metal complex. The color (like the magnitude of **Δ**) depends on the identity of the metal ion, the coordination geometry, and the ligand identity. Chemists don't just "look" at color, though - we measure it using electronic absorption spectroscopy. This is usually done in a lab using a UV-visible spectrophotometer.

An example of such a measurement is shown below in Figure **6.12.1** for a Cu(II) complex. The sample appears a pink color to the eye, and when it is measured using a UV-visible spectrometer, it is shown to absorb visible light at approximately 530 nm. The absorption spectrum can indicate the oxidation state of Cu, the ligands bound to the Cu(II) ion, and the coordination geometry. The color of the solution in Figure **6.12.1** is a shade of pink.

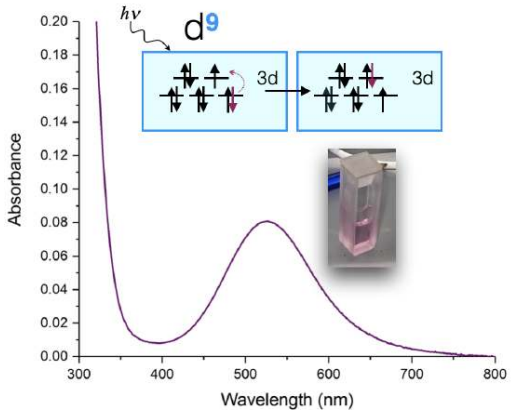


Figure **6.12.1**: A UV-visible spectrum of a Cu(II)-peptide complex. A photo of the sample shows its pink color. The splitting diagram for its approximation as an octahdral complex is shown, where an electronic transition from t_{2g} to e_g is shown. (CC-BY-NC-SA; Kathryn Haas)

The Electromagnetic Spectrum

The electromagnetic spectrum (EM) spectrum is made up of photons of different wavelengths. Photons, unique in displaying the properties of both waves and particles, create visible light and colors in a small portion of the EM spectrum. This visible light portion has wavelengths in approximately the 400-750 nanometer range (a nanometer, "nm," is 10^{-9} meters). Each specific wavelength corresponds to a different color (Figure **6.12.2**), and when all the wavelengths are present, it appears as white light.

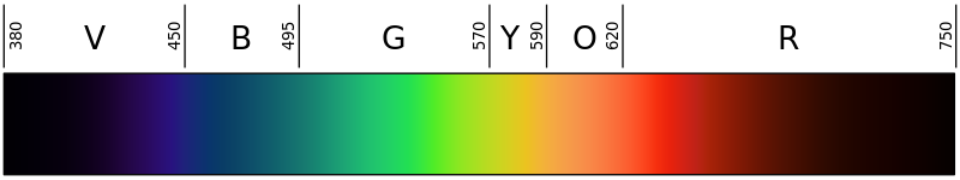


Figure **6.12.2**: A linear representation of the visible light spectrum. (Public Domain; Gringer via Wikipedia)

The wavelength and frequency of a wave are inversely proportional: as one increases, the other decreases; this is a consequence of all light traveling at the same speed.

$$\lambda \propto \nu^{-1}$$

Because of this relationship, blue light has a much higher frequency and more energy than red light.

Perceiving Color

Color is perceived in two ways, through additive mixing, where different colors are made by combining different colors of light, and through subtractive mixing, where different wavelengths of light are taken out so that the light is no longer pure white. For

colors of coordination complexes, subtractive mixing is considered. As shown in Figure **6.12.3**, the idea behind subtractive mixing is that white light (which is made from all the colors mixed together) interacts with an object. The object absorbs some of the light, and then reflects or transmits (or both, depending on the object) the rest of the light, which contacts the eye. The object is perceived as whichever color is not absorbed. In Figure **6.12.3**, white light (simplified as green, red, and blue bands) is shone through a solution. The solution absorbs the red and green wavelengths; however, the blue light is reflected and passes through, so the solution appears blue. This procedure takes place whenever an object displays visible color. If none of the light is absorbed, and all is reflected back off, the object appears white; if all of the light is absorbed, and there is none left to reflect or transmit through, the object appears black.

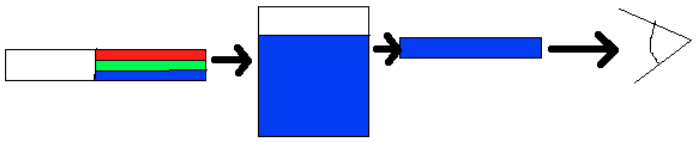
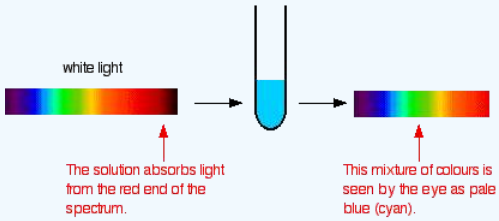


Figure **6.12.3**: Subtractive mixing

Example **6.12.1**: Copper(II) sulfate

If white light (ordinary sunlight, for example) passes through copper(II) sulfate solution, some wavelengths in the light are absorbed by the solution. Copper(II) ions in solution absorb light in the red region of the spectrum. The light which passes through the solution and out the other side will have all the colors in it except for the red. We see this mixture of wavelengths as pale blue (cyan). The diagram gives an impression of what happens if you pass white light through copper(II) sulfate solution.



Working out what color you will see is not easy if you try to do it by imagining "mixing up" the remaining colors. You wouldn't have thought that all the other colors apart from some red would look cyan, for example. Sometimes what you actually see is quite unexpected. Mixing different wavelengths of light doesn't 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.

The absorption spectrum shown above in Figure **6.12.1** is a simple case in which only one absorption band is observed in the visible region of the spectrum. In a simple case like this, the color of a complex can be predicted using a color wheel. When a solution or object absorbs a certain wavelength, we see the complementary color, or the color opposite to the absorbed wavelength on the color wheel in Figure **6.12.4**. In the case of the Cu(II) complex spectrum shown in Figure **6.12.1**, the color of the light absorbed at 530 nm is green, and the predicted color observed is pink. Table **6.12.1** lists the approximate colors of absorption corresponding to wavelengths of light absorbed and gives similar information to that deduced from Figure **6.12.4**.

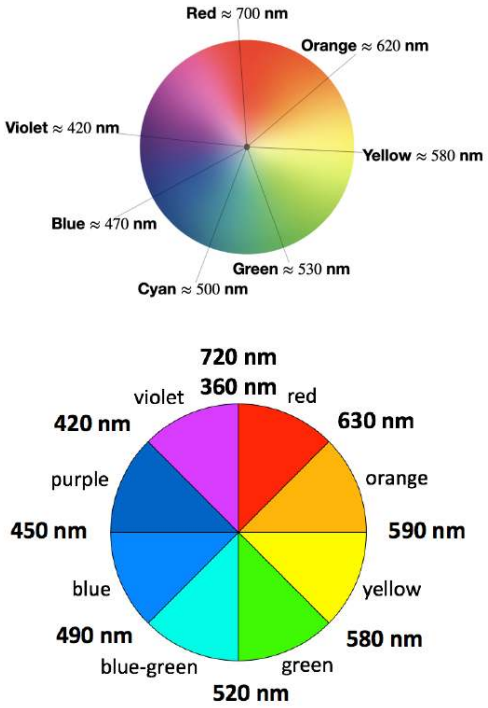


Figure 6.12.4: Color wheels with wavelengths marked (top: CC-BY-NC-SA; Kathryn Haas)(bottom: CC BY-SA 4.0 International; Tem5psu via source)

Table 6.12.1: Approximate wavelengths of absorption and their complementary colors observed. * This prediction is limited to simple cases where there is only one absorption band in the visible spectrum.

λ absorbed	E (cm^{-1})	E (eV)	Approximate color absorbed	Predicted color observed (by eye)
> 700 nm	$< 14,000 \frac{1}{cm}$	< 1.77 eV	Infrared	not observable
$\approx 700 - 635$ nm	$\approx 14,300 - 16,000 \frac{1}{cm}$	$\approx 1.77 - 1.95$ eV	Red	Green
$\approx 635 - 590$ nm	$\approx 15,700 - 16,900 \frac{1}{cm}$	$\approx 1.95 - 2.10$ eV	Orange	Blue
$\approx 590 - 560$ nm	$\approx 16,900 - 17,900 \frac{1}{cm}$	$\approx 2.10 - 2.21$ eV	Yellow	Violet
$\approx 560 - 520$ nm	$\approx 17,900 - 19,200 \frac{1}{cm}$	$\approx 2.21 - 2.38$ eV	Green	Red
$\approx 520 - 490$ nm	$\approx 19,200 - 20,400 \frac{1}{cm}$	$\approx 2.38 - 2.53$ eV	Cyan	Red-Orange
$\approx 490 - 450$ nm	$\approx 20,400 - 22,200 \frac{1}{cm}$	$\approx 2.53 - 2.76$ eV	Blue	Orange
$400 - 450$ nm	$\approx 22,200 - 25,000 \frac{1}{cm}$	$\approx 2.76 - 3.10$ eV	Violet	Yellow
<400 nm	$> 25,000 \frac{1}{cm}$	> 3.10 eV	Ultraviolet (UV)	not observable

Colors of Coordination Complexes: Crystal Field Splitting

When ligands attach to a transition metal to form a coordination complex, electrons in the d orbital split into high energy and low energy orbitals. The difference in energy of the two levels is denoted as Δ, and it is a characteristic a property both of the metal and the ligands. This is illustrated in Figure 6.12.5; the "o" subscript on the Δ indicates that the complex has octahedral geometry.

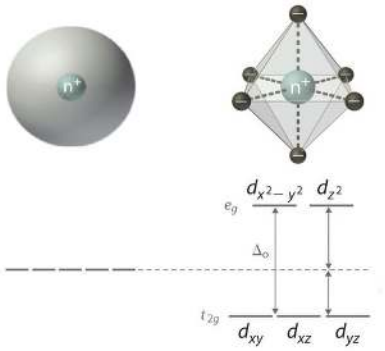


Figure **6.12.5**: d-Orbitals Splitting in an octahedral ligand field. (CC BY-SA-NC; anonymous by request)

If Δ_o is large, and much energy is required to promote electrons into the high energy orbitals, the electrons will instead pair in the lower energy orbitals, resulting in a "low spin" complex (Figure **6.12.6**); however, if Δ_o is small, and it takes little energy to occupy the higher orbitals, the electrons will do so, and remain unpaired (until there are more than five electrons), resulting in a “high spin” complex. Different ligands are associated with either high or low spin —a "strong field" ligand results in a large Δ_o and a low spin configuration, while a "weak field" ligand results in a small Δ_o and a high spin configuration. For more details, see the Crystal Field Theory (CFT) page.

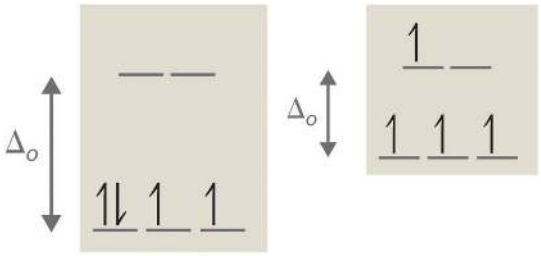


Figure **6.12.6**: (a) Low Spin, Strong Field ($\Delta_o > P$). (b): High Spin, Weak Field ($\Delta_o < P$). (CC BY-SA-NC; anonymous)

A photon equal to the energy difference Δ_o can be absorbed, promoting an electron to the higher energy level. As certain wavelengths are absorbed in this process, subtractive color mixing occurs and the coordination complex solution becomes colored. If the ions have a noble gas configuration, and have no unpaired electrons, the solutions appear colorless; in reality, they still have a measured energy and absorb certain wavelengths of light, but these wavelengths are not in the visible portion of the EM spectrum and no color is perceived by the eye.

In general, a larger Δ indicates that higher energy photons are absorbed, and the solution appears further to the left on the EM spectrum shown in Figure **6.12.2**. This relationship is described in the equation

$$\Delta = \frac{hc}{\lambda}$$

where

- h is Planck's constant ($= 6.626 \times 10^{-34} Js$)
- c is the speed of light ($= 2.998 \times 10^{8} \frac{m}{s}$)
- λ is the wavelength of light absorbed in units of m

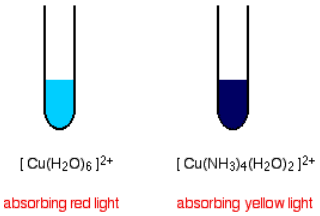
Relating the Colors of Coordination Complexes to the Spectrochemical Series

According to the Crystal Field Theory, ligands that induce smaller CFSE (Δ) values are considered "weak field" and will absorb lower-energy light with longer λ values (ie a "red shift"). Ligands that induce larger CFSE values are considered "strong field" and will absorb higher-energy light with shorter λ values (ie a "blue shift"). Thus, the energy difference, Δ, determines the color of the coordination complex.

The **spectrochemical series**, introduced previously, ranks ligands from weak field/high spin ot strong field/ low spin. It can be used to compare the approximate Δ values of ligands and to predict which wavelengths will be absorbed a complex, and thereby, what color it will appear.

$$\underset{\text{weak-field ligands}}{I^- < Br^- < Cl^- < \underline{S}CN^- < CH_3COO^- < F^- < OH^- < ox^{2-} < ONO^-} < \underset{\text{intermediate-field ligands}}{H_2O < SC\underline{N}^-} < EDTA^{4-} < NH_3 < en < NO_2^- < \underset{\text{strong-field ligands}}{CN^- \approx CO}$$

The greater the CFSE, the more energy that is needed to promote an electron from the lower group of orbitals to the higher ones. In terms of the color of the light absorbed, greater energy corresponds to shorter wavelengths. That means that as the splitting increases, the light absorbed will tend to shift away from the red end of the spectrum towards orange, yellow and so on. There is a fairly clear-cut case in copper(II) chemistry. If you add an excess of ammonia solution to hexaaquacopper(II) ions in solution, the pale blue (cyan) color is replaced by a dark inky blue as some of the water molecules in the complex ion are replaced by ammonia.

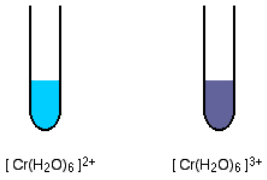


The first complex must be absorbing red light in order to give the complementary color cyan. The second one must be absorbing in the yellow region in order to give the complementary color dark blue. Yellow light has a higher energy than red light. You need that higher energy because ammonia causes more splitting of the d orbitals than water does.

Other Factors

The oxidation state of the metal

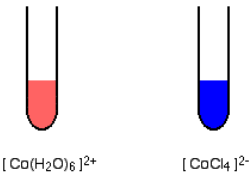
As the oxidation state of the metal increases, so also does the amount of splitting of the d orbitals. Changes of oxidation state therefore change the color of the light absorbed, and so the color of the light you see. Taking another example from chromium chemistry involving only a change of oxidation state (from +2 to +3):



The 2+ ion is almost the same color as the hexaaquacopper(II) ion, and the 3+ ion is the hard-to-describe violet-blue-grey color.

The coordination of the Ion

Splitting is greater if the ion is octahedral than if it is tetrahedral, and therefore the color will change with a change of co-ordination. The problem is that an ion will normally only change co-ordination if you change the ligand - and changing the ligand will change the color as well. Hence, you cannot isolate out the effect of the co-ordination change. For example, a commonly quoted case comes from cobalt(II) chemistry, with the ions $[Co(H_2O)_6]^{2+}$ and $[CoCl_4]^{2-}$.



The difference in the colors is going to be a combination of the effect of the change of ligand, and the change of the number of ligands.

Example 6.12.1

If a solution with a dissolved octahedral complex appears yellow to the eye, what wavelength of light does it absorb? Is this complex expected to be low spin or high spin?

Solution

A solution that looks yellow absorbs light that is violet, which is roughly 410 nm from the color wheel. Since it absorbs high energy, the electrons must be raised to a higher level, and Δ_o is high, so the complex is likely to be low spin.

Example 6.12.2

An octahedral metal complex absorbs light with wavelength 535 nm. What is the crystal field splitting Δ_o for the complex? What color is it to the eye?

Solution

To solve this question, we need to use the equation

$$\Delta_o = \frac{hc}{\lambda}$$

with

- h is Planck's constant and is $6.625 \times 10^{-34} J \cdot s$ and
- c is the speed of light and is $2.998 \times 10^8\, m/s$.

It is also important to remember that 1 nm is equal to 1×10^{-9} meters. With all this information, the final equation looks like this:

$$\Delta_o = \frac{(6.625 \times 10^{-34}\, J \cdot s)(2.998 \times 10^8\, m/s)}{(535nm)\left(\frac{1\, m}{1 \times 10^9\, nm}\right)} = 3.712\, J/molecule$$

It is not necessary to use any equations to solve the second part of the problem. Light that is 535 nm is green, and because green light is absorbed, the complex appears red (refer to Figures **6.12.1** and **6.12.6** for this information).

Note: the fact that the complex is octahedral makes no impact when solving this problem. Although the splitting is different for complexes of different structures, the mechanics of solving the problem are identical.

Example 6.12.3

There are two solutions, one orange and one blue. Both solutions are known to be made up of a cobalt complex; however, one has chloride ions as ligands, while the other has ammonia ligands. Which solution is expected to be orange?

Solution

In order to solve this problem, it is necessary to know the relative strengths of the ligands involved. A sample ligand strength list is given here, but see Crystal Field Splitting for a more complete list:

$$CN^- > en > NH_3 > H_2O > F^- > SCN^- > Cl^-$$

From this information, it is clear that NH_3 is a stronger ligand than Cl^-, which means that the complex involving NH_3 has a greater Δ, and the complex will be low spin. Because of the larger Δ, the electrons absorb higher energy photons, and the solution will have the appearance of a lower energy color. Since orange light is less energetic than blue light, the NH_3 containing solution is predicted to be orange

Example 6.12.4

A *tetrahedral* complex absorbs at 545 nm. What is the respective octahedral crystal field splitting (Δ_o)? What is the color of the complex?

Solution

$$\begin{aligned}\Delta_t &= \frac{hc}{\lambda} \\ &= \frac{(6.626 \times 10^{-34} J \cdot s)(3 \times 10^8 m/s)}{545 \times 10^{-9} m} \\ &= 3.65 \times 10^{-19}\ J\end{aligned}$$

However, the *tetrahedral* splitting (Δ_t) is ~4/9 that of the *octahedral* splitting (Δ_o).

$$\begin{aligned}\Delta_t &= 0.44\Delta_o \\ \Delta_o &= \frac{\Delta_t}{0.44} \\ &= \frac{3.65 \times 10^{-19} J}{0.44} \\ &= 8.30 \times 10^{-18} J\end{aligned}$$

This is the energy needed to promote *one* electron in *one* complex. Often the crystal field splitting is given per mole, which requires this number to be multiplied by Avogadro's Number (6.022×10^{23}).

This complex appears red, since it absorbs in the complementary green color (determined via the color wheel).

Problems

Exercise 6.12.1

What color will a complex be that absorbs light that is 600 nm be?

Answer

Blue. The color absorbed is orange.

Exercise 6.12.2

What color will a complex an octahedral complex appear if it has a Δ_o of $3.75 \times 10^{-19}\ J$?

Answer

It is red. Using $\Delta=hc/\lambda$, $h=6.626*10^{-34}$J*s, $c=2.998*10^8$m/s, wavelength would equal 530 nm. So green is absorbed, and the complementary color of green is red, so red is the color of the complex.

Exercise 6.12.3

Would you expect a violet solution to be high spin or low spin? What about a red solution?

Answer

It would be high spin. The complementary color of violet is yellow, which has a wavelength of 570 nm. For a red solution, the complementary color absorbed is green, with a wavelength of 530 nm, so it would be considered low spin.

? Exercise 6.12.4

There are two solutions, one which is yellow and another which is violet. The solutions are $[Co(H_2O)_6]^{3+}$and $[Co(CN^-)_6]^{3-}$. What are the colors of each solution?

Answer

$[Co(H_2O)_6]^{3+}$ is violet and $[Co(CN^-)_6]^{3-}$ is yellow. Looking at the spectrochemical series, H_2O is a weak field ligand, so it absorbs colors of long wavelengths—in this case, the longer wavelength is yellow, so the color reflected is violet. CN^- is a strong field ligand, so it absorbs colors of shorter wavelengths-in this case, the shorter wavelength is violet, so the color reflected is yellow.

Contributors and Attributions

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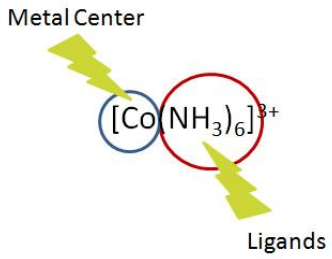
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6.13: Complex-Ion Equilibria

When a metal ion reacts with a Lewis base in solution a complex ion is formed. This reaction can be described in terms of chemical equilibria.

A complex ion is comprised of two important parts: the central atom and its surrounding ligands. The central atom can be any metallic ion (usually a transition metal). The ligands are any combination of anions that can donate an electron pair, effectively meaning they are all Lewis bases. When combined they form coordinate covalent bonds.



Formation Constant

In general, chemical equilibrium is reached when the forward reaction rate is equal to the reverse reaction rate and can be described using an equilibrium constant, K. Complex ion equilibria are no exception to this and have their own unique equilibrium constant. This **formation constant**, K_f, describes the formation of a complex ion from its central ion and attached ligands. This constant may be called a *stability constant* or *association constant*; the units depend on the specific reaction it is describing. Common metal/ligand K_f values are tabulated in Table E4.

At its most basic level, K_f can be explained as the following, where M is a metal ion, L is a ligand, and x and y are coefficients:

$$K_f = \frac{[M_xL_y]}{[M]^x[L]^y}$$

K_f values are very large in magnitude for complex ion formation reactions heavily favor the product and very small for poorly forming complex ions. For example, observe the formation reaction of the dicyanoargentate(I) complex ion

$$\mathrm{Ag^+(aq) + 2\,CN^-(aq) \rightleftharpoons Ag(CN)_2{}^-(aq)}$$

and the resulting formation constant expression:

$$\begin{aligned} K_f &= \frac{[\mathrm{Ag(CN)_2{}^-}]}{[\mathrm{Ag^+}][\mathrm{CN^-}]^2} \\ &= 5.6 \times 10^{18} \end{aligned}$$

The larger the K_f value of a complex ion, the more stable it is. Due to how large formation constants often are it is not uncommon to see them listed as logarithms in the form $\log K_f$. You may also see them in the form of a **dissociation constant**, K_d (which should not be confused with pK_a). This is merely the inverse value of the formation constant and as such describes the instability of a complex ion. It may help to think of K_f and K_d as stability and instability constants, respectively.

Using the above example, the dissociation constant expression would be:

$$\begin{aligned} K_d &= \frac{1}{K_f} \\ &= \frac{[Ag^+][CN^-]^2}{[Ag(CN)_2]^-} \\ &= 1.8 \times 10^{-19} \end{aligned}$$

In logarithm form K_f and K_d would be:

$$\log K_f = \log(5.6 \times 10^{18}) = 18.7$$
$$\log K_d = \log(1.8 \times 10^{-19}) = -18.7$$

Example 6.13.1: Stepwise Equilbria

One might assume that the formation of complex ions is a one step process, however this is not always the case. As an example let's look at the formation of tetraamminecopper(II) ion in solution:

$$[Cu(H_2O)_4]^{2+}(aq) + 4\,NH_3(aq) \rightleftharpoons [Cu(NH_3)_4]^{2+}(aq) + 4\,H_2O(l)$$

The reason for using the hydrated form of the copper ion is that cations in solution usually exist in their hydrated form. It is because of this that the creation of tetraamminecopper(II) ion is a multi-step process, the ammine ligands have to displace the existing aqua ligands. In calculations however, the concentration of water and the number of aqua ligands are effectively constant meaning that they can be safely ignored. Each step of this process has its own formation constant, and as with other chemical equilibria, the overall reaction constant is the product of these stepwise formation constants.

Ligand Exchange Step 1:

$$[Cu(H_2O)_4]^{2+}(aq) + NH_3(aq) \rightleftharpoons [Cu(H_2O)_3(NH_3)]^{2+}(aq) + H_2O(l) \quad \text{(step 1)}$$

$$K_1 = \frac{[[Cu(H_2O)_3(NH_3)]^{2+}]}{[[Cu(H_2O)_4]^{2+}][NH_3]} = 1.9 \times 10^4$$

Ligand Exchange Step 2:

$$[Cu(H_2O)_3(NH_3)]^{2+}(aq) + NH_3(aq) \rightleftharpoons [Cu(H_2O)_2(NH_3)_2]^{2+}(aq) + H_2O(l) \quad \text{(step 2)}$$

$$K_2 = \frac{[[Cu(H_2O)_2(NH_3)_2]^{2+}]}{[[Cu(H_2O)_3(NH_3)]^{2+}][NH_3]} = 3.9 \times 10^3$$

Ligand Exchange Step 3:

$$[Cu(H_2O)_2(NH_3)_2]^{2+}(aq) + NH_3(aq) \rightleftharpoons [Cu(H_2O)(NH_3)_3]^{2+}(aq) + H_2O(l) \quad \text{(step 3)}$$

$$K_3 = \frac{[[Cu(H_2O)(NH_3)_3]^{2+}]}{[[Cu(H_2O)_2(NH_3)_2]^{2+}][NH_3]} = 1.0 \times 10^3$$

Ligand Exchange Step 4:

$$[Cu(H_2O)(NH_3)_3]^{2+}(aq) + NH_3(aq) \rightleftharpoons [Cu(NH_3)_4]^{2+}(aq) + H_2O(l) \quad \text{(step 4)}$$

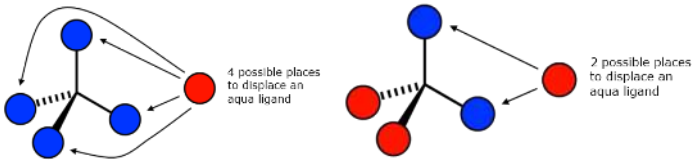
$$K_4 = \frac{[[Cu(NH_3)_4]^{2+}]}{[[Cu(H_2O)(NH_3)_3]^{2+}][NH_3]} = 1.5 \times 10^2$$

Total

$$\begin{aligned} K_f &= K_1 \times K_2 \times K_3 \times K_4 \\ &= \frac{[[Cu(H_2O)_3(NH_3)]^{2+}]}{[[Cu(H_2O)_4]^{2+}][NH_3]} \times \frac{[[Cu(H_2O)_2(NH_3)_2]^{2+}]}{[[Cu(H_2O)_3(NH_3)]^{2+}][NH_3]} \\ &\quad \times \frac{[[Cu(H_2O)(NH_3)_3]^{2+}]}{[[Cu(H_2O)_2(NH_3)_2]^{2+}][NH_3]} \times \frac{[[Cu(NH_3)_4]^{2+}]}{[[Cu(H_2O)(NH_3)_3]^{2+}][NH_3]} \\ &= \frac{[[Cu(NH_3)_4]^{2+}]}{[[Cu(H_2O)_4]^{2+}][NH_3]^4} \\ &= 1.1 \times 10^{13} \end{aligned}$$

If you wanted to find the formation constant of one of the intermediate steps, you would simply take the product of the K values up until that point. For example the formation constant of $[Cu(H_2O)_2(NH_3)_2]^{2+}$ would be $\beta_2 = K_1 \times K_2 = 7.4 \times 10^7$. As seen here and above the standard notation for these values is a lowercase beta.

You may notice that each stepwise formation constant is smaller than the one before it. This decreasing trend is due to the effects of entropy, causing each step to be progressively less likely to occur. You can think of this in the following way, continuing with the previous example:



When the first ammine ligand goes to displace an aqua ligand it has four sites from which to choose from, making it "easier" to displace one. Yet with every step the number of sites decreases making it increasingly more difficult. As always though, there are exceptions to this rule. If the values do not continually decrease then the structure of the complex ion likely changed during one of the steps.

Note: Is it important to show water as a ligand in these reactions?

The lone pairs of electrons in water molecules make water an excellent ligand. Metal ions in any body of water in the environment usually are coordinated to 6 water molecules, e.g. $\mathbf{Ag(H_2O)_6}^{+}$, $\mathbf{Cu(H_2O)_6}^{2+}$, and $\mathbf{Cr(H_2O)_6}^{2+}$, etc. In the literature, these ions are represented by $\mathbf{Ag^{+}(aq)}$, $\mathbf{Cu^{2+}(aq)}$, and $\mathbf{Cr^{3+}(aq)}$ and very often the $\mathbf{(aq)}$ notation is also omitted (although probably should not be).

When a stronger coordinating ligand such as $\mathbf{NH_3}$ is present, its molecules compete with water for the coordination site.

$$\mathbf{Ag(H_2O)_6}^{+} + \mathbf{NH_3} \rightleftharpoons \mathbf{Ag(NH_3)(H_2O)_5}^{+}$$
$$\mathbf{Ag(NH_3)(H_2O)_5}^{+} + \mathbf{NH_3} \rightleftharpoons \mathbf{Ag(NH_3)_2(H_2O)_4}^{+}$$

It is equivalent to represent these reactions by the following with the equilibrium constant as indicated.

$$\mathbf{Ag}^{+} + \mathbf{NH_3} \rightleftharpoons \mathbf{Ag(NH_3)}^{+} \qquad K_1 = 2.0 \times 10^{3}$$
$$\mathbf{Ag(NH_3)}^{+} + \mathbf{NH_3} \rightleftharpoons \mathbf{Ag(NH_3)_2}^{+} \qquad K_2 = 8.0 \times 10^{3}$$

Example 6.13.2: Using Formation Constants as a Metric of Stability

Based on the given values, rank the following complex ions from most to least stable.

- $\mathbf{[Cr(OH)_4]^{-}}$ with $K_f = 8.0 \times 10^{29}$
- $\mathbf{[Ni(CN)_4]^{2-}}$ with $\log(K_d) = -31.3$
- $\mathbf{[Co(NH_3)_6]^{3+}}$ with $K_d = 2.2 \times 10^{-34}$
- $\mathbf{[Cu(CN)_4]^{3-}}$ with $\log(K_f) = 30.3$

Solution

The key to solving this problem is to convert all of the given values into the same form. In this case we will convert all of them into the form K_f though any other form could be used as long as you are consistent.

- $\mathbf{[Cr(OH)_4]^{-}}$ with $K_f = 8.0 \times 10^{29}$
- $\mathbf{[Ni(CN)_4]^{2-}}$ with $\log(K_d) = -31.3 \longrightarrow K_f = 2.0 \times 10^{31}$
- $\mathbf{[Co(NH_3)_6]^{3+}}$ with $K_d = 2.2 \times 10^{-34} \longrightarrow K_f = 4.5 \times 10^{33}$
- $\mathbf{[Cu(CN)_4]^{3-}}$ with $\log(K_f) = 30.3 \longrightarrow K_f = 2.0 \times 10^{30}$

After converting it is easy to rate the ions in terms of stability. From most to least stable:

$$\mathbf{[Co(NH_3)_6]^{3+}} > \mathbf{[Ni(CN)_4]^{2-}} > \mathbf{[Cu(CN)_4]^{3-}} > \mathbf{[Cr(OH)_4]^{-}}.$$

Below are three tables of the formation constants and thermodynamics properties of example ligand-metal complexes; a more complete table can be found in Table E4.

Table **6.13.1**: Reaction of ammonia and 1,2-diaminoethane with Cd^{2+}.

# of ligands	ΔG° (kJmol^{-1})	ΔH° (kJmol^{-1})	ΔS° (JK-1mol^{-1})	log β
2 NH_3(1 en)	-28.24 (-33.30)	-29.79 (-29.41)	-5.19 (+13.05)	4.95 (5.84)
4 NH_3(2 en)	-42.51 (-60.67)	-53.14 (-56.48)	-35.50 (+13.75)	7.44 (10.62)

Table **6.13.2**: Reaction of pyridine and 2,2'-bipyridine with Ni^{2+}.

# of ligands	log β	ΔG° (kJmol^{-1})
2 py (1 bipy)	3.5 (6.9)	-20 (-39)
4 py (2 bipy)	5.6 (13.6)	-32 (-78)
6 py (3 bipy)	9.8 (19.3)	-56 (-110)

Table **6.13.3**: Reaction of ammonia and 1,2-diaminoethane with Ni^{2+}.

# of ligands	log β	ΔG° (kJmol^{-1})
1 NH_3	2.8	-16
2 NH_3 (1 en)	5.0 (7.51)	-28.5 (-42.8)
3 NH_3	6.6	-37.7
4 NH_3 (2 en)	7.87 (13.86)	-44.9 (-79.1)
5 NH_3	8.6	-49.1
6 NH_3 (3 en)	8.61 (18.28)	-49.2 (-104.4)

Solubility Effects

The formation of complex ions can sometimes explain the solubility of certain compounds in solution. For example, let's say we have a saturated solution of silver bromide ($AgBr$) which also contains additional undissolved solid silver bromide. If high enough concentrations of ammonia are added to the solution, the solid silver bromide will dissolve despite the solution previously having been saturated. This is because of the formation diammineargentate(I) ion, illustrated by the following chemical equation:

$$AgBr\,(s) + 2\,NH_3\,(aq) \rightarrow [Ag(NH_3)_2]^+\,(aq) + Br^-\,(l)$$

Example 6.13.3

The creation of $[Ni(en)_3]^{2+}$ is a three step process with the following stepwise formation constants $K_1 = 3.3 \times 10^7$, $K_2 = 1.9 \times 10^6$, and $K_3 = 1.8 \times 10^4$. Using this information find the overall formation constant and the formation constant for each of the intermediate steps.

Solution

Take the product of the stepwise formation constants up until the step you are trying to find.

$[Ni(H_2O)_4\,(en)]^{2+}$ with $\beta_1 = K_1 = 3.3 \times 10^7$

$[Ni(H_2O)_2(en)_2]^{2+}$ with $\beta_2 = K_1 \times K_2 = 6.8 \times 10^{13}$

$[Ni(en)_3]^{2+}$ with $\beta_3 = K_f = K_1 \times K_2 \times K_3 = 1.1 \times 10^{18}$

Problems

Exercise 6.13.1

Write the stepwise reactions that sum to the following overall reaction for formation of the cuprammonium ion $Cu(NH_3)_4^{2+}$:

$$Cu^{2+} + 4NH_3 \rightleftharpoons Cu(NH_3)_4^{2+}$$

Write the K_f for the overall reaction in terms of the K_n values.

Answer

STEP 1:

$$Cu^{2+} + NH_3 \rightleftharpoons Cu(NH_3)^{2+}$$

$$K_1 = \frac{[Cu(NH_3)^{2+}]}{[Cu^{2+}][NH_3]}$$

STEP 2:

$$CuNH_3^{2+} + NH_3 \rightleftharpoons Cu(NH_3)_2^{2+}$$

$$K_2 = \frac{[Cu(NH_3)_2^{2+}]}{[Cu(NH_3)^{2+}][NH_3]}$$

STEP 3:

$$Cu(NH_3)_2^{2+} + NH_3 \rightleftharpoons Cu(NH_3)_3^{2+}$$

$$K_3 = \frac{[Cu(NH_3)_3^{2+}]}{[Cu(NH_3)_2^{2+}][NH_3]}$$

STEP 4:

$$Cu(NH_3)_3^{2+} + NH_3 \rightleftharpoons Cu(NH_3)_4^{2+}$$

$$K_4 = \frac{[Cu(NH_3)_4^{2+}]}{[Cu(NH_3)_3^{2+}][NH_3]}$$

$K_f = K_1 \times K_2 \times K_3 \times K_4$

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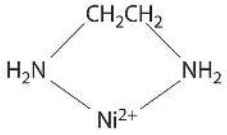
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6.14: The Chelate Effect

The term ligand come from the latin word *ligare*, which meaning to bind) was first used by Alfred Stock in 1916 in relation to silicon chemistry. The first use of the term in a British journal was by H. Irving and R.J.P. Williams in *Nature*, 1948, 162, 746 in their paper describing what is now called the Irving-Williams series. Ligands can be characterised as monodentate, bidentate, tridentate etc. where the concept of teeth (*dent*) is introduced. The term **chelate** was first applied in 1920 by Sir Gilbert T. Morgan and H.D.K. Drew [*J. Chem. Soc.*, 1920, 117, 1456], who stated: "The adjective chelate, derived from the great claw or *chela* (chely- Greek) of the lobster or other crustaceans, is suggested for the caliperlike groups which function as two associating units and fasten to the central atom so as to produce heterocyclic rings." Metal complexation is of widespread interest. It is studied not only by inorganic chemists, but by physical and organic chemists, biochemists, pharmacologists, molecular biologists and environmentalists.



Ligands like chloride, water, and ammonia are said to be monodentate (one-toothed, from the Greek mono, meaning “one,” and the Latin dent-, meaning “tooth”): they are attached to the metal via only a single atom. Ligands can, however, be bidentate (two-toothed, from the Greek di, meaning “two”), tridentate (three-toothed, from the Greek tri, meaning “three”), or, in general, polydentate (many-toothed, from the Greek poly, meaning “many”), indicating that they are attached to the metal at two, three, or several sites, respectively. Ethylenediamine ($H_2NCH_2CH_2NH_2$, often abbreviated as en) and diethylenetriamine ($H_2NCH_2CH_2NHCH_2CH_2NH_2$, often abbreviated as dien) are examples of a bidentate and a tridentate ligand, respectively, because each nitrogen atom has a lone pair that can be shared with a metal ion. When a bidentate ligand such as ethylenediamine binds to a metal such as Ni^{2+}, a five-membered ring is formed. A metal-containing ring like that shown is called a chelate ring . Correspondingly, a polydentate ligand is a chelating agent, and complexes that contain polydentate ligands are called chelate complexes.



A chelate complex

The Chelate Effect

Experimentally, it is observed that metal complexes of polydentate ligands are significantly more thermodynamically stable than the corresponding complexes of chemically similar monodentate ligands; this increase in stability is called the *chelate effect*. For example, the complex of Ni^{2+} with three ethylenediamine ligands, $[Ni(en)_3]^{2+}$, should be chemically similar to the Ni^{2+} complex with six ammonia ligands, $[Ni(NH_3)_6]^{2+}$. In fact, the equilibrium constant for the formation of $[Ni(en)_3]^{2+}$ is almost 10 orders of magnitude larger than the equilibrium constant for the formation of $[Ni(NH_3)_6]^{2+}$ (Table E4):

$$[Ni(H_2O)_6]^{2+} + 6NH_3 \rightleftharpoons [Ni(NH_3)_6]^{2+} + 6H_2O(l) \quad K_f = 4 \times 10^8 \tag{6.14.1}$$

$$[Ni(H_2O)_6]^{2+} + 3en \rightleftharpoons [Ni(en)_3]^{2+} + 6H_2O(l) \quad K_f = 2 \times 10^{18} \tag{6.14.2}$$

The formation constants are formulated as ligand exchange reactions with aqua ligands being displaced by new ligands (NH_3 or en) in the examples above.

> *Chelate complexes are more thermodynamically stable than the analogous complexes with monodentate ligands.*

The stability of a chelate complex depends on the size of the chelate rings. For ligands with a flexible organic backbone like ethylenediamine, complexes that contain five-membered chelate rings, which have almost no strain, are significantly more stable than complexes with six-membered chelate rings, which are in turn much more stable than complexes with four- or seven-membered rings. For example, the complex of nickel (II) with three ethylenediamine ligands is about 363,000 times more stable than the corresponding nickel (II) complex with trimethylenediamine ($H_2NCH_2CH_2CH_2NH_2$, abbreviated as tn):

$$[Ni(H_2O)_6]^{2+} + 3en \rightleftharpoons [Ni(en)_3]^{2+} + 6H_2O(l) \quad K_f = 6.76 \times 10^{17} \tag{6.14.3}$$

$$[Ni(H_2O)_6]^{2+} + 3tn \rightleftharpoons [Ni(tn)_3]^{2+} + 6H_2O(l) \quad K_f = 1.86 \times 10^{12} \tag{6.14.4}$$

*The above measurements were done in a solution of ionic strength 0.15 at 25° C.

Example 6.14.1

Arrange $[Cr(en)_3]^{3+}$, $[CrCl_6]^{3-}$, $[CrF_6]^{3-}$, and $[Cr(NH_3)_6]^{3+}$ in order of increasing stability.

Given: four Cr(III) complexes

Asked for: relative stabilities

Strategy:

A Determine the relative basicity of the ligands to identify the most stable complexes.

B Decide whether any complexes are further stabilized by a chelate effect and arrange the complexes in order of increasing stability.

Solution

A The metal ion is the same in each case: Cr^{3+}. Consequently, we must focus on the properties of the ligands to determine the stabilities of the complexes. Because the stability of a metal complex increases as the basicity of the ligands increases, we need to determine the relative basicity of the four ligands. Our earlier discussion of acid–base properties suggests that ammonia and ethylenediamine, with nitrogen donor atoms, are the most basic ligands. The fluoride ion is a stronger base (it has a higher charge-to-radius ratio) than chloride, so the order of stability expected due to ligand basicity is

$$[CrCl_6]^{3-} < [CrF_6]^{3-} < [Cr(NH_3)_6]^{3+} \approx [Cr(en)_3]^{3+}.$$

B Because of the chelate effect, we expect ethylenediamine to form a stronger complex with Cr^{3+} than ammonia. Consequently, the likely order of increasing stability is

$$[CrCl_6]^{3-} < [CrF_6]^{3-} < [Cr(NH_3)_6]^{3+} < [Cr(en)_3]^{3+}.$$

Entropy

Consider the formation of a complex of Ni^{2+} with ammonia or 1,2-diaminoethane.

$$\begin{array}{lcl} [Ni(H_2O)_6]^{2+} + 6\,NH_3 & \overset{\beta_6}{\Leftrightarrow} & [Ni(NH_3)_6]^{2+} + 6\,H_2O \quad \textbf{1f} \\ [Ni(NH_3)_6]^{2+} & \Leftrightarrow & [Ni(H_2O)_6]^{2+} + 6\,NH_3 \quad \textbf{1d} \\ [Ni(H_2O)_6]^{2+} + 3\,en & \overset{\beta_3}{\Leftrightarrow} & [Ni(en)_3]^{2+} + 6H_2O \quad \textbf{2f} \\ \hline [Ni(NH_3)_6]^{2+} + 3\,en & \Leftrightarrow & [Ni(en)_3]^{2+} + 6NH_3 \quad \textbf{3} \end{array}$$

In reaction 3 above, *three* bidentate ligands replace the *six* monodentate ligands. On the left-hand-side there are 4 species, whereas on the right-hand-side there are 7 species, that is a net gain of 3 species occurs as the reaction proceeds. This represents an increase in entropy since it the disorder of the system increases by the production of additional molecules.

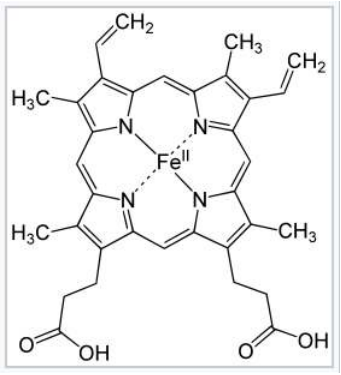
An alternative view comes from trying to understand how the reactions might proceed. To form a complex with 6 monodentates requires 6 separate favorable collisions between the metal ion and the ligand molecules. To form the tris-bidentate metal complex requires an initial collision for the first ligand to attach by one arm but remember that the other arm is always going to be nearby and only requires a rotation of the other end to enable the ligand to form the chelate ring.

If you consider dissociation steps, then when a monodentate group is displaced, it is lost into the bulk of the solution. On the other hand, if one end of a bidentate group is displaced the other arm is still attached and it is only a matter of the arm rotating around

and it can be reattached again. **Both** conditions favor the formation of the complex with bidentate groups rather than monodentate groups.

The Macrocyclic Effect

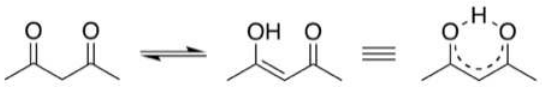
The **macrocyclic effect** follows the same principle as the chelate effect, but the effect is further enhanced by the cyclic conformation of the ligand. Macrocyclic ligands are not only multi-dentate, but because they are covalently constrained to their cyclic form, they allow less conformational freedom. The ligand is said to be "**pre-organized**" for binding, and there is little entropy penalty for wrapping it around the metal ion. For example heme b is a tetradentate cyclic ligand which is strongly complexes transition metal ions, including (in biological systems) Fe^{+2}.



Heme b

Some other common chelating and cyclic ligands are shown below:

Acetylacetonate ($acac^-$, right) is an anionic bidentate ligand that coordinates metal ions through two oxygen atoms. $Acac^-$ is a hard base so it prefers hard acid cations. With divalent metal ions, $acac^-$ forms neutral, volatile complexes such as $Cu(acac)_2$ and $Mo(acac)_2$ that are useful for chemical vapor deposition (CVD) of metal thin films.



2,2'-Bipyridine and related bidentate ligands such as 1,10-phenanthroline (below, center left) form propeller-shaped complexes with metals such as Ru^{2+}. The $[Ru(bpy)_3]^{2+}$ complex (below left) is photoluminescent and can also undergo photoredox reactions, making it an interesting compound for both photocatalysis and artificial photosynthesis. The chiral propellor shapes of metal polypyridyl complexes such as $[Ru(bpy)_3]^{2+}$ coincidentally match the size and helicity of the major groove of DNA. This has led to

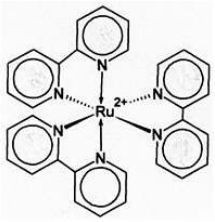
a number of interesting studies of electron transfer reactions along the DNA backbone, initiated by photoexcitation of the metal complex.

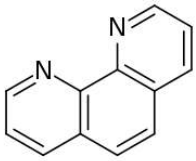


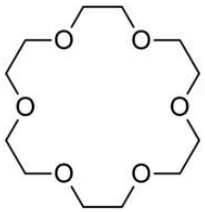
Prof. Jacqueline Barton (Caltech) has used metal polypyridyl complexes to study electron transfer reactions that are implicated in the biological sensing and repair of damage in DNA molecules.

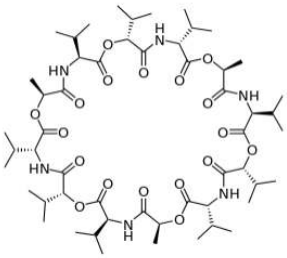
Crown ethers such as 18-crown-6 (below, center right) are cyclic hard bases that can complex alkali metal cations. Crowns can selectively bind Li^+, Na^+, or K^+ depending on the number of ethylene oxide units in the ring.

The chelating properties of crown ethers are mimetic of the natural antibiotic **valinomycin** (below right), which selectively transports K^+ ions across bacterial cell membranes, killing the bacterium by dissipating its membrane potential. Like crown ethers, valinomycin is a cyclic hard base.









Problems

? Exercise 6.14.1

Arrange $[Co(NH_3)_6]^{3+}$, $[CoF_6]^{3-}$, and $[Co(en)_3]^{3+}$ in order of decreasing stability.

Answer

$[Co(en)_3]^{3+} > [Co(NH_3)_6]^{3+} > [CoF_6]^{3-}$

? Exercise 6.14.1

Of $\mathbf{[Ni(en)_3]^{2+}}$, $\mathbf{[Ni(EDTA)]^{2-}}$, and $\mathbf{[Ni(NH_3)_6]^{2+}}$, which would you expect to have the largest $\boldsymbol{K_f}$ value? The smallest? Explain.

Answer

This is a question involving the effects of chelation. When the complex ion with EDTA is formed, the EDTA ligand displaces six aqua ligands at once. Ethylenediamine ligands displace two at a time and ammine ligands displace one at a

time. Based on this we would expect $[Ni(EDTA)]^{2-}$ to be the most stable and $[Ni(NH_3)_6]^{2+}$ to be the least stable.

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6.16: Hard and Soft Acids and Bases

The thermodynamic stability of a metal complex depends greatly on the properties of the ligand and the metal ion and on the type of bonding. Metal–ligand interaction is an example of a Lewis acid–base interaction. Lewis bases can be divided into two categories:

- hard bases contain small, relatively nonpolarizable donor atoms (such as N, O, and F), and
- soft bases contain larger, relatively polarizable donor atoms (such as P, S, and Cl).

Metal ions with the highest affinities for hard bases are hard acids, whereas metal ions with the highest affinity for soft bases are soft acids. Some examples of hard and soft acids and bases are given in Table **6.16.1**. Notice that hard acids are usually cations of electropositive metals; consequently, they are relatively nonpolarizable and have higher charge-to-radius ratios. Conversely, soft acids tend to be cations of less electropositive metals; consequently, they have lower charge-to-radius ratios and are more polarizable. Chemists can predict the relative stabilities of complexes formed by the d-block metals with a remarkable degree of accuracy by using a simple rule: hard acids prefer to bind to hard bases, and soft acids prefer to bind to soft bases.

Table **6.16.1**: Examples of Hard and Soft Acids and Bases

	Acids	Bases
hard	H^+	NH_3, RNH_2, N_2H_4
	Li^+, Na^+, K^+	H_2O, ROH, R_2O
	Be^{2+}, Mg^{2+}, Ca^{2+}, VO^{2+}	OH^-, F^-, Cl^-, $CH_3CO_2^-$
	Al^{3+}, Sc^{3+}, Cr^{3+}	CO_3^{2-}
	Ti^{4+}	PO_4^{3-}
soft	BF_3, Al_2Cl_6, CO_2, SO_3	
	Cu^+, Ag^+, Au^+, Tl^+, Hg_2^{2+}	H^-
	Pd^{2+}, Pt^{2+}, Hg^{2+}	CN^-, SCN^-, I^-, RS^-
	$GaCl_3$, $GaBr_3$, GaI_3	CO, R_2S

> *Hard acids prefer to bind to hard bases, and soft acids prefer to bind to soft bases.*

Because the interaction between hard acids and hard bases is primarily electrostatic in nature, the stability of complexes involving hard acids and hard bases increases as the positive charge on the metal ion increases and as its radius decreases. For example, the complex of Al^{3+} (r = 53.5 pm) with four fluoride ligands (AlF_4^-) is about 10^8 times more stable than InF_4^-, the corresponding fluoride complex of In^{3+} (r = 80 pm). In general, the stability of complexes of divalent first-row transition metals with a given ligand varies inversely with the radius of the metal ion, as shown in Table **6.16.2**. The inversion in the order at copper is due to the anomalous structure of copper(II) complexes, which will be discussed shortly.

Table **6.16.2**

complex stability	Mn^{2+}	$< Fe^{2+}$	$< Co^{2+}$	$< Ni^{2+}$	$< Cu^{2+}$	$> Zn^{2+}$
ionic radius (pm)	83	78	74.5	69	73	74

Because a hard metal interacts with a base in much the same way as a proton, by binding to a lone pair of electrons on the base, the stability of complexes of hard acids with hard bases increases as the ligand becomes more basic. For example, because ammonia is a stronger base than water, metal ions bind preferentially to ammonia. Consequently, adding ammonia to aqueous solutions of many of the first-row transition-metal cations results in the formation of the corresponding ammonia complexes.

In contrast, the interaction between soft metals (such as the second- and third-row transition metals and Cu^+) and soft bases is largely covalent in nature. Most soft-metal ions have a filled or nearly filled d subshell, which suggests that metal-to-ligand π bonding is important. Complexes of soft metals with soft bases are therefore much more stable than would be predicted based on electrostatic arguments.

The hard acid–hard base/soft acid–soft base concept also allows us to understand why metals are found in nature in different kinds of ores. Recall that most of the first-row transition metals are isolated from oxide ores but that copper and zinc tend to occur naturally in sulfide ores. This is consistent with the increase in the soft character of the metals across the first row of the transition metals from left to right. Recall also that most of the second- and third-row transition metals occur in nature as sulfide ores, consistent with their greater soft character.

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SECTION OVERVIEW

6.17: Complex Ion Chemistry

An introduction to the complex ions formed by transition and other metals. Includes bonding, shapes and names, and a simple look at the origin of color. Looks in detail at various ligand exchange reactions and the chemistry of common hexaaqua ions.

6.17.1: Acidity of the Hexaaqua Ions

6.17.2: Ligand Exchange Reactions (Introduction)

6.17.3: Ligand Exchange Reactions (Thermodynamics)

6.17.4: Reactions of the Hexaaqua Ions with Ammonia

6.17.5: Reactions of the Hexaaqua Ions with Carbonate Ions

6.17.6: Reactions of the Hexaaqua Ions with Hydroxide Ions

6.17.7: Stereoisomerism in complex ions

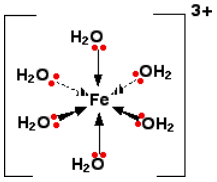
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6.17.1: Acidity of the Hexaaqua Ions

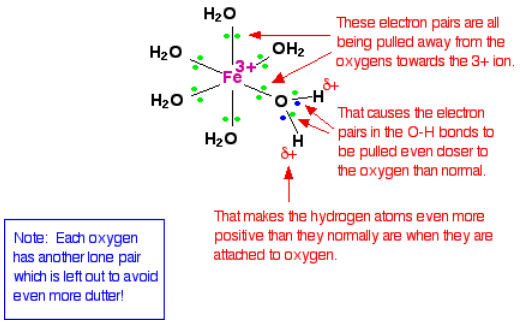
This page explains why complex ions of the type $[M(H_2O)_6]^{n+}$ are acidic.

The Charge Distribution within Complex Ion

The pH's of solutions containing hexaaqua ions vary a lot from one metal to another (assuming you are comparing solutions of equal concentrations). However, the underlying explanation is the same for all of them. We'll take the hexaaquairon(III) ion, $[Fe(H_2O)_6]^{3+}$ as typical. The structure of the ion is:



Each of the six water molecules are attached to the central iron(III) ion via a co-ordinate bond using one of the lone pairs on the oxygen. We'll choose one of these water molecules at random (it doesn't make any difference which one!), and look at the bonding in a bit more detail - showing all the bonds around the oxygen. Imagine for the moment that the 3+ charge is located entirely on the iron.



When the lone pairs on the oxygens form co-ordinate bonds with the iron, there is obviously a movement of electrons towards the iron. That has an effect on the electrons in the O-H bonds. These electrons, in turn, get pulled towards the oxygen even more than usual. That leaves the hydrogen nuclei more exposed than normal. The overall effect is that each of the hydrogen atoms is more positive than it is in ordinary water molecules. The 3+ charge is no longer located entirely on the iron but spread out over the whole ion - much of it on the hydrogen atoms.

The effect of dissolving this ion in water

The hydrogen atoms attached to the water ligands are sufficiently positive that they can be pulled off in a reaction involving water molecules in the solution. The first stage of this process is:

$$Fe(H_2O)_6^{3+} + H_2O \rightleftharpoons Fe(H_2O)_5(OH)^{2+} + H_3O^+ \qquad (6.17.1.1)$$

The complex ion is acting as an (Arrhenius) acid by donating a hydrogen ion to water molecules in the solution. The water is, of course, acting as a (Arrhenius) base by accepting the hydrogen ion. Because of the confusing presence of water from two different sources (the ligands and the solution), it is easier to simplify Equation 6.17.1.1:

$$[Fe(H_2O)_6]^{3+}(aq) \rightleftharpoons [Fe(H_2O)_5(OH)]^{2+}(aq) + H^+(aq) \qquad (6.17.1.2)$$

However, if you write it like this, remember that the hydrogen ion is not just falling off the complex ion. It is being pulled off by a water molecule in the solution. Whenever you write "$H^+(aq)$" what you really mean is a hydroxonium ion, H_3O^+.

The hexaaquairon(III) ion is quite strongly acidic giving solutions with pH's around 1.5, depending on concentration. You can get further loss of hydrogen ions as well, from a second and a third water molecule since the complex ion is a polyprotic acid.

Losing a second hydrogen ion:

$$[Fe(H_2O)_5(OH)]^{2+}(aq) \rightleftharpoons [Fe(H_2O)_4(OH)_2]^{+}(aq) + H^{+}(aq) \quad (6.17.1.3)$$

and a third one:

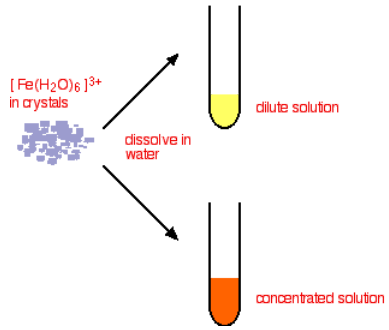
$$[\,Fe(H_2O)_4(OH)_2]^{+}(aq) \rightleftharpoons [\,Fe(H_2O)_3(OH)_3](s) + H^{+}(aq) \quad (6.17.1.4)$$

This time you end up with a neutral complex and because it has no charge, it does not dissolve to any extent in water, and a precipitate is formed.

In practice

What do you actually get in solution if you dissolve an iron(III) salt in water? In fact you get a mixture of all the complexes that you have seen in the equations above. These reactions are all equilibria, so everything will be present. The proportions depend on how concentrated the solution is.

The color of the solution is very variable and depends in part on the concentration of the solution. Dilute solutions containing iron(III) ions can be pale yellow. More concentrated ones are much more orange, and may even produce some orange precipitate. None of these colors represents the true color of the $[Fe(H_2O)_6]^{3+}$ ion - which is a very pale lilac color and is only really easy to see in solids containing the ion.

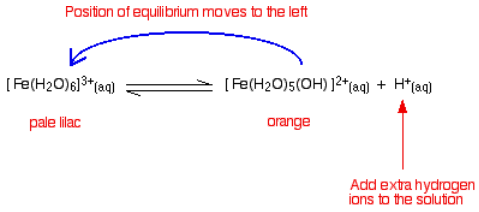


Looking at the equilibrium showing the loss of the first hydrogen ion:

$$\underbrace{Fe(H_2O)_6^{3+}}_{\text{pale lilac}} + H_2O \rightleftharpoons \underbrace{Fe(H_2O)_5(OH)^{2+}}_{\text{orange}} + H_3O^{+}$$

The color of the new complex ion on the right-hand side is so strong that it completely masks the color of the hexaaqua ion. In concentrated solutions, the equilibrium position will be even further to the right-hand side (Le Chatelier's Principle), and so the color darkens. You will also get significant loss of other hydrogen ions (Equation 6.17.1.3 and 6.17.1.4) leading to some formation of the neutral complex and thus some precipitate.

The position of this equilibrium can be shifted by adding extra hydrogen ions from a concentrated acid (e.g., by adding concentrated nitric acid to a solution of iron(III) nitrate). The new hydrogen ions push the position of the equilibrium to the left so that you can see the color of the hexaaqua ion. This is slightly easier to follow if you write the simplified version of the equilibrium (Equation 6.17.1.2).



3+ Ions are More Acidic than 2+ ions

Solutions containing 3+ hexaaqua ions tend to have pH's in the range from 1 to 3. Solutions containing 2+ ions have higher pH's - typically around 5 - 6, although they can go down to about 3. Remember that the reason that these ions are acidic is

because of the pull of the electrons towards the positive central ion. An ion with 3+ charges on it is going to pull the electrons more strongly than one with only 2+ charges.

In 3+ ions, the electrons in the O-H bonds will be pulled further away from the hydrogens than in 2+ ions. That means that the hydrogen atoms in the ligand water molecules will have a greater positive charge in a 3+ ion, and so will be more attracted to water molecules in the solution. If they are more attracted, they will be more readily lost - and so the 3+ ions are more acidic.

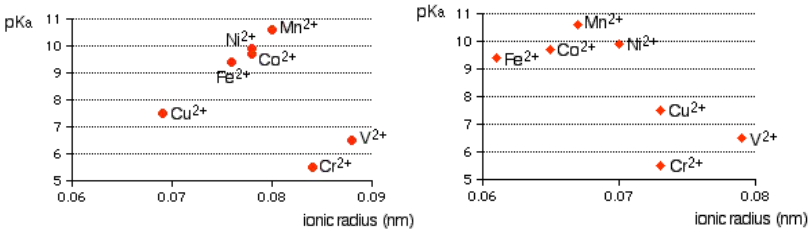
The Effect of ionic radius on acidity

If you have ions of the same charge, it seems reasonable that the smaller the volume this charge is packed into, the greater the distorting effect on the electrons in the O-H bonds. Ions with the same charge but in a smaller volume (a higher charge density) would be expected to be more acidic. You would therefore expect to find that the smaller the radius of the metal ion, the stronger the acid. Unfortunately, it's not that simple!

Unfortunately, almost every data source that you refer to quotes different values for ionic radii. This is because the radius of a metal ion varies depending on what negative ion it is associated with. We are interested in what happens when the metal ion is bonded to water molecules, so haven't got simple ions at all! Whatever values we take are unlikely to represent the real situation. In the graphs which follow I have taken values for ionic radii from two common sources so that you can see what a lot of difference it makes to the argument.

The graphs

If it is true that the smaller the ionic radius, the stronger the acidity of the hexaaqua ion, you would expect some sort of regular increase in pK_a (showing weaker acids) as ionic radius increases. The following graphs plot pK_a against ionic radii for the 2+ ions of the elements in the first transition series from vanadium to copper. The first graph plots pK_a against ionic radii taken from Chemistry Data Book by Stark and Wallace.



You can see that there is a trend for several of the ions, but it is completely broken by vanadium and chromium. The second graph uses ionic radii taken from the Nuffield Advanced Science Book of Data.

There probably is a relationship between ionic radius and acid strength, but that it is nothing like as simple and straightforward as most books at this level pretend. The problem is that there are other more important effects operating as well (quite apart from differences in charge) that can completely swamp the effect of the changes in ionic radius. You have to look in far more detail at the bonding in the hexaaqua ions and the product ions.

Contributors and Attributions

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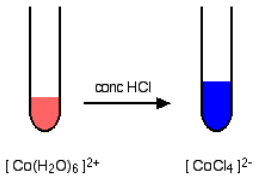
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6.17.2: Ligand Exchange Reactions (Introduction)

This page describes some common ligand exchange (substitution) reactions involving complex metal ions. It assumes that you are familiar with basic ideas about complex ions. A *ligand exchange reaction* involves the substitution of one or more ligands in a complex ion with one or more different ligands.

Replacing aqua with chloro ligands

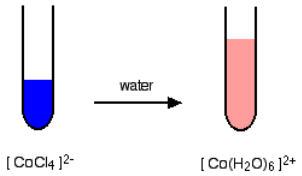
If you add concentrated hydrochloric acid to a solution containing hexaaquacobalt(II) ions (for example, cobalt(II) chloride solution), the solution turns from its original pink color to a dark rich blue. The six aqua molecules are replaced by four chloro ions.



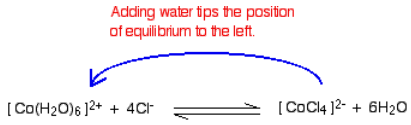
The reaction taking place is reversible.

$$[Co(H_2O)_6]^{2+} + 4\,Cl^- \rightleftharpoons [CoCl_4]^{2-} + 6\,H_2O$$

Concentrated hydrochloric acid is used as the source of chloride ions because it provides a very high concentration compared to what is possible with, say, sodium chloride solution. Concentrated hydrochloric acid has a chloride ion concentration of approximately 10 mol dm^{-3}. The high chloride ion concentration pushes the position of the equilibrium to the right according to Le Chatelier's Principle.

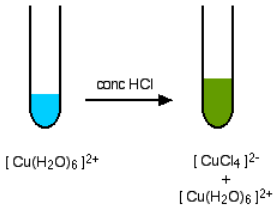


Notice the change in the co-ordination of the cobalt. Chloride ions are bigger than water molecules, and there isn't room to fit six of them around the central cobalt ion. This reaction can be easily reversed by adding water to the solution. Adding water to the right-hand side of the equilibrium has the effect of moving the position of equilibrium to the left. The pink color of the hexaaquacobalt(II) ion is produced again (only paler, of course, because it is more dilute).



Replacing the water in the hexaaquacopper(II) ion

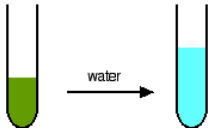
In terms of the chemistry, this is exactly the same as the last example - all that differs are the colors. Unfortunately, these are not quite so straightforward. The color of the tetrachlorocuprate(II) ion is almost always seen mixed with that of the original hexaaqua ion. What you normally see is:



The reaction taking place is reversible, and you get a mixture of colors due to both of the complex ions.

$$[Cu(H_2O)_6]^{2+} \rightleftharpoons [CuCl_4]^{2-} + 6\,H_2O$$

You may find the color of the tetrachlorocuprate(II) ion variously described as olive-green or yellow. Adding water to the green solution, replaces the chloro ligands by water molecules again, and returns the solution to blue.



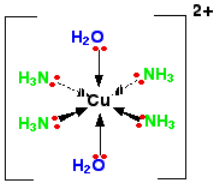
Replacing water molecules by ammonia

Water molecules and ammonia molecules are very similar in size, and so there is no change in co-ordination this time. Unfortunately, the reactions aren't quite so straightforward to describe. Ammonia solution can react with hexaaqua metal ions in two quite distinct ways, because it can act as a base as well as a ligand.

If you add a small amount of ammonia solution you get precipitates of the metal hydroxide - the ammonia is acting as a base. In some cases, these precipitates redissolve when you add more ammonia to give solutions in which a ligand exchange reaction has occurred. In the diagrams below, both steps are shown, but we are only going to consider the chemistry of the overall ligand exchange reaction. The precipitates dissolve because of a complicated series of equilibrium shifts, and we shan't worry about that for the moment.

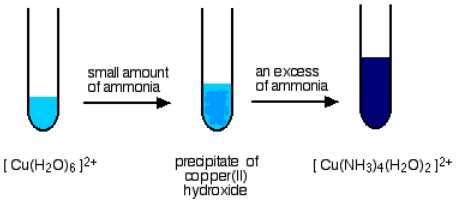
Replacing the water in the hexaaquacopper(II) ion

This is a slightly untypical case, because only four of the six water molecules get replaced to give the tetraamminediaquacopper(II) ion, $[Cu(NH_3)_4(H_2O)_2]^{2+}$.



the tetraamminediaquacopper(II) ion

Notice that the four ammonias all lie in one plane, with the water molecules above and below. What you see in a test tube is:



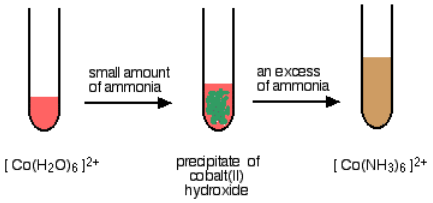
The main equilibrium involved in the ligand exchange reaction is:

$$[Cu(H_2O)_6]^{2+} + 4\,NH_3 \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+} + 4\,H_2O$$

The color of the deep blue complex is so strong that this reaction is used as a sensitive test for copper(II) ions in solution. Even if you try to reverse the change by adding large amounts of water to the equilibrium, the strength of the deep blue (even highly diluted) always masks the pale blue of the aqua ion.

Replacing the water in the hexaaquacobalt(II) ion

This time, all the water molecules get replaced.



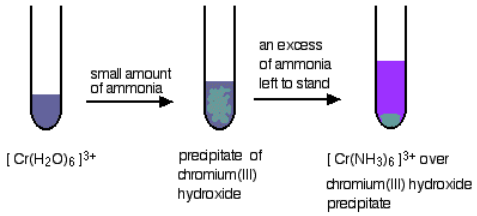
$$[Co(H_2O)_6]^{2+} + 6\,NH_3 \rightleftharpoons [Co(NH_3)_6]^{2+} + 6\,H_2O$$

The straw colored solution formed changes color very rapidly on standing to a deep reddish brown. The hexaamminecobalt(II) ions are oxidised by the air to hexaamminecobalt(III) ions. However, that is a quite separate reaction, and is not a part of the ligand exchange reaction.

Replacing the water in the hexaaquachromium(III) ion

Again, all the agua ligands are replaced by ammine ligands. The difference this time is that the reaction is incomplete. The precipitate has to be left to stand in the presence of excess concentrated ammonia solution for some time to get the fully substituted ammine complex. Even so, you still get left with some unreacted precipitate.

$$[Cr(H_2O)_6\,]^{3+} + 6\,NH_3 \rightleftharpoons [Cr(NH_3)_6]^{3+} + 6\,H_2O$$

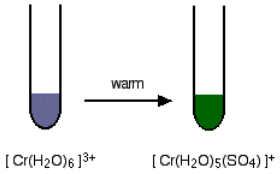


Two more replacements of the water in the hexaaquachromium(III) ion

The color of the hexaaquachromium(III) ion has been shown as a "difficult to describe" violet-blue-grey in all the diagrams above. In practice, when it is produced during a reaction in a test tube, it is often green. A typical example of this is the use of acidified potassium dichromate(VI) as an oxidising agent. Whenever this is used, the orange solution turns green and we nearly always describe the green ion as being $Cr^{3+}_{(aq)}$ - implying the hexaaquachromium(III) ion. That's actually an over-simplification. What happens is that one or more of the ligand water molecules get replaced by a negative ion in the solution - typically sulfate or chloride.

Replacement of the water by sulfate ions

You can do this simply by warming some chromium(III) sulfate solution.



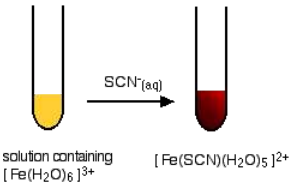
One of the water molecules is replaced by a sulfate ion. Notice the change in the charge on the ion. Two of the positive charges are canceled by the presence of the two negative charges on the sulfate ion.

Replacement of the water by chloride ions

In the presence of chloride ions (for example with chromium(III) chloride), the most commonly observed color is green. This happens when two of the water molecules are replaced by chloride ions to give the tetraaquadichlorochromium(III) ion - $[Cr(H_2O)_4Cl_2]^+$. Once again, notice that replacing water molecules by chloride ions changes the charge on the ion.

A ligand exchange reaction in the test for iron(III) ions

This provides an extremely sensitive test for iron(III) ions in solution. If you add thiocyanate ions, SCN^-, (from, say, sodium or potassium or ammonium thiocyanate solution) to a solution containing iron(III) ions, you get an intense blood red solution containing the ion $[Fe(SCN)(H_2O)_5]^{2+}$.



Contributors and Attributions

- Jim Clark (Chemguide.co.uk)

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6.17.3: Ligand Exchange Reactions (Thermodynamics)

This page explains what is meant by a stability constant for a complex ion, and goes on to look at how its size is governed in part by the entropy change during a ligand exchange reaction.

Replacing aqua ligands with ammine ligands

If you add ammonia solution to a solution containing hexaaquacopper(II) ions, $[Cu(H_2O)_6]^{2+}$, four of the water molecules are eventually replaced by ammonia molecules to give $[Cu(NH_3)_4(H_2O)_2]^{2+}$. This can be written as an equilibrium reaction to show the overall effect:

$$[Cu(H_2O)_6]^{2+} + 4\,NH_3 \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+} + 4\,H_2O \tag{6.17.3.1}$$

In fact, the water molecules get replaced one at a time, and so this is made up of a series of part-reactions:

$$[Cu(H_2O)_6]^{2+} + NH_3 \rightleftharpoons [Cu(NH_3)(H_2O)_5]^{2+} + H_2O \tag{6.17.3.2}$$

$$[Cu(NH_3)(H_2O)_5]^{2+} + NH_3 \rightleftharpoons [Cu(NH_3)_2(H_2O)_4]^{2+} + H_2O \tag{6.17.3.3}$$

$$[Cu(NH_3)_2(H_2O)_4]^{2+} + NH_3 \rightleftharpoons [Cu(NH_3)_3(H_2O)_3]^{2+} + H_2O \tag{6.17.3.4}$$

$$[Cu(NH_3)_3(H_2O)_3]^{2+} + NH_3 \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+} + H_2O \tag{6.17.3.5}$$

Although this can look a bit daunting at first sight, all that is happening is that first you have one, then two, then three, then four water molecules in total replaced by four ammine ligands.

Individual stability constants

Let's take a closer look at the first of these equilibria (Equation 6.17.3.2). Like any other equilibrium, this one has an equilibrium constant, K_c - except that in this case, we call it a stability constant. Because this is the first water molecule to be replaced, we call it K_1 and is given by this expression:

$$K_1 = \frac{[[Cu(NH_3)(H_2O)_5]^{2+}]}{[[Cu(H_2O)_6]^{2+}][NH_3]}$$

There are two points of possible confusion here - one minor, one more important!

- First, the square brackets have changed their meaning! Square brackets are often used to keep everything in a complex ion together and tidy. Here, they have reverted to their other use, which implies concentrations in mol dm^{-3}.
- In order to avoid complete confusion, the square brackets keeping the complexes together have been removed entirely.
- More importantly, if you compare the equilibrium constant expression with the equation, you will see that the water on the right-hand side hasn't been included. That is normal practice with these expressions.
- Because everything is dissolved in water, the water is present as a huge excess. Generating a little bit more during the reaction is going to make no effective difference to the total concentration of the water in terms of moles of water per dm^3.
- The concentration of the water is approximately constant. The equilibrium constant is defined so that you avoid having an extra unnecessary constant in the expression.

With that out of the way, let's go back to where we were - but introduce a value for K_1:

$$[Cu(H_2O)_6]^{2+} + NH_3 \rightleftharpoons [Cu(NH_3)(H_2O)_5]^{2+} + H_2O$$

$$K_1 = \frac{[Cu(NH_3)(H_2O)_5^{2+}]}{[Cu(H_2O)_6^{2+}]\,[NH_3]} = 1.78 \times 10^4 \text{ mol}^{-1} \text{ dm}^3$$

The value of the equilibrium constant is fairly large, suggesting that there is a strong tendency to form the ion containing an ammonia molecule. A high value of a stability constant shows that the ion is easily formed. Each of the other equilibria above also has its own stability constant, K_2, K_3 and K_4. For example, K_2 is given by:

$$[Cu(NH_3)(H_2O)_5]^{2+} + NH_3 \rightleftharpoons [Cu(NH_3)_2(H_2O)_4]^{2+} + H_2O$$

$$K_2 = \frac{[Cu(NH_3)_2(H_2O)_4^{2+}]}{[Cu(NH_3)(H_2O)_5^{2+}]\,[NH_3]}$$
$$= 4.07 \times 10^3 \ \text{mol}^{-1}\,\text{dm}^3$$

The ion with two ammonias is even more stable than the ion with one ammonia. You could keep plugging away at this and come up with the following table of stability constants:

ion	K_n	value (mol^{-1} dm^3)	log K_n
$[Cu(NH_3)(H_2O)_5]^{2+}$	K_1	1.78×10^4	4.25
$[Cu(NH_3)_2(H_2O)_4]^{2+}$	K_2	4.07×10^3	3.61
$[Cu(NH_3)_3(H_2O)_3]^{2+}$	K_3	9.55×10^2	2.98
$[Cu(NH_3)_4(H_2O)_2]^{2+}$	K_4	1.74×10^2	2.24

You will often find these values quoted as log K_1. All this does is tidy the numbers up so that you can see the patterns more easily. The ions keep on getting more stable as you replace up to 4 water molecules, but notice that the equilibrium constants are gradually getting less big as you replace more and more waters. This is common with individual stability constants.

Overall Formation constants

The overall stability constant is simply the equilibrium constant for the total reaction:

$$[Cu(H_2O)_6]^{2+} + 4\,NH_3 \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+} + 4\,H_2O$$

It is given by this expression:

$$\text{overall } K_{stab} = \frac{[Cu(NH_3)_4(H_2O)_2^{2+}]}{[Cu(H_2O)_6^{2+}]\,[NH_3]^4}$$
$$= 1.20 \times 10^{13} \ \text{mol}^{-4}\,\text{dm}^{12}$$

You can see that overall this is a very large equilibrium constant, implying a high tendency for the ammonias to replace the waters. The "log" value is 13.1. This overall value is found by multiplying together all the individual values of K_1, K_2 and so on. To find out why that works, you will need a big bit of paper and some patience! Write down expressions for all the individual values (the first two are done for you above), and then multiply those expressions together. You will find that all the terms for the intermediate ions cancel out to leave you with the expression for the overall stability constant.

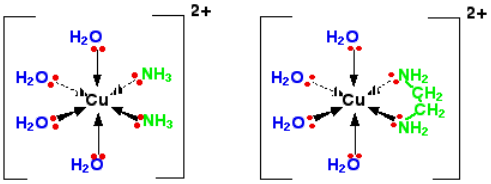
Summary

Whether you are looking at the replacement of individual water molecules or an overall reaction producing the final complex ion, a stability constant is simply the equilibrium constant for the reaction you are looking at. The **larger** the value of the stability constant, the further the reaction lies to the **right**. That implies that complex ions with large stability constants are more stable than ones with smaller ones.

Stability constants tend to be very large numbers. In order to simplify the numbers a "log" scale is often used. Because of the way this works, a difference of 1 in the log value comes from a 10 times difference in the stability constant. A difference of 2 comes from a 100 (in other words, 10^2) times difference in stability constant - and so on.

Stability constants and entropy - the chelate effect

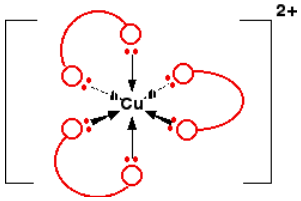
The chelate effect is an effect which happens when you replace water (or other simple ligands) around the central metal ion by multidentate ligands like 1,2-diaminoethane (often abbreviated to "en") or EDTA. Compare what happens if you replace two water molecules around a $[Cu(H_2O)_6]^{2+}$ ion with either 2 ammonia molecules or one molecule of 1,2-diaminoethane.



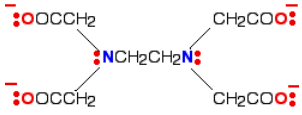
This second structure is known as a chelate from a Greek word meaning a crab's claw. You can picture the copper ion as being nipped by the claw of the 1,2-diaminoethane molecule. Chelates are much more stable than complex ions formed from simple monodentate ligands. The overall stability constants for the two ions are:

ion	log K
$[Cu(NH_3)_2(H_2O)_4]^{2+}$	7.86
$[Cu(H_2O)_4(en)]^{2+}$	10.6

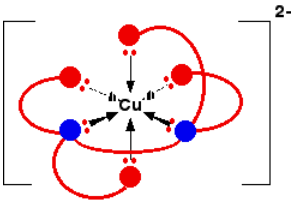
The reaction with the 1,2-diaminoethane could eventually go on to produce a complex ion $[Cu(en)_3]^{2+}$. Simplifying the structure of this:



The overall stability constant for this (as log K) is 18.7. Another copper-based chelate comes from the reaction with EDTA.



the $EDTA^{4-}$ ion



the $[Cu(EDTA)]^{2-}$ ion

This also has a high stability constant - log K is 18.8. However many examples you take, you always find that a chelate (a complex ion involving multidentate ligands) is more stable than ions with only monodentate ligands. This is known as the chelate effect.

The reason for the chelate effect

If you compare the two equilibria below, the one with the 1,2-diaminoethane ("en") has the higher equilibrium (stability) constant (for values, see above).





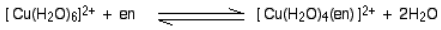
The enthalpy changes of the two reactions are fairly similar. You might expect this because in each case you are breaking two bonds between copper and oxygen atoms and replacing them by two bonds between copper and nitrogen atoms.

If the enthalpy changes are similar, what causes the difference in the extent to which the two reactions happen?

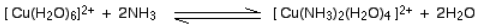
You need to think about the entropy change during each reaction.

Entropy is most easily thought of as a measure of disorder. Any change which increases the amount of disorder increases the tendency of a reaction to happen.

If you look again at the two equiilbria, you might notice that the 1,2-diaminoethane equilibrium does lead to an increase in the entropy. There are only two species on the left-hand side of the equation, but three on the right.



You can obviously get more entropy out of three species than out of only two. Compare that with the other equilibrium. In this case, there is no change in the total number of species before and after reaction, and so no useful contribution to an increase in entropy.



In the case of the complex with EDTA, the increase in entropy is very pronounced.



Here, we are increasing the number of species present from two on the left-hand side to seven on the right. You can get a major amount of increase in disorder by making this change.

Reversing this last change is going to be far more difficult in entropy terms. You would have to move from a highly disordered state to a much more ordered one. That isn't so likely to happen, and so the copper-EDTA complex is very stable.

Summary

Complexes involving multidentate ligands are more stable than those with only monodentate ligands. The underlying reason for this is that each multidentate ligand displaces more than one water molecule. This leads to an increase in the number of species present in the system, and therefore an increase in entropy. An increase in entropy makes the formation of the chelated complex more favorable.

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6.17.4: Reactions of the Hexaaqua Ions with Ammonia

This page describes and explains the reactions between complex ions of the type $[M(H_2O)_6]^{n+}$ and ammonia solution.Reactions of the hexaaqua ions with ammonia solution are complicated by the fact that the ammonia can have two quite different functions. It can act as a base (in the Brønsted-Lowry sense), but it is also a possible ligand which can replace water molecules around the central metal ion. When it acts as a ligand, it is acting as a Lewis base. We need to look at these two functions separately.

Ammonia acting as a (Brønsted-Lowry) base

This is what happens when you only add small amounts of dilute ammonia solution to any of the hexaaqua ions. The ligand effect only happens with an excess of ammonia or with concentrated ammonia - and with some metals you don't even see it then.

We'll talk through what happens if you add a small amount of dilute ammonia solution to a solution containing a 2+ hexaaqua ion. These have the formula $[M(H_2O)_6]^{2+}$, and they are acidic. Their acidity is shown in the reaction of the hexaaqua ions with water molecules from the solution:

$$[M(H_2O)_6]^{2+}(aq) + H_2O \rightleftharpoons [M(H_2O)_5(OH)]^{+}(aq) + H_3O^{+}(aq)$$

They are acting as acids by donating hydrogen ions to water molecules in the solution. Because of the confusing presence of water from two different sources (the ligands and the solution), it is easier to simplify this:

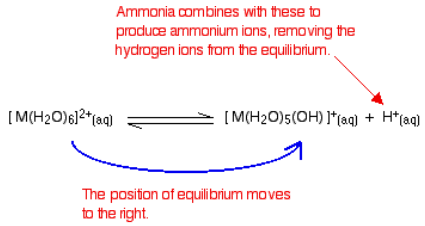
$$[M(H_2O)_6]^{2+}(aq) \rightleftharpoons [M(H_2O)_5(OH)]^{+}(aq) + H^{+}(aq)$$

Adding ammonia solution to this equilibrium - stage 1

There are two possible reactions.

1. Reaction of ammonia with the hydroxonium ions (hydrogen ions)
2. Ammonia will react with these to produce ammonium ions.

According to Le Chatelier's Principle, the position of equilibrium will move to the right, producing more of the new complex ion.



Reaction of ammonia with the hexaaqua ion

Statistically, there is far more chance of an ammonia molecule hitting a hexaaqua metal ion than of hitting a hydrogen ion. There are far more hexaaqua ions present. If that happens, you get exactly the same new complex ion formed as above.

$$[M(H_2O)_6]^{2+}(aq) + NH_3 \rightleftharpoons [M(H_2O)_5(OH)]^{+}(aq) + NH_4^{+}(aq)$$

Notice that this is still a reversible change (unlike the corresponding change when you add hydroxide ions). Ammonia is only a weak base.

The second stage of the reaction

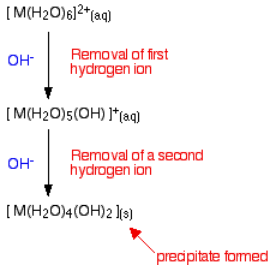
Whichever of the above reactions happens, you end up with $[M(H_2O)_5(OH)]^{+}$ ions in solution. These are also acidic, and can lose hydrogen ions from another of the water ligands. Taking the easier version of the equilibrium:

$$[M(H_2O)_5(OH)]^{+}(aq) \rightleftharpoons [M(H_2O)_4(OH)_2](s) + H^{+}(aq)$$

Adding ammonia again tips the equilibrium to the right - either by reacting with the hydrogen ions, or by reacting directly with the complex on the left-hand side. When this happens, the new complex formed no longer has a charge - this is a "neutral complex". It

is insoluble in water - and so a precipitate is formed. This precipitate is often written without including the remaining water ligands. In other words we write it as $M(OH)_2$. A precipitate of the metal hydroxide has been formed.

Summarizing what has happened



You can also usefully write the complete change as an overall equilibrium reaction. This will be important for later on.

$$[M(H_2O)_6]^{2+}(aq) + 2\,NH_3 \rightleftharpoons [M(H_2O)_4(OH)_2](s) + 2\,NH_4{}^+(aq)$$

If you did the same reaction with a 3+ ion, the only difference is that you would have to remove a total of 3 hydrogen ions in order to get to the neutral complex. That would give the overall equation:

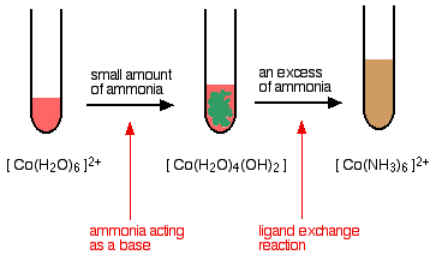
$$[M(H_2O)_6]^{3+}(aq) + 3\,NH_3 \rightleftharpoons [M(H_2O)_3(OH)_3](s) + 4\,NH_4{}^+(aq)$$

Ions of specific metals

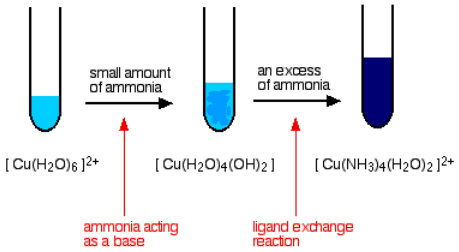
Remember that we are concentrating for the moment on the ammonia acting as a base - in other words, on the formation of hydroxide precipitates when you add small amounts of ammonia solution to solutions containing hexaaqua metal The diagrams, however, will show the complete change so I don't have to repeat them later on. Ignore the cases where the precipitate dissolves in excess ammonia for the moment.

2+ ions

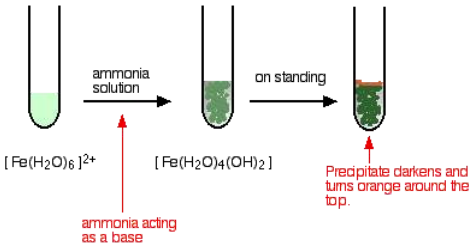
hexaaquacobalt(II)



hexaaquacopper(II)

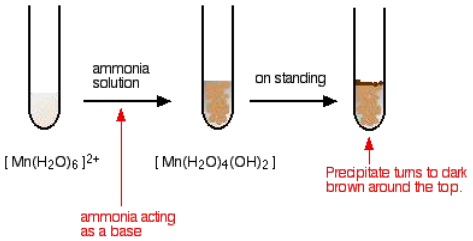


hexaaquairon(II)



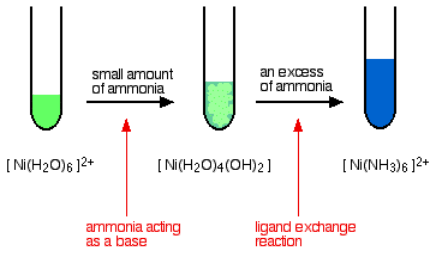
Iron is very easily oxidized under alkaline conditions. Oxygen in the air oxidizes the iron(II) hydroxide precipitate to iron(III) hydroxide especially around the top of the tube. The darkening of the precipitate comes from the same effect. This is NOT a ligand exchange reaction.

hexaaquamanganese(II)

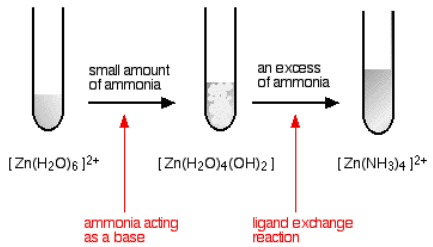


I have shown the original solution as very pale pink (the palest I can produce!), but in fact it is virtually colorless. The pale brown precipitate is oxidized to darker brown manganese(III) oxide in contact with oxygen from the air. Again, this isn't a ligand exchange reaction.

hexaaquanickel(II)



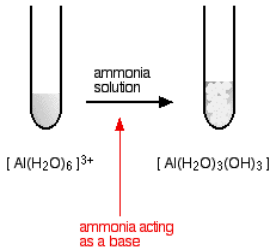
hexaaquazinc



You start and finish with colourless solutions, producing a white precipitate on the way.

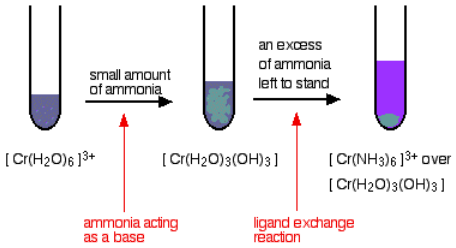
3+ ions

hexaaquaaluminium

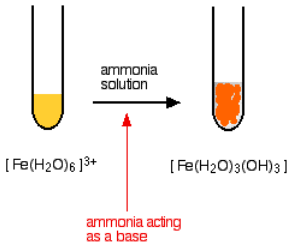


Starting from a colorless solution, you get a white precipitate.

hexaaquachromium(III)



hexaaquairon(III)



Summary of the effect of adding small amounts of ammonia solution

In each case you get a precipitate of the neutral complex - the metal hydroxide. Apart from minor differences in the exact shade of color you get, these are almost all exactly the same as the precipitates you get when you add a little sodium hydroxide solution to the solutions of the hexaaqua ions. The only real difference lies in the color of the cobalt precipitate.

Ammonia acting as a ligand

The ligand exchange reaction

In some cases, ammonia replaces water around the central metal ion to give another soluble complex. This is known as a ligand exchange reaction, and involves an equilibrium such as this one:

$$[Cu(H_2O)_6]^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+} + 4H_2O$$

The formation of this new soluble complex causes the precipitate to dissolve. The ammonia attaches to the central metal ion using the lone pair of electrons on the nitrogen atom. Because it is a lone pair donor, it is acting as a Lewis base.

Explaining why the precipitate dissolves

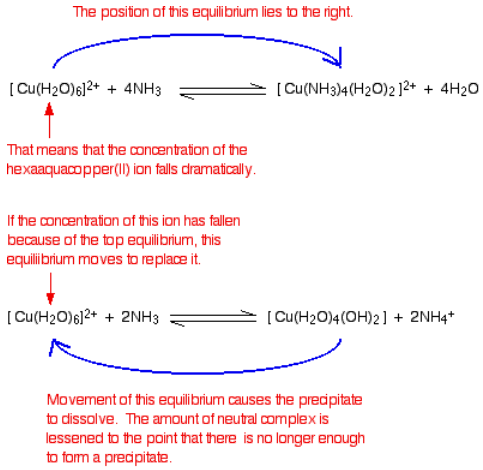
Almost all text books leave the argument at this point, assuming that it is obvious why the formation of the complex causes some precipitates to dissolve - it is not! Consider the copper case as typical of any of them. There are two equilibria involved in this. The first is the one in which ammonia is acting as a base and producing the precipitate:

$$[Cu(H_2O)_6]^{2+} + 2NH_3 \rightleftharpoons [Cu(H_2O)_4(OH)_2] + 2NH_4^+$$

The other one is the ligand exchange reaction:

$$[Cu(H_2O)_6]^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+} + 4H_2O$$

Notice that the hexaaqua ion appears in both of these. There is now an interaction between the two equilibria:



Looking at it like this is helpful in explaining why some precipitates dissolve in excess ammonia while others don't. It depends on the positions of the equilibria. To get the precipitate to dissolve, you obviously need the ligand exchange equilibrium to lie well to the right, but you need the acid-base equilibrium to be easy to pull back to the left.

Contributors and Attributions

- Jim Clark (Chemguide.co.uk)

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6.17.5: Reactions of the Hexaaqua Ions with Carbonate Ions

This page describes and explains the reactions between complex ions of the type $[M(H_2O)_6]^{n+}$ and carbonate ions from, for example, sodium carbonate solution. There is a difference in the reactions depending on whether the metal at the center of the hexaaqua ion carries a 2+ or a 3+ charge. We need to look at each cases separately.

3+ ions reacting with carbonate ions

The 3+ hexaaqua ions are sufficiently acidic to react with carbonate ions to release carbon dioxide gas and precipitate a metal hydroxide.

The acidity of the 3+ hexaaqua ions

These have the formula $[M(H_2O)_6]^{3+}$, and they are fairly acidic. They react with water molecules from the solution:

$$[M(H_2O)_6]^{3+}(aq) + H_2O \rightleftharpoons [M(H_2O)_6]^{2+}(aq) + H_3O^+(aq)$$

They are acting as acids by donating hydrogen ions to water molecules in the solution. Because of the confusing presence of water from two different sources (the ligands and the solution), it is easier to simplify this:

$$[M(H_2O)_6]^{3+}(aq) \rightleftharpoons [M(H_2O)_6]^{2+}(aq) + H^+(aq)$$

Carbonate ions acting as a base

Carbonate ions combine with hydrogen ions in two stages - first to make hydrogencarbonate ions, and then to give carbon dioxide and water.

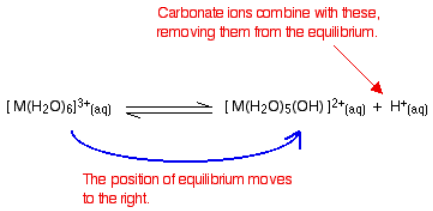
$$CO_3^{2-}(aq) + H^+(aq) \rightleftharpoons HCO_3^-(aq) + H_2O(l)$$

$$HCO_3^-(aq) + H^+(aq) \rightleftharpoons CO_2(g) + H_2O(l)$$

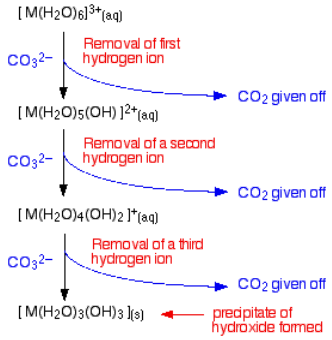
Reacting carbonate ions with the 3+ hexaaqua ions

Provided the proportions are right, the 3+ hexaaqua ions are sufficiently acidic for the reactions to go all the way to carbon dioxide. There are two possible reactions.

1. Reaction of carbonate ions with the hydroxonium ions (hydrogen ions). According to Le Chatelier's Principle, as the hydrogen ions are removed, the position of equilibrium will move to the right, producing more of the new complex ion.



2. Reaction of carbonate ions with the hexaaqua ion. Statistically, there is far more chance of a carbonate ion hitting a hexaaqua metal ion than of hitting a hydrogen ion. It removes a hydrogen ion directly from the hexaaqua complex. If that happens, you get exactly the same new complex ion formed as above. But it doesn't stop there. Carbonate ions keep on removing hydrogen ions from the complex until you end up with a neutral complex. You see that as a precipitate of the metal hydroxide.



You can also usefully write the complete change as an overall reaction.

$$2\,[M(H_2O)_6]^{3+}(aq) + 3\,CO_3^{2-} \longrightarrow 2\,[M(H_2O)_3(OH)_3](s) + 3\,CO_2(g) + 3\,H_2O(l)$$

2+ ions reacting with carbonate ions

The 2+ hexaaqua ions aren't strongly acidic enough to release carbon dioxide from carbonates. In these cases, you still get a precipitate - but it is a precipitate of what is loosely described as the "metal carbonate".

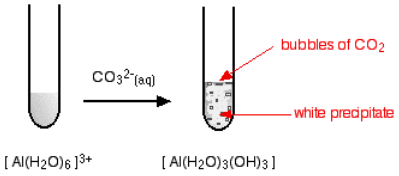
$$M^{2+}(aq) + CO_3^{2-}(aq) \rightarrow MCO_3(s)$$

Looking at the ions of specific metals

We'll look at the reactions of three 3+ ions and three 2+ ions. The important ones are the 3+ ions.

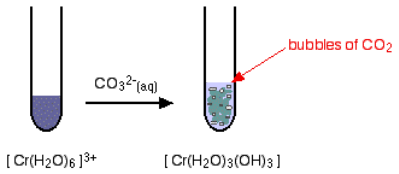
The 3+ ions

hexaaquaaluminium



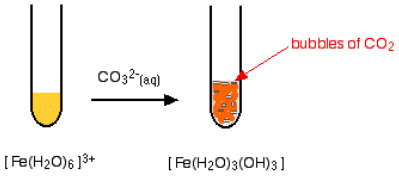
Starting from a colourless solution, you get a white precipitate - but with bubbles of gas as well. The precipitate is identical to the one you get if you add small amounts of either sodium hydroxide or ammonia solutions to a solution of the hexaaquaaluminium ions.

hexaaquachromium(III)



Again, the precipitate is just the same as if you had added small amounts of either sodium hydroxide or ammonia solution.

hexaaquairon(III)



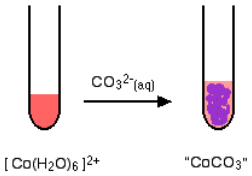
. . . and again, exactly the same precipitate as if you had added any other base.

Summary

In each case you get a precipitate of the neutral complex - the metal hydroxide. This is exactly the same precipitate that you get if you add small amounts of either sodium hydroxide solution or ammonia solution to solutions of these ions. Bubbles of carbon dioxide are also given off.

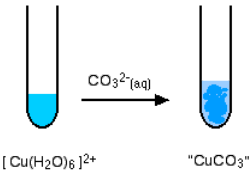
2+ ions

hexaaquacobalt(II)



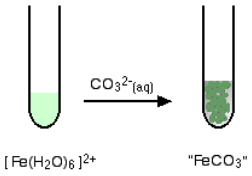
No gas this time - just a precipitate of "cobalt(II) carbonate".

hexaaquacopper(II)



Again, there isn't any carbon dioxide - just a precipitate of the "copper(II) carbonate".

hexaaquairon(II)



You get a precipitate of the "iron(II) carbonate", but no carbon dioxide.

Summary

Hexaaqua ions with a 2+ charge aren't sufficiently acidic to liberate carbon dioxide from carbonate ions. Instead you get a precipitate which you can think of as being the metal carbonate.

Contributors and Attributions

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6.17.6: Reactions of the Hexaaqua Ions with Hydroxide Ions

This page describes and explains the reactions between complex ions of the type $[M(H_2O)_6]^{n+}$ and hydroxide ions from, for example, sodium hydroxide solution. It assumes that you know why these ions are acidic, and are happy about the equilibria involved.

The general case

Although there are only minor differences, for simplicity we will look at 2+ ions and 3+ ions separately.

Adding hydroxide ions to 2+ hexaaqua ions

These have the form $[M(H_2O)_6]^{2+}$. Their acidity is shown in the reaction of the hexaaqua ions with water molecules from the solution:

$$[M(H_2O)_6]^{2+}(aq) + H_2O(l) \rightleftharpoons [M(H_2O)_5(OH)]^{+}(aq) + H_3O^{+}(aq)$$

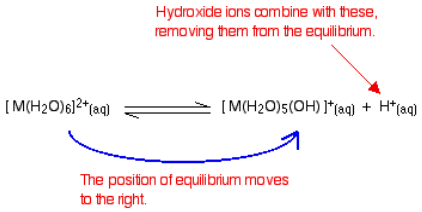
They are acting as acids by donating hydrogen ions to water molecules in the solution. Because of the confusing presence of water from two different sources (the ligands and the solution), it is easier to simplify this:

$$[M(H_2O)_6]^{2+}(aq) \rightleftharpoons [M(H_2O)_5(OH)]^{+}(aq) + H^{+}(aq)$$

Disturbing this equilibrium by adding hydroxide ions - stage 1

What happens if you add hydroxide ions to this equilibrium? There are two possible reactions.

1. Reaction of hydroxide ions with the hydroxonium ions (hydrogen ions). According to Le Chatelier's Principle, the position of equilibrium will move to the right, producing more of the new complex ion.



2. Reaction of hydroxide ions with the hexaaqua ion. Statistically, there is far more chance of a hydroxide ion hitting a hexaaqua metal ion than of hitting a hydrogen ion. There are far more hexaaqua ions present. If that happens, you get exactly the same new complex ion formed as above.

$$[M(H_2O)_6]^{2+}(aq) + OH^{-}(aq) \rightleftharpoons [M(H_2O)_5(OH)]^{+}(aq) + H_2O(l)$$

Notice that this isn't a ligand exchange reaction. The hydroxide ion has removed a hydrogen ion from one of the ligand water molecules. The reaction has also become essentially irreversible.

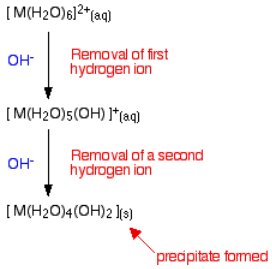
The second stage of the reaction

Whichever of the above reactions happens, you end up with $[M(H_2O)_5(OH)]^{+}$ ions in solution. These are also acidic, and can lose hydrogen ions from another of the water ligands. Taking the easier version of the equilibrium:

$$[M(H_2O)_5(OH)]^{+}(aq) \rightleftharpoons [M(H_2O)_4(OH)_2](s) + H^{+}(aq)$$

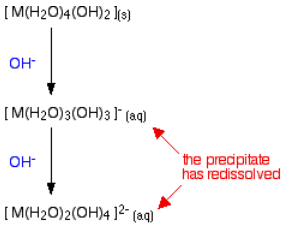
Adding hydroxide ions again tips the equilibrium to the right - either by reacting with the hydrogen ions, or by reacting directly with the complex on the left-hand side. When this occurs, the new complex formed no longer has a charge - we describe it as a "neutral complex". In all the cases we are looking at, this neutral complex is insoluble in water - and so a precipitate is formed. This precipitate is often written without including the remaining water ligands. In other words we write it as $M(OH)_2$. A precipitate of the metal hydroxide has been formed.

Summarizing what has happened so far



Going further

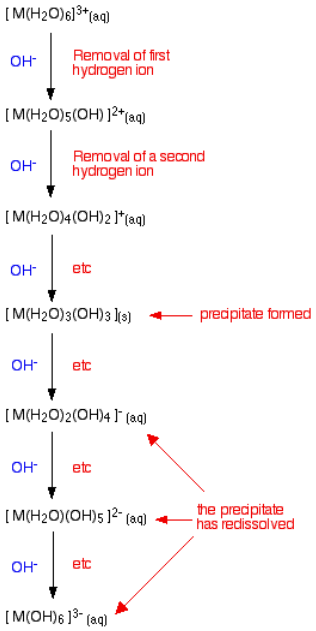
There is no logical reason why the removal of hydrogen ions from the complex should stop at this point. Further hydrogen ions can be removed by hydroxide ions to produce anionic complexes - complexes carrying negative charges. Whether this actually happens in the test tube to any extent varies from metal to metal.



In fact, if you do this using sodium hydroxide solution of the usual concentrations, most of the 2+ ions that you will meet at this level don't go beyond the precipitate. The only one you are likely to come across is the zinc case - and that has a complication. The final ion is $[Zn(OH)_4]^{2-}$ - a tetrahedral ion which has lost the remaining 2 water ligands.

Adding hydroxide ions to 3+ hexaaqua ions

The argument here is exactly as before - the only difference is the number of hydrogen ions which have to be removed from the original hexaaqua complex to produce the neutral complex. Going beyond the neutral complex is also rather more common with 3+ than with 2+ ions, and may go as far as having a hydrogen ion removed from each of the six water molecules. This is summarized in the same sort of flow scheme as before:

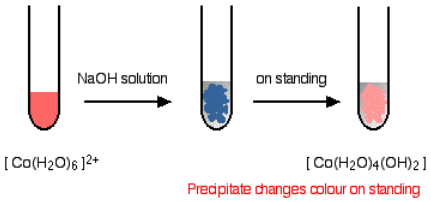


Looking at the ions of specific metals

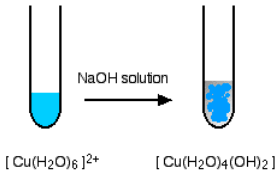
In each case the formula of the precipitate will be given as if it were the simple neutral complex. In fact, these "hydroxide" precipitates sometimes rearrange by losing water from combinations of the attached OH groups. This produces oxides closely associated with the lost water. These changes are beyond the scope of this site.

2+ ions

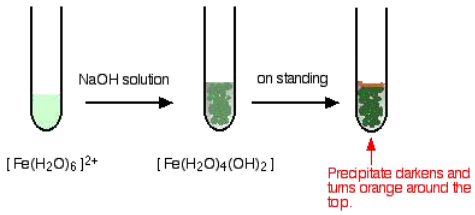
hexaaquacobalt(II)



hexaaquacopper(II)

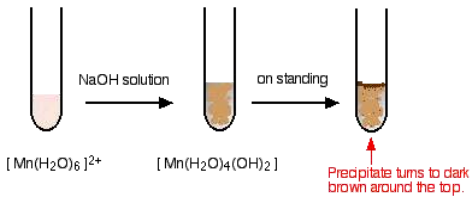


hexaaquairon(II)



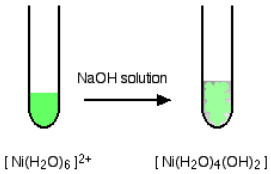
Iron is very easily oxidized under alkaline conditions. Oxygen in the air oxidizes the iron(II) hydroxide precipitate to iron(III) hydroxide especially around the top of the tube. The darkening of the precipitate comes from the same effect.

hexaaquamanganese(II)

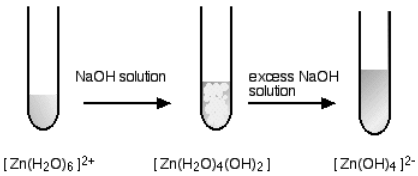


I have shown the original solution as very pale pink (the palest I can produce!), but in fact it is virtually colourless. The pale brown precipitate is oxidized to darker brown manganese(III) oxide in contact with oxygen from the air.

hexaaquanickel(II)



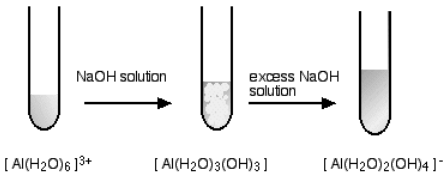
hexaaquazinc



You start and finish with colorless solutions, producing a white precipitate on the way.

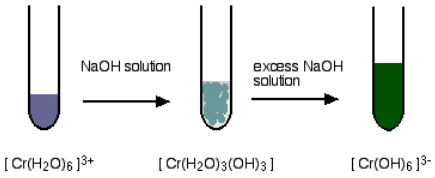
3+ ions

hexaaquaaluminium

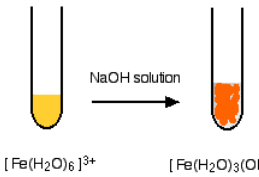


This looks exactly the same in the test tube as the corresponding zinc reaction above - but beware the different formulae of the precipitate and the final solution.

hexaaquachromium(III)



hexaaquairon(III)



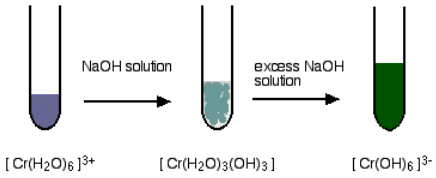
Reversing the process

If adding hydroxide ions removes hydrogen ions from the hexaaqua complex one at a time, it doesn't seem unreasonable that you could put them back again by adding an acid. That's just what happens!

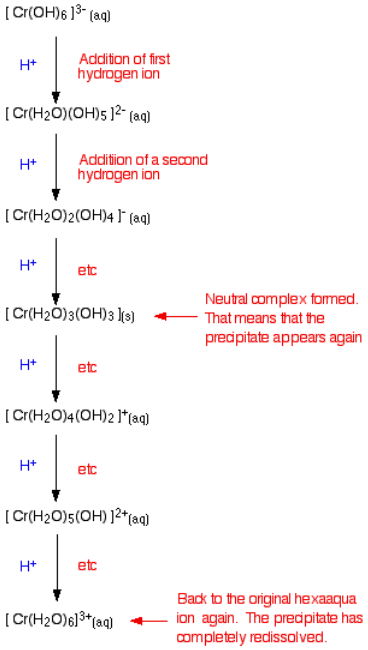
We'll look in detail at what happens in the chromium(III) case, but exactly the same principle applies to all the other examples we've looked at - whether for 2+ or 3+ ions. As long as you understand what is happening, you can work out the details if you need to

Adding acid to hexahydroxochromate(III) ions

These are the ions formed at the end of the sequence in which you add hydroxide ions to a solution containing hexaaquachromium(III) ions. Their formula is $[Cr(OH)_6]^{3-}$. A reminder of the color changes when you add sodium hydroxide solution to a solution containing hexaaquachromium(III) ions:



If you add an acid (dilute sulphuric acid, for example), the hydrogen ions get put back on one at a time.



You already know the colors of the significant stages (the beginning, the end, and the neutral complex). It isn't a separate bit of learning! You can apply this to any case. If you know the colors as you remove hydrogen ions, you automatically know them as you put the hydrogen ions back on again. It also doesn't matter where you start from either - whether, for example, you add acid to an ionic complex like $[Cr(OH)_6]^{3-}$, or a neutral one like $[Fe(H_2O)_4(OH)_2]$.

You will know that the $[Fe(H_2O)_4(OH)_2]$ is a dirty green precipitate. When you add the hydrogen ions back to it, it will revert to the very pale green solution of the $[Fe(H_2O)_6]^{2+}$ ion. None of this is a new bit of learning - you just have to re-arrange what you already know!

Amphoteric hydroxides

An amphoteric substance has both acidic and basic properties. In other words, it will react with both bases and acids. Some of the metal hydroxides we've been looking at are doing exactly that.

Chromium(III) hydroxide as an amphoteric hydroxide

"Chromium(III) hydroxide" is a simple way of naming the neutral complex $[Cr(H_2O)_3(OH)_3]$. You have seen that it reacts with bases (hydroxide ions) to give $[Cr(OH)_6]^{3-}$. It also reacts with acids (hydrogen ions) to give $[Cr(H_2O)_6]^{3+}$. This is a good example of amphoteric behavior.

Other examples of amphoteric hydroxides are zinc hydroxide and aluminium hydroxide.

Copper(II) hydroxide as a basic oxide

Quite a lot of metal hydroxides won't react any further with hydroxide ions if you use sodium hydroxide solution at the sort of concentrations normally used in the lab. That means that they don't have any significant acidic nature.

"Copper(II) hydroxide" is what we would normally call the neutral complex $[Cu(H_2O)_4(OH)_2]$. This doesn't dissolve in sodium hydroxide solution at any concentration normally used in the lab. It doesn't show any acidic character.

On the other hand, it will react with acids - replacing the lost hydrogen ions on the water ligands. Because it is accepting hydrogen ions, it is acting as a base. Hydroxides like this (which react with acids, but not bases) are not amphoteric - they are just simple bases.

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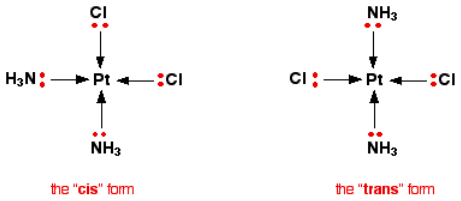
- **Reactions of the Hexaaqua Ions with Hydroxide Ions** by Jim Clark is licensed CC BY-NC 4.0.

6.17.7: Stereoisomerism in complex ions

Some complex ions can show either optical or geometric isomerism.

Geometric Isomerism

This occurs in planar complexes like the $Pt(NH_3)_2Cl_2$ we've just looked at. There are two completely different ways in which the ammonias and chloride ions could arrange themselves around the central platinum ion:



the "**cis**" form the "**trans**" form

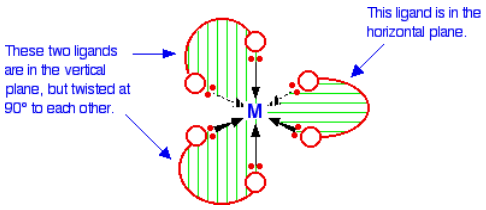
The two structures drawn are isomers because there is no way that you can just twist one to turn it into the other. The complexes are both locked into their current forms.

The terms *cis* and *trans* are used in the same way as they are in organic chemistry. Trans implies "opposite" - notice that the ammine ligands are arranged opposite each other in that version, and so are the chloro ligands. Cis means "on the same side" - in this instance, that just means that the ammine and chloro ligands are next door to each other.

Optical isomerism

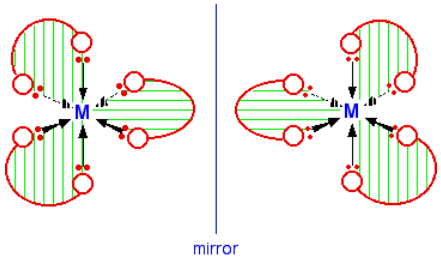
You recognize optical isomers because they have no plane of symmetry. In the organic case, it is fairly easy to recognize the possibility of this by looking for a carbon atom with four different things attached to it. It isn't qute so easy with the complex ions - either to draw or to visualize! The examples you are most likely to need occur in octahedral complexes which contain bidentate ligands - ions like $[Ni(NH_2CH_2CH_2NH_2)_3]^{2+}$ or $[Cr(C_2O_4)_3]^{3-}$.

The diagram below shows a simplified view of one of these ions. Essentially, they all have the same shape - all that differs is the nature of the "headphones". The charges are left off the ion, because obviously they will vary from case to case. The shape shown applies to any ion of this kind.



If your visual imagination will cope, you may be able to see that this ion has no plane of symmetry. If you find this difficult to visualize, the only solution is to make the ion out of a lump of plasticene (or a bit of clay or dough) and three bits of cardboard cut to shape.

A substance with *no plane of symmetry is going to have optical isomers* - one of which is the mirror image of the other. One of the isomers will rotate the plane of polarization of plane polarized light clockwise; the other rotates it counter-clockwise. In this case, the two isomers are:



If you have a really impressive visual imagination, you may be able to see that there is no way of rotating the second isomer in space so that it looks exactly the same as the first one.

Contributors and Attributions

- Jim Clark (Chemguide.co.uk)

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SECTION OVERVIEW

6.18: Crystal Field Theory

One of the most striking characteristics of transition-metal complexes is the wide range of colors they exhibit. Crystal field theory (CFT) is a bonding model that explains many important properties of transition-metal complexes, including their colors, magnetism, structures, stability, and reactivity. The central assumption of CFT is that metal–ligand interactions are purely electrostatic in nature.

6.18.1: Metals, Tetrahedral and Octahedral

6.18.2: Non-octahedral Complexes

6.18.3: Octahedral vs. Tetrahedral Geometries

6.18.4: Tetrahedral vs. Square Planar Complexes

6.18.5: Thermodynamics and Structural Consequences of d-Orbital Splitting

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6.18.1: Metals, Tetrahedral and Octahedral

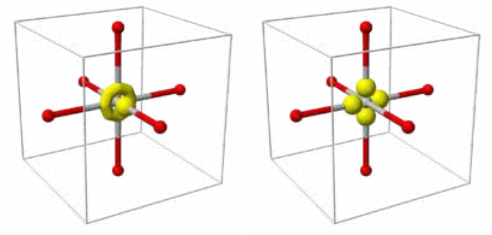
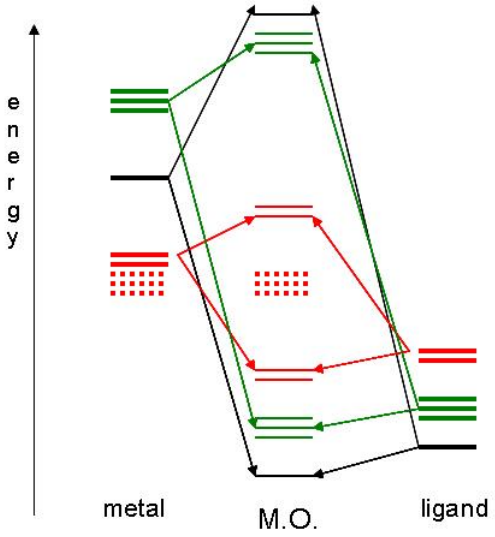


Figure 1: The d_{z^2} (left) and $d_{x^2-y^2}$ (right) orbitals. Images used with permission from Wikipedia.

Let us continue to consider an octahedral complex. The remaining d orbitals, d_{xy}, d_{xz} and d_{yz} see their energy increase to a lesser extent. We refer to the d_{xy}, d_{xz} and d_{yz} orbitals collectively as the t_{2g} d orbitals.

Hybrid orbital theory can be used to describe how metals bond to ligands. When metals bond to ligands, magnetic data shows that some electrons are paired when there is no obvious reason for them to be paired. Molecular orbitals begin to account for this phenomenon by allowing wave functions to interfere in a constructive, low energy (bonding) or destructive, or high energy (antibonding) manner. Thus, the electrons can fill the lowest energy molecular orbitals available to them. However, the electron pairing may be different if the electrons were allowed to fill the lowest energy atomic orbitals available to them.



This diagram shows the field splitting of a metal with ligands in an octahedral configuration. The thick horizontal lines represent atomic orbitals of the metal (left) and ligands (right). The colors correspond to s (black), p (green) and d (red) orbitals. The middle column of horizontal lines represents molecular orbitals made of bonding (lower energy) and antibonding (higher energy) components.

If the ligands are oriented on the cartesian coordinate axes, the metal will still own 3 d orbitals, xy, xz, and xz, which do not intersect (and therefore do not interact) with the ligands. These are considered "nonbonding" orbitals, and are represented by dotted lines in the diagram.

References

1. Jean, Yves; "molecular orbitals of transition metal complexes"; Oxford University Press, 2005

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6.18.2: Non-octahedral Complexes

Learning Objectives

- Understand the d-orbital degeneracies of square planar and tetrahedral metal complexes.

Tetragonal and Square Planar Complexes

If two *trans*- ligands in an octahedral complex are either chemically different from the other four (as in *trans*-$[Co(NH_3)_4Cl_2]^+$), or at a different distance from the metal than the other four, the result is a tetragonally distorted octahedral complex. The electronic structures of such complexes are best viewed as the result of distorting an octahedral complex. Consider, for example, an octahedral complex such as $[Co(NH_3)_6]^{3+}$: two *trans*- NH_3 molecules are slowly removed from the metal along the ±z axes, as shown in the top half of Figure **6.18.2.1**. As the two axial Co–N distances increase simultaneously, the d-orbitals that interact most strongly with the two axial ligands decrease in energy due to a decrease in electrostatic repulsions between the electrons in these orbitals and the negative ends of the ligand dipoles. The affected d orbitals are those with a component along the ±z axes—d_{z^2}, d_{xz}, and d_{yz}. These orbitals are not affected equally, however: because the d_{z^2} orbital points directly at the two ligands being removed, its energy will decrease much more rapidly than the degenerate energies of the d_{xz} and d_{yz}, as shown in the bottom half of Figure **6.18.2.1**. In addition, the effective positive charge on the metal increases somewhat as the axial ligands are removed, increasing the attraction between the four remaining ligands and the metal. This increases the extent of their interactions with the other two d orbitals and increases their energies. Again, the two d orbitals are not affected equally: because the $d_{x^2-y^2}$ orbital points directly at the four in-plane ligands, its energy increases to a greater extent than the energy of the d_{xy} orbital, which points between the in-plane ligands. If the two axial ligands are moved infinitely far away from the metal, a square planar complex is formed. The energy of the d_{xy} orbital actually surpasses that of the d_{z^2} orbital in the process. The largest orbital splitting in a square planar complex, between the $d_{x^2-y^2}$ and d_{xy} energy levels, is identical in magnitude to Δ_o.

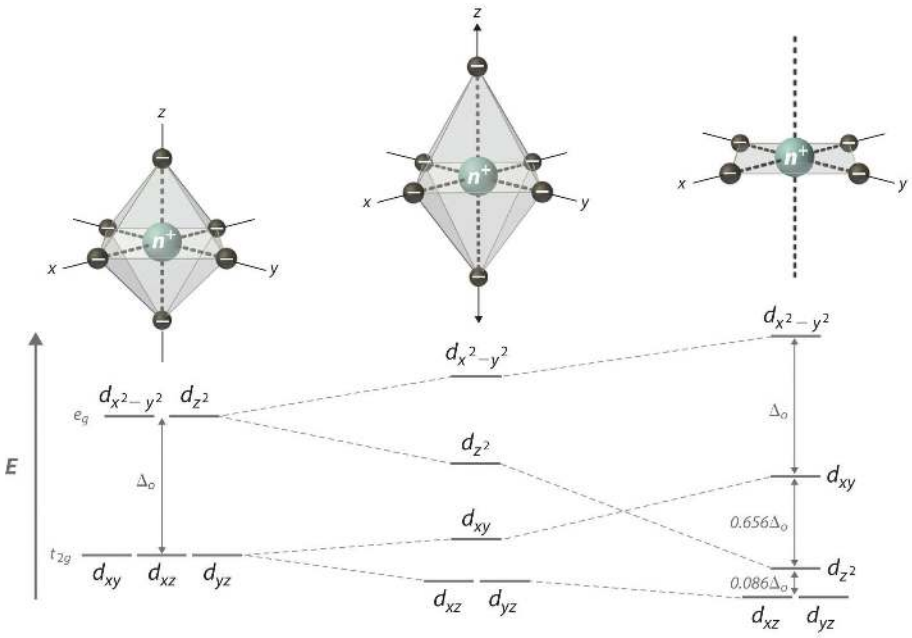


Figure **6.18.2.1** d-Orbital Splittings for Tetragonal and Square Planar Complexes. (CC BY-SA-NC; anonymous by request)

Moving the two axial ligands away from the metal ion along the z axis initially generates an elongated octahedral complex (the center compound of Figure **6.18.2.1**) and eventually produces a square planar complex (right). As shown below the structures, an axial elongation causes the d_{z^2} d_{xz} and d_{yz} orbitals to decrease in energy and the $d_{x^2-y^2}$ and d_{xy} orbitals to increase in energy. The change in energy is not the same for all five d orbitals. The d_{z^2} orbital has a smaller xy component than does the d_{xy} orbital, so it reaches a lower energy level; thus, the order of these orbitals is reversed.

Tetrahedral Complexes

In a tetrahedral arrangement of four ligands around a metal ion, none of the ligands lies on any of the three coordinate axes (illustrated in part (a) in Figure **6.18.2.2**); consequently, none of the five d orbitals points directly at the ligands. Nonetheless, the d_{xy}, d_{xz}, and d_{yz} orbitals interact more strongly with the ligands than do $d_{x^2-y^2}$ and d_{z^2}; this again results in a splitting of the five d orbitals into two groups. The splitting of the energies of the orbitals in a tetrahedral complex (Δ_t) is much smaller than that for an octahedral complex (Δ_o), however, for two reasons: first, the d orbitals interact less strongly with the ligands in a tetrahedral arrangement; second, there are only four negatively-charged regions rather than six, which decreases the electrostatic interactions by one-third if all other factors are equal. It can be shown that for complexes of the same metal ion with the same charge, the same ligands, and the same M–L distance, $\Delta_t = \frac{4}{9}\Delta_o$. The relationship between the splitting of the five d orbitals in octahedral and tetrahedral crystal fields imposed by the same ligands is shown schematically in part (b) in Figure **6.18.2.2**.

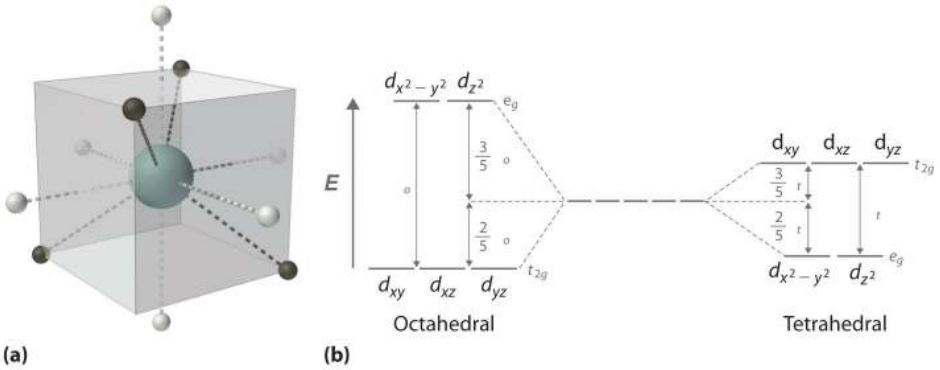


Figure **6.18.2.2**: d-Orbital Splittings for a Tetrahedral Complex. (a) In a tetrahedral complex, none of the five d orbitals points directly at or between the ligands. (b) Because the d_{xy}, d_{xz}, and d_{yz}orbitals (the t_{2g} orbitals) interact more strongly with the ligands than do the $d_{x^2-y^2}$ and d_{z^2} orbitals (the e_g orbitals), the order of orbital energies in a tetrahedral complex is the opposite of the order in an octahedral complex. (CC BY-SA-NC; anonymous by request)

> *Δ_t < Δ_o because of weaker d-orbital–ligand interactions and decreased electrostatic interactions.*

Example 6.18.2.1: Predicting Structure

For each complex, predict its structure, whether it is high spin or low spin, and the number of unpaired electrons present.

1. $[Cu(NH_3)_4]^{2+}$
2. $[Ni(CN)_4]^{2-}$

Solution

Because Δ_o is so large for the second- and third-row transition metals, all four-coordinate complexes of these metals are square planar due to the much higher crystal field stabilization energy (CFSE) for square planar versus tetrahedral structures. The only exception is for d^{10} metal ions such as Cd^{2+}, which have zero CFSE and are therefore tetrahedral as predicted by the VSEPR model. Four-coordinate complexes of the first-row transition metals can be either square planar or tetrahedral; the former is favored by strong-field ligands, whereas the latter is favored by weak-field ligands. For example, the $[Ni(CN)_4]^{2-}$ ion is square planar, while the $[NiCl_4]^{2-}$ ion is tetrahedral.

1.

The copper in this complex is a d^9 ion and it has a coordination number of 4. So it is probably either square planar or tetrahedral. To estimate which, we need to fill in the CFT splitting diagrams for each with 9 electrons and ask which has a lower energy. Comparing the square planer (Figure **6.18.2.1**) splitting diagram with tetrahedral (Figure **6.18.2.2**), suggests that 9 electrons will have a net lower total energy for square planar (since the $d_{x^2-y^2}$ orbital is high in energy, the others are lower).

For the square planar structure, neither high nor low spin states are possible (only one state) with a single unpaired electron.

2.

The nickle in this complex is a d^8 ion and it has a coordination number of 4. So it is probably either square planar or tetrahedral. To estimate which, we need to fill in the CFT splitting diagrams for each with 8 electrons and ask which has a lower energy. Comparing the square planer (Figure **6.18.2.1**) splitting diagram with tetrahedral (Figure **6.18.2.2**), suggests that 8 electrons will have a net lower total energy for square planar (since the $d_{x^2-y^2}$ orbital is high in energy, the others are lower).

For the square planar structure, it is a low spin complex since a high spin requires a lot of energy to promote to the $d_{x^2-y^2}$ orbital. Hence, there are no unpaired electrons

? Exercise 6.18.2.1

What are the geometries of the following two complexes?

1. $[AlCl_4]^-$
2. $[Ag(NH_3)_2]^+$

Answer 1

tetrahedral

Answer 2

linear

Summary

Distorting an octahedral complex by moving opposite ligands away from the metal produces a tetragonal or square planar arrangement, in which interactions with equatorial ligands become stronger. Because none of the d orbitals points directly at the ligands in a tetrahedral complex, these complexes have smaller values of the crystal field splitting energy Δ_t. In tetrahedral molecular geometry, a central atom is located at the center of four substituents, which form the corners of a tetrahedron. Tetrahedral geometry is common for complexes where the metal has d^0 or d^{10} electron configuration. The CFT diagram for tetrahedral complexes has $d_{x^2-y^2}$ and d_{z^2} orbitals equally low in energy because they are between the ligand axis and experience little repulsion. In square planar molecular geometry, a central atom is surrounded by constituent atoms, which form the corners of a square on the same plane. The square planar geometry is prevalent for transition metal complexes with d^8 configuration. The CFT diagram for square planar complexes can be derived from octahedral complexes yet the $d_{x^2-y^2}$ level is the most destabilized and is left unfilled.

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6.18.3: Octahedral vs. Tetrahedral Geometries

How do we tell whether a particular complex is octahedral, tetrahedral, or square planar? Obviously if we know the formula, we can make an educated guess: something of the type ML_6 will almost always be octahedral (there is an alternative geometry for 6-coordinate complexes, called trigonal prismatic, but it's pretty rare), whereas something of formula ML_4 will usually be *tetrahedral* unless the metal atom has the d^8 electron configuration, in which case it will probably be *square planar*. But what if we take a particular metal ion and a particular ligand? Can we predict whether it will form an octahedral or a tetrahedral complex, for example? To an extent, the answer is yes... we can certainly say what factors will encourage the formation of tetrahedral complexes instead of the more usual octahedral.

The Crystal Field Stabilization Energy (CFSE) is the additional stabilization gained by the splitting of the orbitals according to the crystal field theory, against the energy of the original five degenerate d orbitals. So, for example, in a d^1situation such as $[Ti(OH_2)_6]^{3+}$, putting the electron into one of the orbitals of the t_{2g} level gains -0.4 Δ_o of CFSE. Generally speaking, octahedral complexes will be favored over tetrahedral ones because:

- It is more (energetically) favorable to form six bonds rather than four
- The CFSE is usually greater for octahedral than tetrahedral complexes. Remember that Δ_o is bigger than Δ_{tet} (in fact, Δ_{tet} is approximately 4/9 Δ_o).

If we make the assumption that Δ_{tet} = 4/9 Δ_o, we can calculate the difference in stabilization energy between octahedral and tetrahedral geometries by referencing everything in terms of Δ_o.

Example 6.18.3.1: d^3 Stabilized Structures

Which is the preferred configuration for a d^3 metal: tetrahedral or octahedral?

Solution

To answer this, the *Crystal Field Stabilization Energy* has to be calculated for a (d^3 metal in both configurations. The geometry with the greater stabilization will be the preferred geometry.

- For a d^3 *octahedral* configuration, the *Crystal Field Stabilization Energy* is

$$3 \times -0.4\Delta_o = -1.2\Delta_o$$

- For a d^3 *tetrahedral* configuration (assuming high spin), the *Crystal Field Stabilization Energy* is

$$-0.8\Delta_{tet}$$

Remember that because Δ_{tet} is less than half the size of Δ_o, tetrahedral complexes are often high spin. We can now put this in terms of Δ_o (we can make this comparison because we're considering the same metal ion and the same ligand: all that's changing is the geometry)

So for tetrahedral d^3, the Crystal Field Stabilization Energy is:

$$\text{CFSE} = -0.8 \text{ x } 4/9\ \Delta_o = -0.355\ \Delta_o.$$

And the difference in Crystal Field Stabilization Energy between the two geometries will be:

$$1.2 - 0.355 = 0.845\ \Delta_o.$$

If we do a similar calculation for the other configurations, we can construct a Table of Δ_o, Δ_{tet} and the difference between them (we'll ignore their signs since we're looking for the difference between them).

Table 6.18.3.1: Crystal Field Stabilization Energies (not splitting parameters). This table compares the values of the CFSE for octahedral and tetrahedral geometries, assuming high spin configurations. The units are Δ_o, and we're assuming that Δ_{tet} = 4/9 Δo.

	Octahedral	Tetrahedral	Difference
d^0, d^5, d^{10}	0	0	0
d^1, d^6	0.4	0.27	0.13
d^2, d^7	0.8	0.53	0.27
d^3, d^8	1.2	0.36	0.84
d^4, d^9	0.6	0.18	0.42

These values can be plotted:.

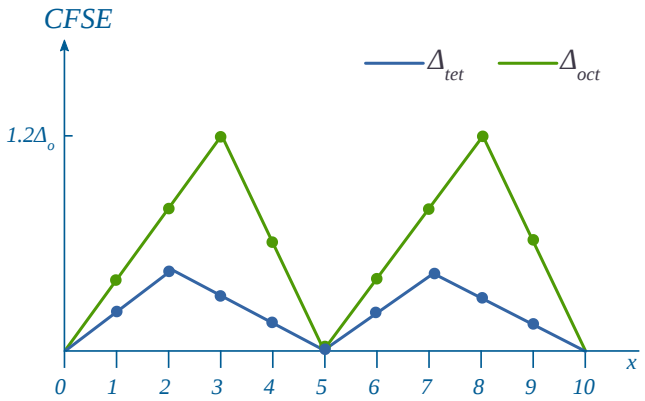


Figure **6.18.3.1**: Crystal Field Stabilization Energy as a function of d-electrons for a hypothetical molecule in the octahedral (green curve) and tetrahedral (blue curve) geometries. (CC BY-NC; Ümit Kaya)

Notice that the Crystal Field Stabilization Energy almost always favors octahedral over tetrahedral in most cases, but the degree of favorability varies with the *electronic configuration*. In other words, for d^1 there's only a small gap between the oct and tet lines, whereas at d^3 and d^8 there's a big gap. However, for d^0, d^5 high spin and d^{10}, there is **no** CFSE difference between octahedral and tetrahedral. The ordering of favorability of octahedral over tetrahedral is:

$$d^3, d^8 > d^4, d^9 > d^2, d^7 > d^1, d^6 > d^0, d^5, d^{10}$$

The units of the graph are Δ_o. So if we have strong field ligands present, Δ_o will be bigger anyway (according to the spectrochemical series), and any energy difference between the oct and tet lines will be all the greater for it. A bigger Δ_o might also push the complexes over to low spin. Similarly, as we saw previously, high oxidation states and metals from the 2nd and 3rd rows of the transition series will also push up Δ_o.

On the other hand, if large or highly charged ligands are present, they may suffer large interligand repulsions and thus prefer a lower coordination number (4 instead of 6). Consequently if you set out to make something that would have a tetrahedral geometry, you would use large, negatively charged, weak field ligands, and use a metal atom with a d^0, d^5 or d^{10} configuration from the first row of the transition series (though of course having weak field ligands doesn't matter in these three configurations because the difference between oct and tet is 0 Δ_o). As Table 2 shows, you can find tetrahedral complexes for most configurations, but there are very few for d^3 and d^8.

Table **6.18.3.2**: Tetrahedral complexes of different d electron counts

d^0	MnO_4^-	d^5	$MnCl_4^{2-}$
d^1	$TiCl_4^-$	d^6	$FeCl_4^{2-}$
d^2	$Cr(OR)_4$	d^7	$CoCl_4^{2-}$

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- Dr Mike Morris, March 2001

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6.18.4: Tetrahedral vs. Square Planar Complexes

Learning Objectives

- Discuss the d-orbital degeneracy of square planar and tetrahedral metal complexes.

Tetrahedral Geometry

Tetrahedral geometry is a bit harder to visualize than square planar geometry. Tetrahedral geometry is analogous to a pyramid, where each of corners of the pyramid corresponds to a ligand, and the central molecule is in the middle of the pyramid. This geometry also has a coordination number of 4 because it has 4 ligands bound to it. Finally, the bond angle between the ligands is 109.5^{o}. An example of the tetrahedral molecule $\mathbf{CH_4}$, or methane.

In a tetrahedral complex, $\mathbf{\Delta_t}$ is relatively small even with strong-field ligands as there are fewer ligands to bond with. It is rare for the $\mathbf{\Delta_t}$ of tetrahedral complexes to exceed the pairing energy. Usually, electrons will move up to the higher energy orbitals rather than pair. Because of this, *most tetrahedral complexes are high spin.*

Square Planar Complexes

In square planar molecular geometry, a central atom is surrounded by constituent atoms, which form the corners of a square on the same plane. The geometry is prevalent for transition metal complexes with d^8 configuration. This includes Rh(I), Ir(I), Pd(II), Pt(II), and Au(III). Notable examples include the anticancer drugs cisplatin ($\mathbf{PtCl_2(NH_3)_2}$).

A square planar complex also has a coordination number of 4. The structure of the complex differs from tetrahedral because the ligands form a simple square on the x and y axes. Because of this, the crystal field splitting is also different (Figure **6.18.4.1**). Since there are no ligands along the z-axis in a square planar complex, the repulsion of electrons in the $\boldsymbol{d_{xz}}$, $\boldsymbol{d_{yz}}$, and the $\boldsymbol{d_{z^2}}$ orbitals are considerably lower than that of the octahedral complex (the $\boldsymbol{d_{z^2}}$ orbital is slightly higher in energy to the "doughnut" that lies on the x,y axis). The $\boldsymbol{d_{x^2-y^2}}$ orbital has the most energy, followed by the $\boldsymbol{d_{xy}}$ orbital, which is followed by the remaining orbtails (although $\boldsymbol{d_{z^2}}$ has slightly more energy than the $\boldsymbol{d_{xz}}$ and $\boldsymbol{d_{yz}}$ orbital). This pattern of orbital splitting remains constant throughout all geometries. Whichever orbitals come in direct contact with the ligand fields will have higher energies than orbitals that slide past the ligand field and have more of indirect contact with the ligand fields. So when confused about which geometry leads to which splitting, think about the way the ligand fields interact with the electron orbitals of the central atom.

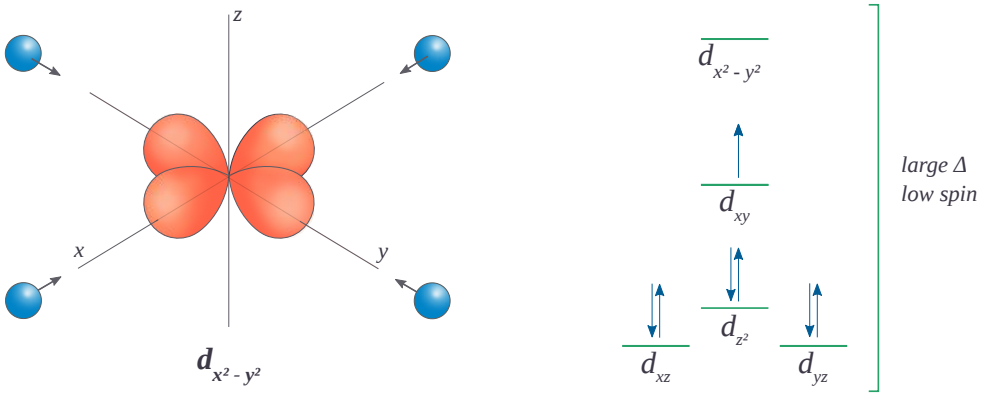


Figure **6.18.4.1**: In square planar complexes Δ will almost always be large, even with a weak-field ligand. Electrons tend to be paired rather than unpaired because paring energy is usually much less than Δ. Therefore, square planar complexes are usually low spin. (CC BY-SA; Ümit Kaya)

In square planar complexes $\mathbf{\Delta}$ will almost always be large (Figure **6.18.4.1**), even with a weak-field ligand. Electrons tend to be paired rather than unpaired because paring energy is usually much less than $\mathbf{\Delta}$. Therefore, *square planar complexes are usually low spin.*

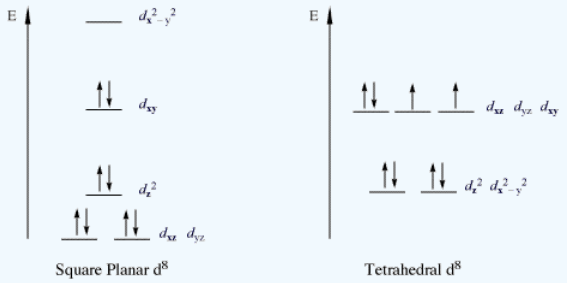
Advanced: $[PdCl_4]^{2-}$ is square planar and $[NiCl_4]^{2-}$ is tetrahedral

The molecule $[PdCl_4]^{2-}$ is diamagnetic, which indicates a square planar geometry as all eight d-electrons are paired in the lower-energy orbitals. However, $[NiCl_4]^{2-}$ is also d^8 but has two unpaired electrons, indicating a tetrahedral geometry. Why is $[PdCl_4]^{2-}$ square planar if Cl^- is not a strong-field ligand?

Solution

The geometry of the complex changes going from $[NiCl_4]^{2-}$ to $[PdCl_4]^{2-}$. Clearly this cannot be due to any change in the ligand since it is the same in both cases. It is the other factor, the metal, that leads to the difference.

Consider the splitting of the d-orbitals in a generic d^8 complex. If it were to adopt a square planar geometry, the electrons will be stabilized (with respect to a tetrahedral complex) as they are placed in orbitals of lower energy. However, this comes at a cost: two of the electrons, which were originally unpaired in the tetrahedral structure, are now paired in the square-planer structure:



Square Planar d^8 Tetrahedral d^8

We can label these two factors as ΔE (stabilization derived from occupation of lower-energy orbitals) and P (spin pairing energy) respectively. One can see that:

- If $\Delta E > P$, then the complex will be square planar
- If $\Delta E < P$, then the complex will be tetrahedral.

This is analogous to deciding whether an octahedral complex adopts a high- or low-spin configuration; where the crystal field splitting parameter Δ_o ΔE does above. Unfortunately, unlike Δ_o in octahedral complexes, there is no simple graphical way to represent ΔE on the diagram above since multiple orbitals are changed in energy between the two geometries.

Interpreting the origin of metal-dependent stabilization energies can be tricky. However, we know experimentally that Pd^{2+} has a larger splitting of the d-orbitals and hence a larger ΔE than Ni^{2+} (moreover P is also smaller).

Practically all 4d and 5d d^8 ML_4 complexes adopt a square planar geometry, irrespective if the ligands are strong-field ligand or not. Other examples of such square planar complexes are $[PtCl_4]^{2-}$ and $[AuCl_4]^-$.

Summary

- In tetrahedral molecular geometry, a central atom is located at the center of four substituents, which form the corners of a tetrahedron.
- Tetrahedral geometry is common for complexes where the metal has d^0 or d^{10}electron configuration.
- The CFT diagram for tetrahedral complexes has $d_{x^2-y^2}$ and d_{z^2} orbitals equally low in energy because they are between the ligand axis and experience little repulsion.
- In square planar molecular geometry, a central atom is surrounded by constituent atoms, which form the corners of a square on the same plane.
- The square planar geometry is prevalent for transition metal complexes with d^8 configuration.
- The CFT diagram for square planar complexes can be derived from octahedral complexes yet the dx2-y2 level is the most destabilized and is left unfilled.

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6.18.5: Thermodynamics and Structural Consequences of d-Orbital Splitting

The energy level splitting of the d-orbitals due to their interaction with the ligands in a complex has important structural and thermodynamic effects on the chemistry of transition-metal complexes. Although these two types of effects are interrelated, they are considered separately here.

Structural Effects

There are two major kinds of structural effects: effects on the ionic radii of metal ions with regular octahedral or tetrahedral geometries, and structural distortions observed for specific electron configurations.

Ionic Radii

Figure 6.18.5.1 is a plot of the ionic radii of the divalent fourth-period metal ions versus atomic number. The dashed line represents the behavior predicted based on the effects of screening and variation in effective nuclear charge (Z_{eff}), assuming a spherical distribution of the 3d electrons. Because these radii are based on the structures of octahedral complexes and Cr^{2+} and Cu^{2+} do not form truly octahedral complexes, the points for these ions are shown as open circles.

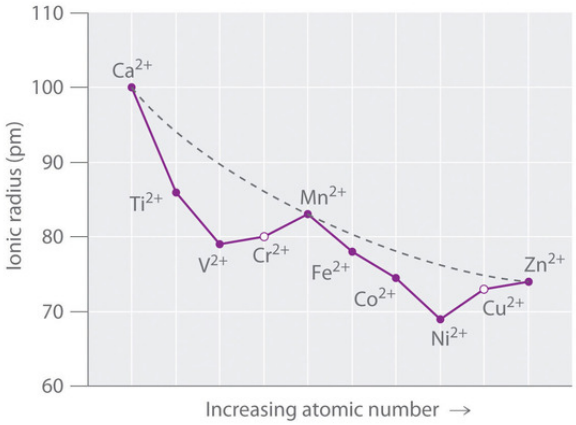


Figure 6.18.5.1: The Effect of d-Orbital Splittings on the Radii of the Divalent Ions of the Fourth-Period Metals. Only $Ca^{2+}(d^0)$, Mn^{2+} (high-spin d^5), and Zn^{2+} (d^{10}) lie on the smooth dashed curve. All other divalent ions fall below this curve because they have asymmetrical distributions of d electrons. To explain why an asymmetrical distribution of d electrons makes a metal ion smaller than expected, consider the Ti^{2+} ion, which has a d^2 configuration with both electrons in the t_{2g} orbitals. Because the t_{2g} orbitals are directed between the ligands, the two d-electrons are unable to shield the ligands from the nuclear charge. Consequently, the ligands experience a higher effective nuclear charge than predicted, the metal–ligand distance is unusually short, and the ionic radius is smaller than expected. If instead the two electrons were distributed uniformly over all five d orbitals, they would be much more effective at screening the ligands from the nuclear charge, making the metal–ligand distances longer and giving the metal a larger ionic radius.

A similar effect is observed for the V^{2+} ion, which has a d^3 configuration. Because the three electrons in the t_{2g} orbitals provide essentially no shielding of the ligands from the metal, the ligands experience the full increase of +1 in nuclear charge that occurs from Ti^{2+} to V^{2+}. Consequently, the observed ionic radius of the V^{2+} ion is significantly smaller than that of the Ti^{2+} ion.

Skipping the Cr^{2+} ion for the moment, consider the d^5 Mn^{2+} ion. Because the nuclear charge increases by +2 from V^{2+} to Mn^{2+}, Mn^{2+} might be expected to be smaller than V^{2+}. The two electrons added from V^{2+} to Mn^{2+} occupy the e_g orbitals, however, which are oriented directly toward the six ligands. Because these electrons are localized directly between the metal ion and the ligands, they are effective at screening the ligands from the increased nuclear charge. As a result, the ionic radius actually increases significantly from V^{2+} to Mn^{2+}, despite the higher nuclear charge of the latter.

The same effects are observed in the second half of the first-row transition metals. In the Fe^{2+}, Co^{2+}, and Ni^{2+} ions, the extra electrons are added successively to the t_{2g} orbitals, resulting in increasingly poor shielding of the ligands from the nuclei and in abnormally small ionic radii. Skipping over Cu^{2+}, adding the last two electrons causes a significant increase in the ionic radius of Zn^{2+}, despite its greater nuclear charge.

The Jahn–Teller Effect

Because simple octahedral complexes are not observed for the Cr^{2+} and Cu^{2+} ions, only estimated values for their radii are shown in Figure **6.18.5.1**. Since both Cr^{2+} and Cu^{2+} ions have electron configurations with an odd number of electrons in the e_g orbitals. Because the single electron (in the case of Cr^{2+}) or the third electron (in the case of Cu^{2+}) can occupy either one of two degenerate e_g orbitals, both systems have degenerate ground states. The Jahn–Teller theorem states that such non-linear systems are not stable; they undergo a distortion that makes the complex less symmetrical and splits the degenerate states, which decreases the energy of the system. The distortion and resulting decrease in energy are collectively referred to as the Jahn–Teller effect. Neither the nature of the distortion nor its magnitude is specified, and in fact, they are difficult to predict. In principle, Jahn–Teller distortions are possible for many transition-metal ions; in practice, however, they are observed only for systems with an odd number of electrons in the e_g orbitals, such as the Cr^{2+} and Cu^{2+} ions.

Consider an octahedral Cu^{2+} complex, $[Cu(H_2O)_6]^{2+}$, which is elongated along the z axis. As indicated in Figure **6.18.5.2**, this kind of distortion splits both the e_g and t_{2g} sets of orbitals. Because the axial ligands interact most strongly with the d_{z^2} orbital, the splitting of the e_g set (δ_1) is significantly larger than the splitting of the t_{2g} set (δ_2), but both δ_1 and δ_2 are much, much smaller than the Δ_o. This splitting does not change the centerpoint of the energy within each set, so a Jahn–Teller distortion results in no net change in energy for a filled or half-filled set of orbitals. If, however, the e_g set contains one electron (as in the d^4 ions, Cr^{2+} and Mn^{3+}) or three electrons (as in the d^9 ion, Cu^{2+}), the distortion decreases the energy of the system. For Cu^{2+}, for example, the change in energy after distortion is $2(-\delta_1/2) + 1(\delta_1/2) = -\delta_1/2$. For Cu^{2+} complexes, the observed distortion is always an elongation along the z axis by as much as 50 pm; in fact, many Cu^{2+} complexes are distorted to the extent that they are effectively square planar. In contrast, the distortion observed for most Cr^{2+} complexes is a compression along the z axis. In both cases, however, the net effect is the same: the distorted system is more stable than the undistorted system.

Jahn–Teller distortions are most important for d^9 and high-spin d^4 complexes; the distorted system is more stable than the undistorted one.

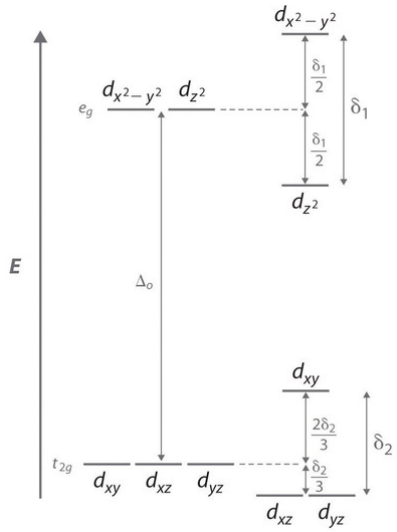


Figure **6.18.5.2**: The Jahn–Teller Effect

Increasing the axial metal–ligand distances in an octahedral d^9 complex is an example of a Jahn–Teller distortion, which causes the degenerate pair of e_g orbitals to split in energy by an amount δ_1; δ_1 and δ_2 are much smaller than Δ_o. As a result, the distorted system is more stable (lower in energy) than the undistorted complex by $\delta_1/2$.

Thermodynamic Effects

As previously noted, crystal field splitting energies (CFSEs) can be as large as several hundred kilojoules per mole, which is the same magnitude as the strength of many chemical bonds or the energy change in most chemical reactions. Consequently, CFSEs are important factors in determining the magnitude of hydration energies, lattice energies, and other thermodynamic properties of the transition metals.

Hydration Energies

The hydration energy of a metal ion is defined as the change in enthalpy for the following reaction:

$$M^{2+}_{(g)} + H_2O_{(l)} \rightarrow M^{2+}_{(aq)} \tag{6.18.5.1}$$

Although hydration energies cannot be measured directly, they can be calculated from experimentally measured quantities using thermochemical cycles. In Figure **6.18.5.3*a***, a plot of the hydration energies of the fourth-period metal dications versus atomic number forms a curve with two valleys. Note the relationship between the plot in Figure **6.18.5.3*a*** and the plot of ionic radii in Figure **6.18.5.1** the overall shapes are essentially identical, and only the three cations with spherically symmetrical distributions of d electrons (Ca^{2+}, Mn^{2+}, and Zn^{2+}) lie on the dashed lines. In Figure **6.18.5.3*a***, the dashed line corresponds to hydration energies calculated based solely on electrostatic interactions. Subtracting the CFSE values for the $[M(H_2O)_6]^{2+}$ ions from the experimentally determined hydration energies gives the points shown as open circles, which lie very near the calculated curve. Therefore, CFSEs are primarily responsible for the differences between the measured and calculated values of hydration energies.

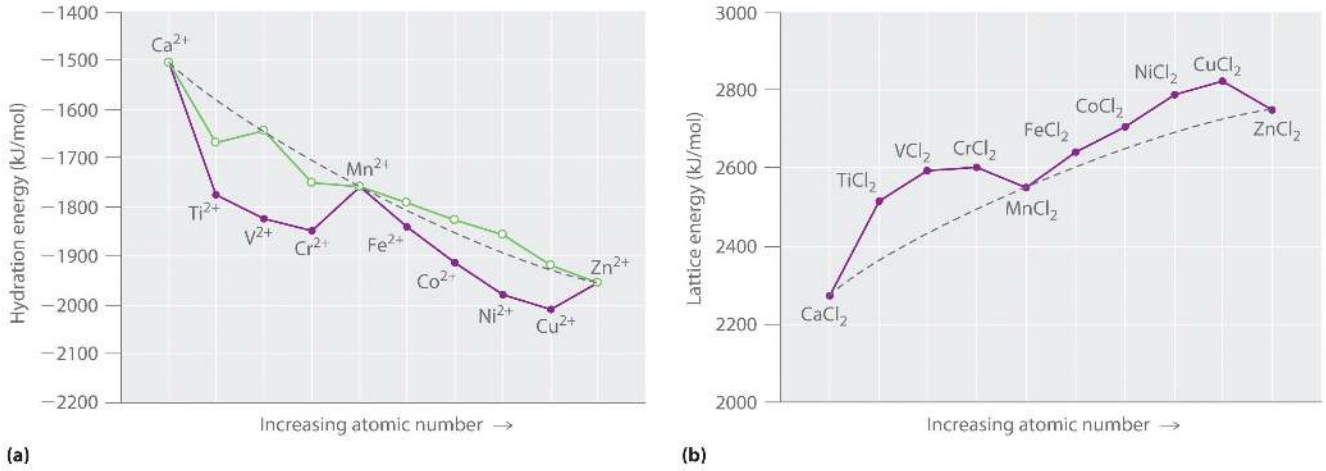


Figure **6.18.5.3**: Thermochemical Effects of d-Orbital Splittings. (a) A plot of the hydration energies of the divalent fourth-period metal ions versus atomic number (solid circles) shows large deviations from the smooth curve calculated, assuming a spherical distribution of d electrons (dashed line). Correcting for CFSE gives the points shown as open circles, which, except for Ti^{2+} and Cr^{2+}, are close to the calculated values. The apparent deviations for these ions are caused by the fact that solutions of the Ti^{2+} ion in water are not stable, and Cr^{2+} does not form truly octahedral complexes. (b) A plot of the lattice energies for the fourth-period metal dichlorides versus atomic number shows similar deviations from the smooth curve calculated, assuming a spherical distribution of d electrons (dashed lines), again illustrating the importance of CFSEs.

Lattice Energies

Values of the lattice energies for the fourth-period metal dichlorides are plotted against atomic number in part (b) of Figure **6.18.5.3**. Recall that the lattice energy is defined as the negative of the enthalpy change for the reaction below. Like hydration energies, lattice energies are determined indirectly from a thermochemical cycle.

$$M^{2+}(g) + 2Cl^-(g) \rightarrow MCl_2(s) \tag{6.18.5.2}$$

The shape of the lattice-energy curve is essentially the mirror image of the hydration-energy curve in part (a) of Figure **6.18.5.3**, with only Ca^{2+}, Mn^{2+}, and Zn^{2+} lying on the smooth curve. It is not surprising that the explanation for the deviations from the curve is exactly the same as for the hydration energy data: all the transition-metal dichlorides, except $MnCl_2$ and $ZnCl_2$, are more stable than expected due to CFSE.

Summary

Distorting an octahedral complex by moving opposite ligands away from the metal produces a tetragonal or square planar arrangement, in which interactions with equatorial ligands become stronger. Because none of the d orbitals points directly at the ligands in a tetrahedral complex, these complexes have smaller values of the crystal field splitting energy Δ_t. The crystal field stabilization energy (CFSE) is the additional stabilization of a complex due to placing electrons in the lower-energy set of d orbitals. CFSE explains the unusual curves seen in plots of ionic radii, hydration energies, and lattice energies versus atomic

number. The Jahn–Teller theorem states that a non-linear molecule with a spatially degenerate electronic ground state undergoes a geometrical distortion to remove the degeneracy and lower the overall energy of the system.

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CHAPTER OVERVIEW

Unit 7: Descriptive Chemistry

7.1: Electron Configuration of Transition Metals

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7.1: Electron Configuration of Transition Metals

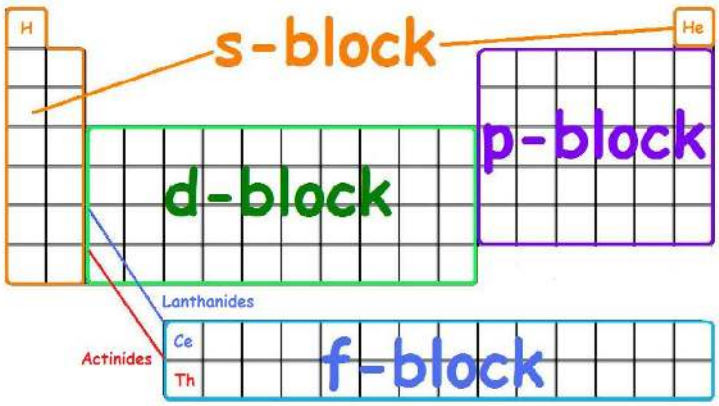
Electron configuration describes the distribution of electrons among different orbitals (including shells and subshells) within atoms and molecules.

Introduction

There are four principle orbitals (s, p, d, and f) which are filled according to the energy level and valence electrons of the element. All four orbitals can hold different number of electrons. The s-orbital can hold 2 electrons, and the other three orbitals can hold up to 6, 10, and 14 electrons, respectively. The s-orbital primarily denotes group 1 or group 2 elements, the p-orbital denotes group 13, 14, 15, 16, 17, or 18 elements, and the f-orbital denotes the Lanthanides and Actinides group. The main focus of this module however will be on the electron configuration of transition metals, which are found in the d-orbitals (d-block).

The electron configuration of transition metals is special in the sense that they can be found in numerous oxidation states. Although the elements can display many different oxidation states, they usually exhibit a common oxidation state depending on what makes that element most stable. For this module, we will work only with the first row of transition metals; however the other rows of transition metals generally follow the same patterns as the first row.

The s, p, d, and f-orbitals are identified on the periodic table below:



First Row Transition Metals

In the first row of the transition metals, the ten elements that can be found are: **Scandium (Sc), Titanium (Ti), Vanadium (V), Chromium (Cr), Manganese (Mn), Iron (Fe), Cobalt (Co), Nickel (Ni), Copper (Cu), and Zinc (Zn).**

Below is a table of the oxidation states that the transition metals can or cannot form. As stated in the boxes, the “No” indicates that the elements are not found with that oxidation state. The “Rare” signifies the oxidation states that the elements are rarely found in. Lastly, the “**Common**” identifies the oxidation states that the elements readily found in.

Oxidation States vs. First Row Transition Metals

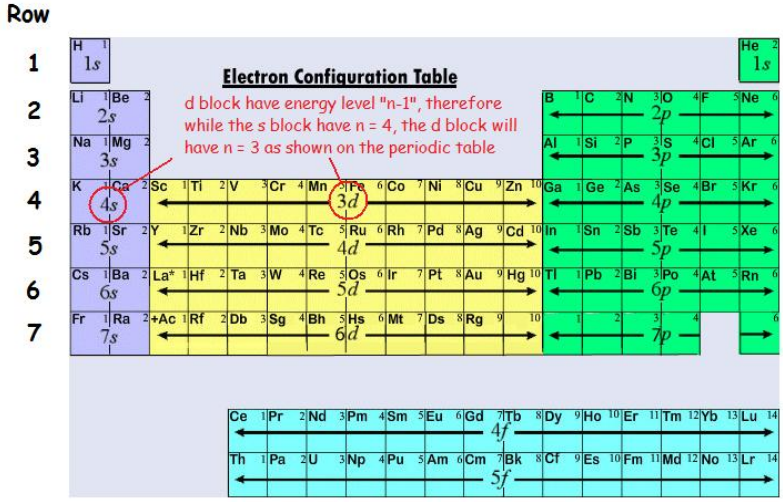
First Row Transition Metals		Oxidation States						
Element Symbol	Atomic Number	+1	+2	+3	+4	+5	+6	+7
Sc	21	No	Rare	**Common**	No	No	No	No
Ti	22	No	Rare	Rare	**Common**	No	No	No
V	23	Rare	**Common (lilac)**	**Common (green)**	**Common (blue)**	**Common (yellow)**	No	No
Cr	24	Rare	**Common**	**Common (Most stable)**	Rare	Rare	**Common**	No
Mn	25	Rare	**Common (Most stable) (pink/red)**	**Common (purple/red)**	**Common**	Rare **(blue)**	**Common (green)**	**Common (purple)**
Fe	26	Rare	**Common (ferrous)**	**Common (ferric)**	Rare	Rare	Rare	No
Co	27	Rare	**Common**	**Common**	Rare	Rare	Rare	No
Ni	28	Rare	**Common**	Rare	Rare	No	No	No
Cu	29	Rare	**Common (blue/green)**	No	No	No	No	No
Zn	30	No	**Common**	No	No	No	No	No

Filling Transition Metal Orbitals

The electron configuration for the **first row transition metals** consists of 4s and 3d subshells with an argon (noble gas) core. This only applies to the first row transition metals, adjustments will be necessary when writing the electron configuration for the other rows of transition metals. The noble gas before the first row of transition metals would be the core written with brackets around the element symbol (i.e. [Ar] would be used for the **first row** transition metals), and the electron configuration would follow a [Ar] $ns^x nd^x$ format. In the case of first row transition metals, the electron configuration would simply be [Ar] $4s^x 3d^x$. The energy level, "n", can be determined based on the periodic table, simply by looking at the row number in which the element is in. However, there is an exception for the d-block and f-block, in which the energy level, "n" for the d block is "n-1" ("n" minus 1) and for the f block is "n-2" (See following periodic table for clarification). In this case, the "x" in ns^x and nd^x is the number of electrons in a specific orbital (i.e. s-orbitals can hold up to a maximum of 2 electrons, p-orbitals can hold up to 6 electrons, d-orbitals can hold up to 10 electrons, and f-orbitals can hold up to 14 electrons). To determine what "x" is, simply count the number of boxes that you come across before reaching the element you are attempting to determine the electron configuration for.

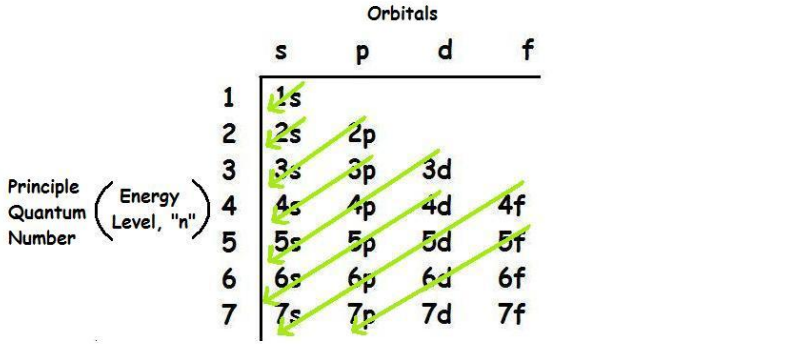
Example of Determining Energy Levels (n)

For example, if we want to determine the electron configuration for Cobalt (Co) at ground state, we would first look at the row number, which is 4 according to the periodic table below; meaning **n = 4 for the s-orbital**. In addition, since we know that the energy level for the d orbital is "n-1", therefore **n = 3 for the d-orbital** in this case. Thus, the electron configuration for Cobalt at ground state would simply be Co: [Ar] $4s^2 3d^7$. The reason why it is $3d^7$ can be explained using the periodic table. As stated, you could simply count the boxes on the periodic table, and since Cobalt is the 7th element of the first row transition metals, we get Co: [Ar] $4s^2 3d^7$.



Order of Filling the Subshells

The following image shows the order for filling the subshells:



Order: 1s 2s 2p 3s 3p 4s 3d 4p 5s 4d 5p 6s 4f 5d 6p 7s 5f 6d 7p

Transition Metals with an Oxidation State

In the ground state, the electron configuration of the transition metals follows the format, ns^2nd^x. As for the electron configuration for transition metals that are charged (i.e. Cu^+), the electrons from the s orbital will be moved to the d-orbital to form either ns^0nd^x or ns^1nd^x.

It is helpful to first write down the electron configuration of an element at its ground state before attempting to determine the electron configuration of an element with an oxidation state. See examples below.

Example 1: Vanadium

Vanadium at Ground State (Neutral):
V: 5 **d**-electrons = [Ar] $4s^2 3d^3$
Vanadium with an Oxidation State of +4:
V^{4+}: [Ar] $4s^0 3d^1$
Or you can also write it as V^{4+}: [Ar] $3d^1$

Example 2: Nickel



Above is a video showing how to write the electron configuration for Nickel (Ni) and Zirconium (Zr) from the d-block.
Nickel at Ground State:
Ni: 8 **d**-electrons = [Ar] $4s^2 3d^8$
Nickel with an Oxidation State of +2:
Ni^{2+}: [Ar] $4s^0 3d^8$
Or simply Ni^{2+}: [Ar] $3d^8$
In this example, the electron configuration for Ni^{2+} still kept its $3d^8$, but lost the $4s^2$ (became $4s^0$) because the s-orbital has the highest energy level of n = 4 in this case. Therefore, the s-orbital will lose its electrons first, before the d-orbital, and so Ni^{2+} can be written as [Ar] $4s^0 3d^8$ OR [Ar] $3d^8$.

Electron Configuration of a Second Row Transition Metal (Rhodium)

Rhodium at Ground State:

Rh: 7 **d**-electrons = [Kr] $5s^2 4d^7$

Rhodium with an Oxidation State of +3:

Rh^{3+}: [Kr] $5s^0 4d^6$

Or simply Rh^{3+}: [Kr] $4d^6$

Example 3: Osmium

Note: Osmium is stable with oxidation states of +2, +3, +4, as well as +8.
Osmium at Ground State:
Os: 6 **d**-electrons = [Xe] $6s^2 4f^{14} 5d^6$
Osmium with an Oxidation State of +2:
Os: [Xe] $4f^{14} 5d^6$
Osmium with an Oxidation State of +3:
Os: [Xe] $4f^{14} 5d^5$
For fourth row transition metals, the electron configuration is very similar to the electron configuration of the third row transition metals. However, for a fourth row transition metal, you would follow the format of [Rn] 7sx5fx6dx rather than the third row transition metal formating of [Xe] 6sx4fx5dx.

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2. Hein, et al. Introduction to General, Organic, and Biochemistry. 9th ed. Hoboken, NJ 2009.

Problems

1. What is the maximum number of electrons each orbital (s, p, d, f) can hold, respectively?
2. Write the electron configuration for Sc^{3+}.
3. Write the electron configuration for Ti^{2+}.
4. Which first row transition metal is the only element that forms an oxidation state of +7?
5. For additional practice, try to write the electron configuration of all the first row transition metals with their common oxidation states:

To see an example of an element from the second row or third row transition metals, see "Electron Configuration of a Second Row Transition Metal (Rhodium)" and "Electron Configuration of a Third Row Transition Metal (Osmium)".)

A) V^{2+} B) V^{3+} C) V^{5+} D) Cr^{2+} E) Cr^{3+} F) Cr^{6+} G) Mn^{2+} H) Mn^{3+}

I) Mn^{4+} J) Mn^{6+} K) Mn^{7+} L) Fe^{2+} M) Fe^{3+} N) Co^{2+} O) Co^{3+} P) Cu^{2+} Q) Zn^{2+}

Solutions

See File Attachment for Solutions. (You will probably need Adobe Reader to open the PDF file.)

Contributors

- Liza Chu (UCD)

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