CHEM 2101 OER



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CHEM 2101 OER

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1.1.3: Atomic Number, Mass Number and Isotopes

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1.1.4: Successes in Early Quantum Theory

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1.1.4A: Some Important Successes of Classical Quantum Theory

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1.1.4B: Bohr's Theory of the Atomic Spectrum of Hydrogen

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1.1.5: AN INTRODUCTION TO WAVE MECHANICS

- Topic hierarchy

1.1.5A: Wave Mechanics of Electrons

1.1.5B: The Uncertainty Principle

1.1.5C: The Schrödinger Wave Equation

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1.1.5A: Wave Mechanics of Electrons

All matter has intrinsic wave properties. These are described mathematically by the Schrödinger Equations and it's solutions. The wavenature of electrons and other fundamental principles (eg charge and momentum) together produce the wave mechanics of electron. The effects of electron wave mechanics are far reaching, responsible for such phenomena as electricity, emission and absorption, and bonding and hybridization.

Background

Wave-Nature of Matter

Accurate explanations of atomic natural physical chemical phenomena are dependent on energy quantization. The realization of this fundamental characteristic of matter was developed through treatment of a couple well known experiments, notably Max Planck's explanation of black body radiation and Einstein's explanation of the photoelectric effect. The conclusions of energy quantization were consolidated by Louis De Broglie as

$$\Lambda = \frac{h}{p}$$

and, by rearrangement:

$$f = \frac{E}{h}$$

On Waves

Quantum mechanically, an electron can be described by a wave function oscillating in space and time that has mean values equal to the expectation values of observables corresponding to given operators. According to the Born interpretation of quantum mechanics, the complex conjugate of this wavefunction correlates to the electron's positional probability density.

Electrons are fermions. They are charged particles. When they are confined by a potential to a limited space they display harmonics analogous to those of other wavelike phenomena. This occurs most notable in atoms and molecules. The hydrogen atom proves the most simple atomic example. The three dimensional harmonics of an electron bound within the potential energy well of a proton results in what are conventionally called orbitals. Orbitals are commonly depicted as contours of some percent of the complex conjugate of the electron's approximate wave function, though realistically without external potentials they diffuse infinitely.

A bound electron occupies higher harmonics of the bound state with increasing energy. Energy can only be increased in specific quanta as demanded for the wave function to exist. The discrete energy levels of higher harmonics correspond to higher orbitals.

Electrons can gain energy to exist in a higher orbital. When this process occurs via interaction with electromagnetic radiation, it is referred to as absorption. Similarly, the regression of an electron into a lower energy orbital results in the release of electromagnetic radiation, and is referred to as emission. Because of the quantized energy levels demanded by a bound system, electrons in a molecule or atom can only absorb or emit light at specific frequencies, which depend on the properties of the system.

Certain materials have energy level spacing such that excitation by an energy source can produce a greater number of electrons in an excited state than in the ground state. This is known as population inversion. When this happens for a transition which releases light upon relaxation, light of a specific nature is produced that has great practical importance. This light is monochromatic, and can be channeled back and forth through the medium (gain medium) and allowed only to disperse through a very narrow slit to produce monochromatic, directional, coherent light source. The apparatus is called a LASER, which is an acronym for light amplification by stimulated emission of radiation.

The inherent charge of electron incites movement of the particle in accordance to the forces described by coulomb's law. Rotational motion of a charged particle produces an electric field. The potential of an electron attraction to positive charge can

be used to store energy in chemical form. The motion of electrons by batteries or other sources through conductive media, such as copper wire can be facilitated to do work. Computer. Light.

Electronic absorption and emission within roughly 350 to 750 nm produces radiation that is in the visible spectrum. the sky is blue because of the interaction of light from the sun with electrons in atoms in the atmosphere in what's known as scattering. Scattering of this type occurs to the inverse cube of wavelength so light with shorter wavelength (blue in the visible) is scattered much more than other wavelengths. The other light passes through the atmosphere or something. maybe i have this backwards.

electrons can tunnel due to their wave nature. quantum mechanical tunneling is where a particle goes somewhere that is classically impossible, meaning that it simply did not have enough energy to to past a potential barrier, ut it did. We experts in science call this quantum weirdness. There are a lot of electrons, but perhaps not more than there are stupid people in the world. This page needs revision.

Most basic wave to satisfy boundary conditions (which are...) is

$$A\sin(n\pi x/L)$$

The superposition principle allows for the fourier theorem which allows an infinite number of such waves to be combined to form any any curve that obeys the requirements of a bound system.

Such a wave provides an accurate (nonrelativistic) description of the electron.

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2. P. W. Atkin and R. S. Friedman, Molecular Quantum Mechanics, 4th Ed. Oxford University Press, 2005.

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1.1.6: ATOMIC ORBITALS

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1.1.6A: Electronic Quantum Numbers

1.1.6B: The Radial Part of the Wave Function

1.1.6C: The Radial Distribution Function

1.1.6D: The Angular Part of the Wave Function

1.1.6E: Orbital Energies in a Hydrogen-like Species

1.1.6F: Size of Orbitals

1.1.6G: The Spin and Magnetic Spin Quantum Number's

1.1.6H: The ground state of Hydrogen

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1.1.6A: Electronic Quantum Numbers

There are four quantum numbers (n, l, m_l, m_s). No two electrons in the same atom can have the same four quantum numbers. Each quantum number describes a different aspect of the electron and its orbital. These numbers are obtained from the solution of the Schrödinger Equation for atoms in spherical coordinates.

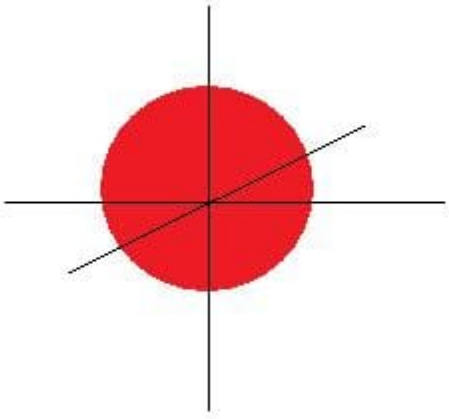
n, the principal quantum number

n tells you about the size of the orbital. It is related to how far the electron is from the atom. It is also related to the energy of the electron. n can be any positive integer number. An orbital has $n-1$radial nodes as well, which describe a radius at which the probability of finding the electron is 0.

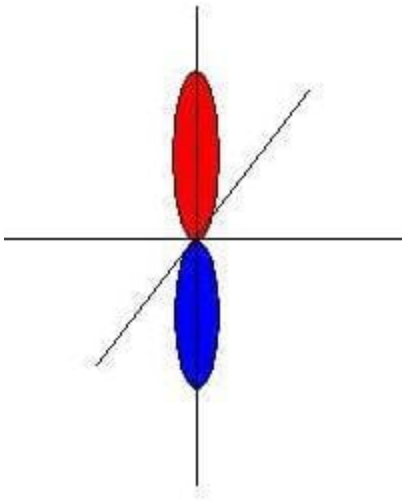
l, azimuthal quantum number

lt tells you about the angular momentum of the electron in the orbital. It defines the shape of the orbital. lt can be any integer between (and including) 0 and $(n-1)$. Each orbital has $l$planar nodes.
Some examples of orbitals with different l:

$l=0$is an s orbital, with no planar nodes.



$l=1$gives a p orbital, which has one planar node.

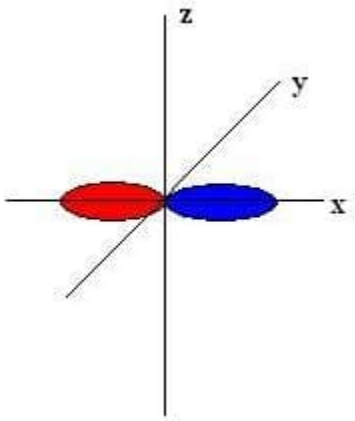


m_l, magnetic quantum number

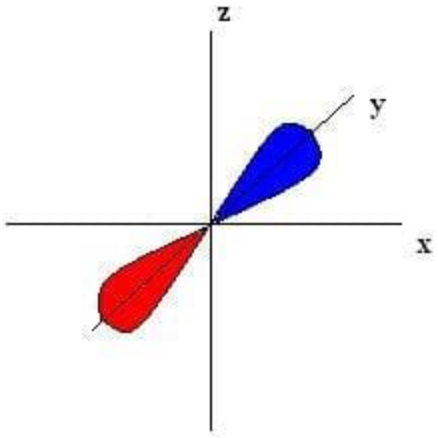
m_l tells you about the angular momentum projected on to the z axis. It tells you of the orientation of the orbital. It can be any integer between $-l$ and l.

$l = 1$ has 3 different (but degenerate) m_l possible values:-1,0 or 1.

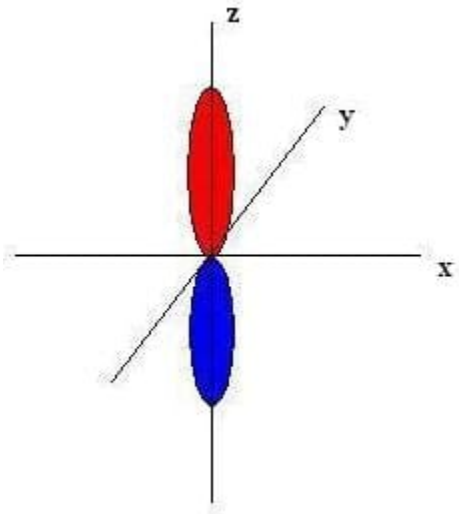
p_x



p_y



p_z



m_s spin projection quantum number

m_s tells you about the spin of the electron. An electron is a fermion, a type of quantum particle which is only allowed to have m_s equal to -1/2 or 1/2.

Pauli Exclusion Principle

The Pauli Exclusion principle states that no two identical fermions can share the same quantum state simultaneously. An electron, being a fermion, obeys this principle, so no two electrons in the same atom can have the same quantum numbers. Each orbital has space for 2 electrons, with m_s values with opposite sign. These electrons are considered spin-paired.

Energies of the Orbitals

The energies of the orbitals depend solely on n and l so there are degenerate states that result from various m_l values. For example, there are 3 p orbitals, all of which are equal in energy and therefore degenerate. Here is a table of possible quantum number arrangements and the corresponding orbitals from $n = 1$ to $n = 5$:

n	l	m_l	m_s	Orbital
1	0	0	$\pm\frac{1}{2}$	$1s$
2	0	0	$\pm\frac{1}{2}$	$2s$
2	1	±1 or 0	$\pm\frac{1}{2}$	$2p_x, 2p_y \ or \ 2p_z$
3	0	0	$\pm\frac{1}{2}$	$3s$
3	1	±1 or 0	$\pm\frac{1}{2}$	$3p_x, 3p_y \ or \ 3p_z$
3	2	$\pm2, \pm1$ or 0	$\pm\frac{1}{2}$	$3d_{z^2}, 3d_{x^2-y^2}, 3d_{xy}, 3d_{xz} \ or \ 3d_{yz}$
4	0	0	$\pm\frac{1}{2}$	$4s$
4	1	±1 or 0	$\pm\frac{1}{2}$	$4p_x, 4p_y \ or \ 4p_z$
4	2	$\pm2, \pm1$ or 0	$\pm\frac{1}{2}$	$4d_{z^2}, 4d_{x^2-y^2}, 4d_{xy}, 4d_{xz} \ or \ 4d_{yz}$
4	3	$\pm3, \pm2, \pm1$ or 0	$\pm\frac{1}{2}$	$4f_{x^3}, 4f_{y^3}, 4f_{z^3}, 4f_{x(z^2-y^2)}, 4f_{y(z^2-x^2)}, 4f_{z(x^2-y^2)} or \ 4f_{xyz}$
5	0	0	$\pm\frac{1}{2}$	$5s$
5	1	±1or 0	$\pm\frac{1}{2}$	$5p_x, 5p_y \ or \ 5p_z$
5	2	$\pm2, \pm1$ or 0	$\pm\frac{1}{2}$	$5d_{z^2}, 5d_{x^2-y^2}, 5d_{xy}, 5d_{xz} \ or \ 5d_{yz}$
5	3	$\pm3, \pm2, \pm1$ or 0	$\pm\frac{1}{2}$	$5f_{x^3}, 5f_{y^3}, 5f_{z^3}, 5f_{x(z^2-y^2)}, 5f_{y(z^2-x^2)}, 5f_{z(x^2-y^2)} or \ 5f_{xyz}$
5	4	$\pm4, \pm3, \pm2, \pm1$ or 0	$\pm\frac{1}{2}$	$5g_{z^4}, 5g_{z^3x}, 5g_{z^3y}, 5g_{z^2xy}, 5g_{z^2(x^2-y^2)}, 5g_{zx^3}, 5g_{zy^3}, 5g_{xy(x^2-y^2)} \ or 5g_{x^4+y^4}$

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Example 1.1.6A.1

How many electrons can have the quantum numbers $n = 2$ and $l = 0$? List the acceptable values for m_l and m_s for these values.

Solution

There may be 2 electrons with these quantum numbers, one with $m_l = 0$ and $m_s = \frac{1}{2}$ and the other with $m_l = 0$ and $m_s = -\frac{1}{2}$.

Example 1.1.6A.2

How many electrons can have the quantum numbers $n = 2$ and $l = 2$?

Solution

This is not a permitted value of l for $n = 2$, since the greatest acceptable value is given by $l = n - 1$.

Example 1.1.6A.3

Which set of orbitals do the quantum numbers $n = 3$ and $l = 2$describe? How many radial and planar nodes do these orbitals have?

Solution

This represents the 3d orbitals. They have 2 planar orbitals and 0 radial nodes.

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1.1.6D: The Angular Part of the Wave Function

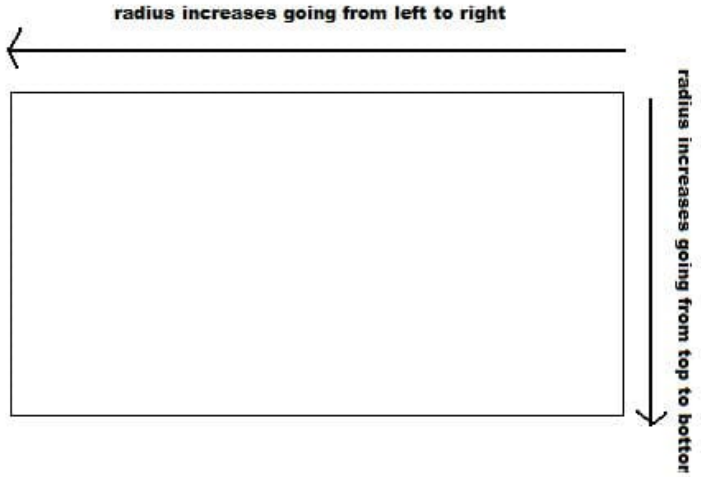
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1.1.6F: Size of Orbitals

Figure 1. General Trend of how the radius change within the Periodic Table



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1.1.6G: The Spin and Magnetic Spin Quantum Number's

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1.1.6H: The ground state of Hydrogen

Hydrogen is the simplest atoms, which only contains an electron and a proton. The ground state of hydrogen is the lowest allowed energy level and has zero angular momentum. However, it is the most stable state in which a single electron occupied the 1s atomic orbital.

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1.1.7: MANY ELECTRON ATOMS



- Topic hierarchy

1.1.7A: The Helium Atom - Two Electrons

1.1.7B: Ground State Electronic Configurations - Experimental Data

1.1.7C: Penetration and Shielding (Slater's rules)

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1.1.7A: The Helium Atom - Two Electrons

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1.1.7B: Ground State Electronic Configurations - Experimental Data

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1.1.7C: Penetration and Shielding (Slater's rules)

Learning Objective

- To quantify the shielding effect experienced by atomic electrons.

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 the impact of electron shielding, and then use that to calculate 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).

Slater's Rules

The general principle behind Slater's Rule is that the actual charge felt by an electron is equal to what you'd expect the charge to be from a certain number of protons, but minus a certain amount of charge from other electrons. Slater's rules allow you to estimate the effective nuclear charge Z_{eff} from the real number of protons in the nucleus and the effective shielding of electrons in each orbital "shell" (e.g., to compare the effective nuclear charge and shielding 3d and 4s in transition metals). Slater's rules are fairly simple and produce fairly accurate predictions of things like the electron configurations and ionization energies.

Slater's Rules

- **Step 1**: Write the electron configuration of the atom in the following form:

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

- **Step 2**: Identify the electron of interest, and ignore all electrons in higher groups (to the right in the list from Step 1). These do not shield electrons in lower groups
- **Step 3**: Slater's Rules is now broken into two cases:
  - the shielding experienced by an s- or p- electron,
    - electrons within same group shield **0.35**, except the 1s which shield **0.30**
    - electrons within the n-1 group shield **0.85**
    - electrons within the n-2 or lower groups shield **1.00**
  - the shielding experienced by n*d* or n*f* valence electrons
    - electrons within same group shield **0.35**
    - electrons within the lower groups shield **1.00**

These rules are summarized in Figure $1.1.7C.1$ and Table $1.1.7C.1$.

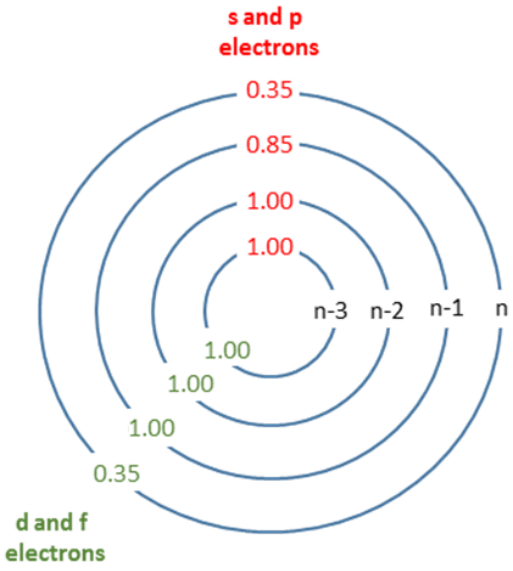


Figure $1.1.7C.1$: Graphical depiction of Slater's rules with shielding constants indicated.

Shielding happens when electrons in lower valence shells (or the same valence shell) provide a repulsive force to valence electrons, thereby "negating" some of the attractive force from the positive nucleus. Electrons really close to the atom (n-2 or lower) pretty much just look like protons, so they completely negate. As electrons get closer to the electron of interest, some more complex interactions happen that reduce this shielding.

Table $1.1.7C.1$*: Slater's Rules for calculating shielding constants*

Group	Other electrons in the same group	Electrons in group(s) with principal quantum number n and azimuthal quantum number < l	Electrons in group(s) with principal quantum number n-1	Electrons in all group(s) with principal quantum number < n-1
[1s]	0.30	-	-	-
[*n*s,*n*p]	0.35	-	0.85	1
[*n*d] or [*n*f]	0.35	1	1	1

The shielding numbers in Table $1.1.7C.1$ 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, which is outside the scope of this Module.

Calculating S

Sum together the contributions as described in the appropriate rule above to obtain an estimate of the shielding constant, S, which is found by totaling the screening by **all electrons** except the one in question.

$$S = \sum n_i S_i \tag{1.1.7C.1}$$

where

- n_i is the number of electrons in a specific shell and subshell and
- S_i is the shielding of the electrons subject to Slater's rules (Table $1.1.7C.1$)

Example 1.1.7C.1: The Shielding of 3*p* Electrons of Nitrogen Atoms

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

Given:

Nitrogen (N)

Asked for:

S, the shielding constant, for a 2*p* electron (Equation 1.1.7C.1)

Strategy:

A. Determine the electron configuration of nitrogen, then write it in the appropriate form.
B. Use the appropriate Slater Rule to calculate the shielding constant for the electron.

Step A

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

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

Step B

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

As Table 1.1.7C.1 indicates,

- the 1s electrons shield the other 2p electron to 0.85 "charges".
- the 2s and 2p electrons shield the other 2p electron equally at 0.35 "charges".

Exercise 1.1.7C.1: The Shielding of valence *p* Electrons of Bromine Atoms

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

Answer available at the end of this section.

Example 1.1.7C.2: The Shielding of 3*d* Electrons of Bromine Atoms

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

Given:

Bromine (Br)

Asked for:

S, the shielding constant, for a 3*d* electron

Strategy:

A. Determine the electron configuration of bromine, then write it in the appropriate form.
B. Use the appropriate Slater Rule to calculate the shielding constant for the electron.

Step A

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 do not contribute to the shielding constant.

Step B

$$S[3d] = 1.00(18) + 0.35(9) = 21.15$$

Exercise 1.1.7C.2: The Shielding of 3*d* Electrons of Copper Atoms

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

Answer available at the end of this section.

Calculating Effective Nuclear Charge

Previously, we described Z_{eff} as being 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:

$$S = Z - Z_{eff} \tag{1.1.7C.2}$$

Rearranging this formula to solve for Z_{eff} we obtain:

$$Z_{eff} = Z - S \tag{1.1.7C.3}$$

We can then substitute the shielding constant obtained using Equation 1.1.7C.3 to calculate an estimate of Z_{eff} for the corresponding atomic electron.

Example 1.1.7C.3: The Effective Charge of p Electrons of Boron Atoms

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

Given:

Boron (B)

Asked for:

Z_{eff} for a valence *p*- electron

Strategy:

A. Determine the electron configuration of boron and identify the electron of interest.
B. Use the appropriate Slater Rule to calculate the shielding constant for the electron.
C. Use the Periodic Table to determine the actual nuclear charge for boron.
D. Determine the effective nuclear constant.

Step A

B: $1s^2\ 2s^2\ 2p^1$. The valence p- electron in boron resides in the 2*p* subshell.

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

Step B

S[2*p*] = 1.00(0) + 0.85(2) + 0.35(2) = 2.40

Step C

Z = 5

Step D

Using Equation 1.1.7C.3,

$$\begin{aligned} Z_{eff} &= Z - S \\ &= 5 - 2.50 \\ &= 2.60 \end{aligned}$$

Exercise $1.1.7C.3$

What is the effective nuclear charge experienced by a valence d-electron in copper?

Answer available at the end of this section.

Summary

Slater's Rules can be used as a model of shielding. This permits us to quantify both the amount of shielding experienced by an electron and the resulting effective nuclear charge. Others performed better optimizations of Z_{eff} using variational Hartree-Fock methods. For example, Clementi and Raimondi published "Atomic Screening Constants from SCF Functions." J Chem Phys (1963) 38, 2686–2689.

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Answers

Exercise $1.1.7C.1$: The Shielding of valence *p* Electrons of Bromine Atoms

The electronic configuration of Bromine is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^5$

We are asked about shielding of a 4p electron so the electrons that contribute to the calculation (in a reorganized configuration)

Reorganized the configuration is ($1s^2$)($2s^2$,$2p^6$)($3s^2$,$3p^6$)($3d^{10}$)($4s^2$,$4p^4$)

$$S[4p] = \underbrace{(2 \times 1)}_{1s\text{ electrons}} + \underbrace{(8 \times 1)}_{2s\text{ and }2p\text{ electrons}} + \underbrace{(8 \times 0.85)}_{3s\text{ and }3p\text{ electrons}} + \underbrace{(10 \times 1)}_{3d\text{ electrons}} + \underbrace{(6 \times 0.35)}_{4s\text{ and }4p\text{ electrons}} = 28.9$$

Exercise $1.1.7C.2$: The Shielding of 3*d* Electrons of Copper Atoms

S = 21.15

Exercise $1.1.7C.3$

$Z_{eff} = 7.85$

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1.1.8: The Periodic Table

For the most part, the introduction to this chapter is about why inorganic chemistry tends to be more complicated to understand and learn than organic:

- Number of elements
- Variation of properties (size, DH_{IP}, DH_{EA}, c) even among similar ones
- Covalency, electrovalency and multiple valencies
- Physical state, molecular aggregation and stability range (temperature) and solubility
- Air and water stability
- Coordination number and respect for the octet rule
- s, pp-pp, pp-dp and dp-dp bonding possibilities

Much order can be introduced into this potential chaos by relating the properties of the elements to their position in the periodic table (or, as was originally done by Mendeleev et al, arranging the elements into the periodic table according to their properties.

Heavier Elements

There is little chemistry to learn about for many of the transuranium elements especially the newest (104 - 108) because of their extremely short half-lives. In some cases only one or two atoms have been made!

The rest of the chapter is divided into secions A and B which, respectively, describe the pure elements themselves and then the general group trends and non-trends.

Part A - The Nature and types of the Elements

Monatomic Elements

Includes all the noble gases and many metal vapours. The noble gases do not form bonds to each other because of their closed valence shell configuration, and the metals have their own kind of bonding which does not work in the gas phase (see below).

Diatomic Elements

These are H_2, the simplest of all neutral molecules, the halogens which also have single bonds, and N_2 and O_2 which have multiple pp-pp bonding.

Discrete (Small) Polyatomic Molecules: S_n and Se_8, P_4.

Since pp-pp bonding is not a very useful option for elements below the first short period because of core-core repulsion at useful p-bonding distances, P, S and Se can form clusters (or chains - see the next group).

Sulphur, which can form two single bonds to itself, comes in various ring sizes up to S_{20}, S_8 being the most stable ("orthorhombic" sulphur).

White phosphorus, which can form three, comes as P_4 with P-P at 2.21 Å, which is more or less normal. A particularly strained P-P, i.e. "bent" would be longer. Nevertheless, P_4 is the most reactive form of phosphorus, for example, spontaneously inflaming in air.

Boron and carbon, capable of forming 3 and 4 bonds, respectively, could have been included here too, but see below.

Elements with Extended Structures

Boron is a somewhat anomalous case because it is electron deficient. The allotropic forms of boron are all hased on the icosahedral B_{12} unit. In this unit, each boron has 5 nearest neighbours, and since the units are weakly bonded to form more extended 3-frameworks, the borons that will have more remote neighbours as well. There are nowhere near enough electrons and atomic orbitals to do this using localized 2-electron - 2-centre Lewis type bonds. As usual molecular orbital theory comes to the rescue, but the B_{12} cage alone is a rather complex system to use as an example. The topic of the boranes (boron hydrides), to be covered later, might help shed some light on how the molecular orbitals might be set up. The allotropes of crystalline boron are the most complex of the structures of the elements, and their study has been futher complicated by the presence of small (but stoichiometric) amounts of carbon or nitrogen leading to some false ones.

altThe basic icosohedral B_{12} unit

Depending on the number of bonds that they can form the following elements can form chain, sheet, or three dimensional structures:

C	P	S
Si	As	Se
Ge	Sb	Te
Sn	Bi	

"Plastic" sulphur (S_n) has a rubbery texture and is thermally unstable at room temperature with respect to conversion to S_8. Selenium also forms chains, but infinite spirals in an ordered (crystalline) structure. Tellurium is similar and the solid has semiconductor propeties.

alt

Crystalline black phosphorus has a "double sheet" structure. This structure is shared by its cogeners (members of the same group) but they are metals. Red phosporus, the other common form, contains chains of phosphorus tetrahedra.)

alt

Graphite has 2-dimensional sheets of trigonal sp^2 carbon atom arranged in aromatic six membered rings. Because of the extended delocalized orbitals, graphite is a conductor, especially parallel to the sheets.

alt

Diamond is a 3-dimensional lattice of tetrahedral sp^3 carbon atoms arranged in saturated six-membered rings all in the chair form. Diamond is an insulator.

alt

A number of additional carbon structures have been discovered quite recently. Buckmeisterfullerene C_{60}, the simplest of the "bucky balls" is shown on the right. It was discovcerd in soot. (Its shape, like an international soccer ball, is an icosahedron with all 10 corners cut off to 1/3 of the way along each edge which generates 10 new pentagonal faces and converts the old triangular ones to hexagons.) There are a number of elongated spheroidal structures and tubes capped by hemispheres known all made by cooling carbon vapour from and arc or plasma discharge. Chemists are still trying to make them do something useful!

Heats of formation for carbon forms are: Graphite, 0 ; diamond, 2.9; and C_{60}, 38.1 kJ mol^{-1}.

Metals

The structures of many metals are based on hexagonal or cubic close packing (Chapter 4 section 7), or the less efficient body-centered cubic (Fig 8-6). Figure 8-7 shows the distribution of these structures.

Metals are sometimes described as a regular array of cations immersed in a sea of valence electrons which are completely delocalized and free to roam through the entire mass. A simplified theoretical picture of this follows:

In the molecule Li_2 the bond results from overlap of the 2s orbitals each of which contains 2 electrons. The diagram below shows several representations of this:

alt

The part of the diagram on the left shows the energy levels at the observed internuclear distance marked with a vertical dotted line on the right hand diagram. A crude representation of the two molecular orbitals is also shown. (The internal spherical nodes that the 2s orbitals possess are omitted.)

The next four diagrams show orbital energies (and orbitals) for hypothetical linear molecules, Li_3, Li_4, Li_5 and $Li_¥$.

alt

Variation of orbital enery with internuclear separation for a hypothetical linear Li_3 molecule

alt.

Variation of orbital enery with internuclear separation for a hypothetical linear Li_4 molecule.

alt

Variation of orbital enery with internuclear separation for a hypothetical linear Li_5 molecule.

alt

At the left is the diagram for the hypothetical $Li_¥$. The infinite number of morse curves merge together to give the "band" shown.

Because lithium has the $2s^1$ valence shell configuration, only half of this band will be filled, and electrons can easily move into the empty orbitals accounting for the metallic conduction observed. The occupied levels/orbitals are shown by the shaded area in the diagram below:

alt

The situation described above is not real. Real crystals are three-dimensional, and in addition to the molecular orbitals formed by the atomic s-orbitals, there will be another set formed by overlap of the atomic p-orbitals. The text figures 8.8 and 8.9 are a more realistic representation.

Cohesive Energies of the Metals

See figure 8-10. Note that the main group metals have relatively low enthalpies of atomization correlating roughly with the number of valence electrons. Maxima occur at the half-filled shell after which antibonding parts of the conduction bands begin to be populated.

Part B - The Chemistry of the Elements in Relation to their Position in the Periodic Table

Hydrogen: $1s^1$

With an intermediate electronegativity and one valence electron, hydrogen might range from H+ to H- in its compounds:

- The proton (radius = 1.5×10^{-13} cm) cannot exist in condensed states (liquid or solids) because it exerts too powerful a polarizing influence on molecules near to itself. Therefore, it is always complexed, for example as H_3O^+.
- Covalent compounds are the normal situation.
- When combined with very electropositive elements e.g. Na, K, Ca it behaves as H^- (hydride ion) and is a very powerful reducing agent.

Helium ($1s^2$) and the noble gases (ns^2np^6)

- The energy necessary to make a valence state is not compensated by bond formation above krypton which forms a few flourides. The rest of the group have fairly extensive chemistry with fluorine, chlorine and oxygen.

  (The first noble gas compound, originally thought to be $Xe^{2+}[PtF_6]^{2-}$ by analogy with $[O_2]^{2+}[PtF_6]^{2-}$, was made by Bartlett in 1962. Prior to that they had been thought to be inert.)

Elements of the First Short Period (Li - F)

They are poor representatives of their groups. (The second short period elements are much better for this.) The reason is connected to their small size and lack of (empty) d-orbitals which limits their coordination number to 4 in the absence of multicentre bonding.

- To achieve their normal valencies, Be, B and C "use" a valence state where one of the 1s electrons is promoted to the p-subshell.
- "Electron deficient" Li, Be and B compounds are Lewis acids. This involves a change in hybridization. The extent to which the coordination number can be increased is limited by negative charge build-up on the acceptor.
- Li, Be and B also tend to be involved in molecules featuring 3-centre, 2 e^- bonding as a way to reduce their electron deficiency.
- N, O and (perhaps) F compounds can be Lewis bases because of the available electon pairs on these atoms. The sharing of more than one pair is opposed by positive charge build-up on the donor atom, and sometimes steric factors.
- Li^+ exists in rather few compounds because of its small size. Covalent and multicenter bonding is common e.g. the lithium alkyls.
- Be^{2+} would be even more polarizing than Li^+ so no compounds containing it exist. Covalency is the norm e.g. BeF_2 and $[Be(H_2O)_4]^{2+}$, which hydrolyses extensively to BeOH containing species.
- for Li, Be and B there is a marked similarity to the diagonally related Mg, Al and C. Although the valencies differ, the chemical behaviour such as covalency of halides or coordination chemistry tends to be somewhat similar. For example, there are close parallels between the lithium alkyls and the magnesium alkyls or between beryllium halides and the aluminium halides.
- For B, C and N, there are no (long-lived) compounds in which the elements are cationic. Covalency dominates the chemistry of these elements.
- There are compounds containing anions e.g. C_2^{2-} (acetylide) and N^{3-}, which is a major product when Mg burns in air.

- The chemistry of O and F is dominated by anion formation and covalency. Remember, O^{2-} is too strong a base to exist in water though solid compounds are known. Fluoride, F^- is only a weak base and so known in solids and aqueous solution.
- C, N and O commonly participate in multiple bonding by the use of p-orbitals. N_2 is a rather unreactive molecule because of the great strength of the triple bond. O_2 is much more reactive, partly because it is a bi-radical. F_2 is very reactive because the filled p-orbitals perpendicular to the bond repel each other.

Covalent Bonds

Covered as part of the previous section.

Elements of the Second Short Period (Na to Ar)

These elements are much more representative of the chemistry of the elements below them in their groups. This specially true for the non-metalic elements:

- The elements of this period and those below it do not tend to use their p-orbitals for π-bonding. Rather the empty d-orbitals are used if π-bonding occcurs.

  For example, aside from special sterically encumbered cases, there are few compounds containing Si=Si, P=P or S=S bonds. An example of an exception is $(CH_3)_3C\text{-}P{=}P\text{-}C(CH_3)$. $p\pi\text{-}p\pi$-bonding is not stable with respect to addition reactions: a kinetic effect.

- Multiple bonding that does occur usually involves a first short period element such as oxygen or nitrogen. Examples include Cl_3PO, SO_2 or ClO_2. Such molecules may contain $p\pi\text{-}d\pi$-bonding, and the octet rule is often violated. On the other hand, there is no analogue in silicon chemistry of O=C=O. SiO_2 is a network solid although the Si-O-Si groupings are linear which does hint and π-interactions.
- The d-obitals can be invoked to explain valence states where the coordination number exceeds 4 (and the octet is exceeded also.) Examples include PCl_5, SF_6 and IF_7. The possibility of higher coordination numbers lead also to different reactivity, e.g. CCl_4 which is inert to hydrolysis and $SiCl_4$.
- The metals differ from the first memeber of their group, e.g. sodium does not form covalent compounds, aluminum is a cation-forming metal quite unlike boron, and the coordination numbers are often 6 rather than 4 for these second row elements.

The Remainder of the Non-Transition Elements

This section contains a group-by-group summary of the properties characterizing each group and indicating, again, how the top member of each group differs. The following is list of key properties appropriate for comparisions:

1. Metallic character.
2. Properties of the oxides:
   a. Ionic *vs* covalent
   b. Acidic *vs* basic
3. Properties of the halides:
   a. Ionic *vs* molecular
   b. Ease of hydrolysis
4. General trends in electrovalence and covalence.
5. Trends in structure:
   a. Coordination numbers for discrete species
   b. Aggregation in the solid state to increase coordination number
6. Properties of the hydrides.
7. Tendency to catenate.
8. The relative importance of $p\pi\text{-}p\pi$ *vs* $p\pi\text{-}d\pi$ *vs* $d\pi\text{-}d\pi$ bonding.
9. The general strength of covalent bonding.
10. The relative importance of the lower valent states vs the hight valent states.

Group IA or 1

See text Table 8.1. The elements have chemistry dominated by the ionic 1+ state. The behaviour going down a group is well-behaved. The following decrease down a group:

a. melting points and heats of sublimation.
b. lattice energies (mostly).
c. Effective hydrated radii and hydration energies.
d. Ionization Enthalpies.

Group IIA or 2 and IIB or 12

See text Table 8.2. For group IIA (Mg, Ca, Sr, Ba and Ra) which all form the 2+ ionic state there are again well-behaved trends including those mentioned for group IA and adding:

a. Solubility of the sulphates and carbonates.
b. Thermal *instability* of the carbonates and nitrates.

which decrease going down the group. Group IIB metals (Zn, Cd and Hg) have two s-electrons outside filled d-subshells. In Zn and Cd the d-electrons do a somewhat poorer screening job than the closed shells of the group IIA so that the 2+ ions (which are more polarizing) are more inclined to form complex ions with NH_3, halides and CN^-.

Mercuric ion, Hg^{2+}, where the f-subshell also has been filled, is quite different in that it is even more inclined to form complexes. The oxidation potential for mercury is positive, whereas the others are all negative, which means that mercury metal is rather easily produced in its reactions. It also readily forms the mercurous ion, Hg_2^{2+}.

Group IIIA or 3 and IIIB or 13

See text Table 8.3. The text includes the group IIIA elements and the rest of the lanthanides among the non-transition metals because of the relative simplicity of their chemistry. They all behave as quite electropositive elements and form the 3+ ion. Scandium behaves as if it falls somewhere between aluminum and gallium in terms of its covalency. The lanthanides are so similar to each another that separation is difficult. (Cation exchange chromatography is used.)

All the group IIIB elements form compounds containing the 3+ ion, but there is a marked tendency towards covalency especially for aluminum e.g. its alkyls are volatile liquids and its chloride sublimes.

Group IIIB is the first group to clearly demonstrate the "inert pair effect". On descending the group, there is a tendency for the 1+ ions to become more and more stable. Tl^+ is more stable than Tl^{3+} and its chemistry is complicated by its redox behaviour.

(The unusual stability of Hg^0 could also be ascribed to the inert pair effect.)

Group IVB or 14

See text Table 8.4. This is the group in which the property differences between the first member, carbon, and the rest is perhaps most marked. Knowing the chemistry of carbon is almost useless for predicting the chemistry of the remaining elements! The chemistry of carbon is dominated by its extraordinary ability to catenate. While silicon can form analogues to the hydrocarbons, multiple bonding is not viable, and the Si-O bond is the important bond in silicon chemistry.

The chemistry of the group IVB elements in their IV oxidation state is predominantly covalent: $SiCl_4$ is a liquid as is $Pb(C_2H_5)_4$, the infamous anti-knock gasoline additive.

The covalent bonds generally weaken on descending the group.

The divalent state of carbon (in carbenes) is very reactive and it comes in both singlet and triplet forms. Silicon has virtually no chemistry in this state.

For the rest of the group, the II state becomes successively more stable going down the group. The "inert pair" is usually stereoactive in both molecular and solid state aggregated compounds. The M(II) compounds can never be considered truly ionic. The trend is probably associated with decreasing covalent bond strengths compared to the energy needed to obtain the valence state because the ionization potential differences are small:

$GeCl_2 + Cl_2$ alt $GeCl_4$ (Rapid at 25 ^oC)

$SnCl_2 + Cl_2$ alt $SnCl_4$ (Slow at 25 ^oC)

$PbCl_2 + Cl_2$ alt $PbCl_4$ (Does not go except at higher temperature and pressure)

$PbBr_4$ and PbI_4 cannot be made.

Group VB or 15

See text Table 8.5. The oxidation states V and III are normal for this group. Phosphorus compounds are all covalent, but the tendency towards ionic behaviour increases down the group especially for the III state, *but*, the only species that can be considered as predominantly cations are $SbO^+$and BiO^+ and Bi^{3+} in its fluoride.

Group VIB or 16

See text Table 8.6. This group is relatively well-behaved so that its features can be tablulated:

a. The 2- ions exist in salts with electropositive elements.
b. There are also anions containing one covalent bond e.g. RS^- or HS^-.
c. There are covalent compounds of type (for example) R_2E or X_2E (R is organic, X is a halogen and E is the group VIB element).
d. There are monocations of type R_3E^+
e. There are anionic ompounds where the group VI element is in the IV or VI state, and with coordination numbers 4, 5 and 6 e.g. SCl_4, SeF_5^-, TeF_6. There are stereoactive lone pairs to worry about!
f. The hydrides, H_2E decrease in stability down the group.
g. The elements themselves become gradually more metallic.
h. The tendency to form anionic complexes increases e.g. $SeBr_6^{2-}$, $TeBr_6^{2-}$ and even PoI_6^{2-}.

Group VIIB or 17

See text Table 8.7. With the elements of group IA, this group is the most well-behaved. The properties progress nicely down the group:

a. The elements all form th X^- ion and compounds with one covalent bond e.g. RX or HX.
b. Interhalogens e.g. ClF have properties somewhat intermediate between the parent dihalogens, but they are polar in the expected sense.
c. The higher oxidation states are II, V and VII.
d. There are no simple cationic ions X^+ but Br_2^+, I_2^+, Cl_3^+, Br_3^+ and several larger iodine cations have been prepared.

The Transition Elements of the d and f-Blocks

Not covered in Chem 242. (Winter 1999)

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1.1.9: THE AUFBAU PRINCIPLE



- Topic hierarchy

1.1.9A: Ground State Electronic Configurations

1.1.9B: Valence and Core Electrons

1.1.9C: Diagrammatic Representations of Electronic Configurations

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1.1.9A: Ground State Electronic Configurations

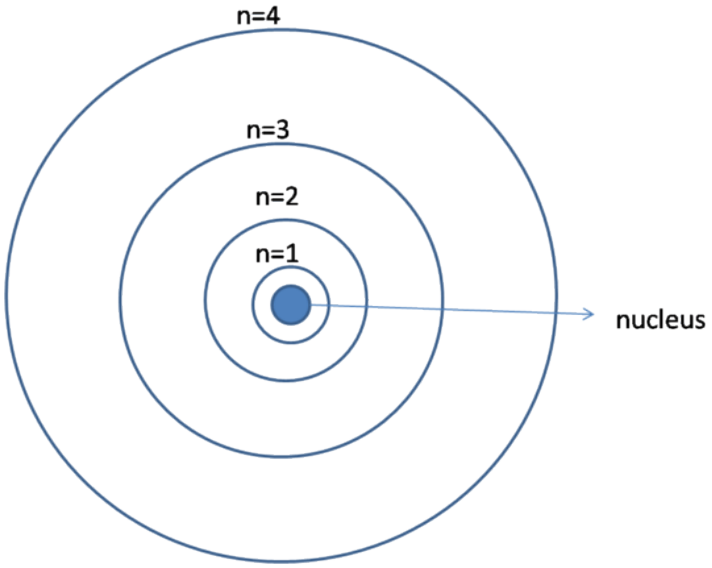
Ground state electron configurations are the foundation for understanding molecular bonding, properties, and structures. From the electrons in an atom, to the differing orbitals and hybridization, the ground state electron configuration sheds light on many different atomic properties. Fundamentally, understanding electron configuration leads to an understanding of the periodic table.

Introduction

In 1913, Niels Bohr proposed that electrons could orbit an atom at a certain distance without collapsing into the atom, and that each orbit distance had its own energy level. He proposed that each orbital's angular momentum, M, was equal to a multiple, n, of Plank's constant, h, divided by 2π. This gives the equation:

$$M = n\hbar \text{ where } \hbar = h/2\pi \text{ and } n = 1,2,3,4$$

This model proposed the Bohr atom, which shows circular orbits surrounding the nucleus.



Orbitals

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 one s orbital, three p orbitals, five d orbitals and seven f orbitals. Therefore, an s orbital can hold two electrons, a p orbital can hold six electrons, a d orbital can hold ten electrons, and an f orbital can hold 14 electrons.

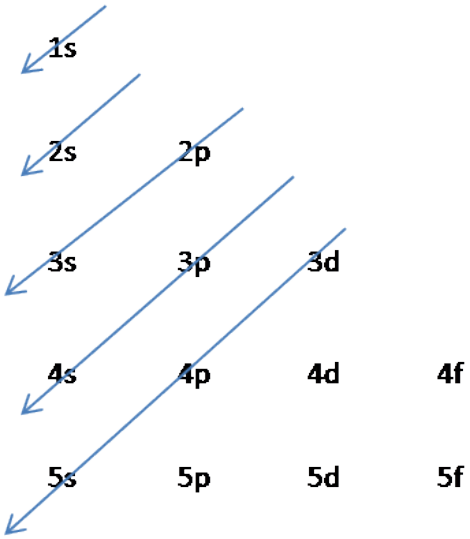
Ground State Electron Configuration

Quantum numbers

There are four quantum numbers *n, l,* m_l, and m_s. The principal quantum number *n* is a positive integer (1,2,3,4) and it represents the energy of the orbital. The angular momentum quantum number *l*, is from 0 to *n* – 1. The *l* values of 0, 1, 2, and 3 correspond to the s, p, d and f orbitals, respectively. The magnetic quantum number m_l ranges from –*l* to +*l*. This quantum number dictates the orbital orientation, such as p_x, p_y, or p_z. The quantum spin number m_s, is either +1/2 or -1/2 and it dictates the electron spin.

Aufbau Principle

The Aufbau principle states that electrons must fill lowest energy shells first.



Following the model, electrons fill the 1s orbital with two electrons, then the 2s with two electrons, then the 2p with six electrons, then the 3s with two electrons, etc.

There are some exceptions to the Aufbau Principle. This occurs mainly with electrons in the d orbital where extra stability is obtained from a half filled or fully filled d orbital. Therefore, if there are 4 electrons, or 9 electrons in the d orbital, it will move one electron from the s orbital below it to fill the extra space.

Example 1.1.9A.1: Chromium

The electron configuration of chromium

Solution

Cr's electron configuration, following the model would be: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^4 \backslash 0, but instead it is \backslash (1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$, because there is extra stability gained from the half-filled d orbital.

Hund's Rule

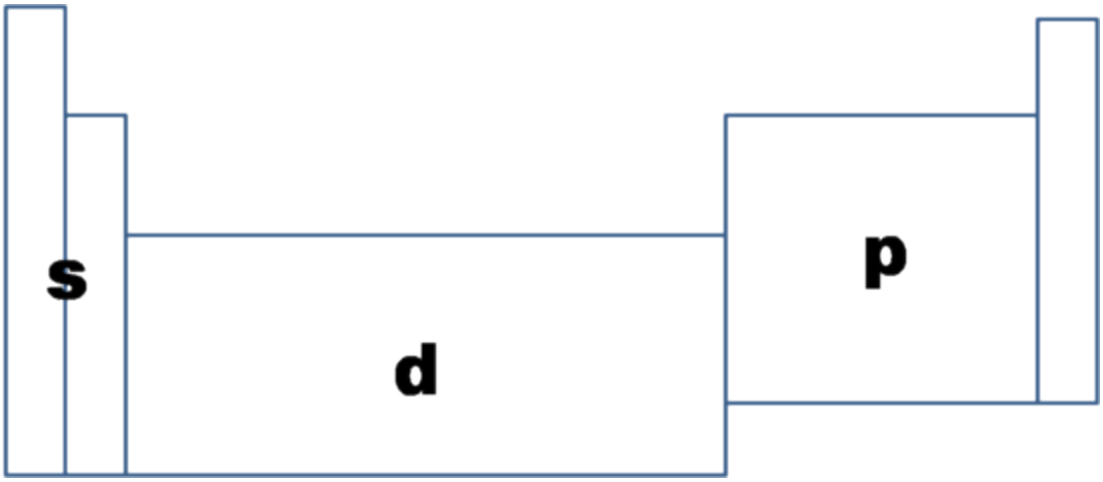
Hund's rule states that when filled sub-levels other than s orbital, electrons must not be spin paired in the orbitals until each orbital contains one electron, and no orbital can have two electrons with the same spin (m_s).

Pauli Exclusion Principle

Pauli Exclusion Principle states that no two electrons can have the same quantum numbers. An orbital can only hold 0, 1, or 2 electrons. They must have opposite spins if there are 2 electrons in the orbittal.

Periodic Trend

Valence electron shells in the periodic table follow a trend. This can be referred to as the s block, the p block, the d block and the f block (lanthanides and actinides) meaning that, in its ground state, an element in a certain "block" will have its valence electrons in the s, p, d, or f orbitals depending.

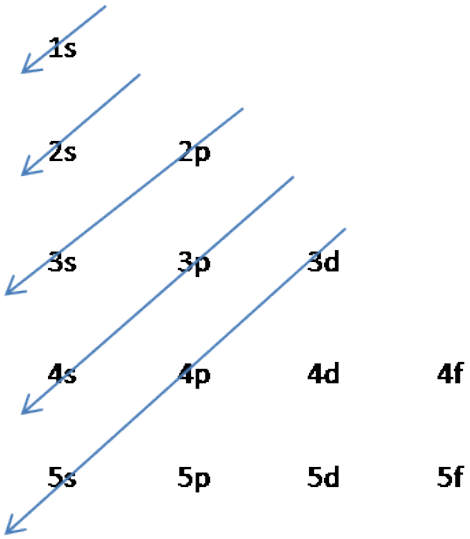


How to Write Ground State Electron Configurations

Basics

Electron configurations are written using the principal quantum number n, followed by the orbital (s, p, d, or f) with the total number of electrons written as a superscript. Example: $1s^2$ For writing ground state electron configurations, a few main steps should be followed.

1. Find the amount of electrons in the atom. Example: Na: 11 e^- Na^+: 10 e^-
2. Fill orbitals following the model until all electrons have been accounted for.



Example: Na: 11 e^- $1s^2$ $2s^2$ $2p^6$ $3s^1$ or Na^+: $1s^2$ $2s^2$ $2p^6$

3. After that, it is important to check for a nearly half-filled or filled d orbital (d^4 or d^9) and adjust accordingly by removing an electron from the s orbital beneath it.

Example 1.1.9A.2: Chromium

What is the electronic configuration of chromium

Solution

Cr: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$ **$4s^2 3d^4$** half filled orbital, s orbital beneath it

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$ **$4s^1 3d^5$**

Shorthand

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: Na: [Ne] $3s^1$

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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.

Problems

1. Write the expanded and shortened ground state electron configuration for Cl.
2. Write the expanded and shortened ground state electron configuration for Cr.
3. Write the expanded and shortened ground state electron configuration for Cu.
4. Write the expanded and shortened ground state electron configuration for Co^{2+}
5. Write the ground state electron configuration for P^{3-}

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

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

Solution 2. Expanded: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1 3d^5$

Shorthand: [Ar] $4s^1 3d^5$

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

Shorthand: [Ar] $4s^1 3d^{10}$

Solution 4. Expanded: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2 3d^5$

Shorthand: [Ar} $4s^2 3d^5$

Solution 5. $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$

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1.1.9B: Valence and Core Electrons

The electrons of an atom are typically divided into two categories: valence and core electrons. Valence electrons occupy the outermost shell or highest energy level of an atom while core electrons are those occupying the innermost shell or lowest energy levels. This difference greatly influences the role of the two types of electrons in a chemical reaction. Generally, valence electrons can participate in the formation of chemical bonding, but core electrons cannot. While core electrons are not involved in bonding, they influence the chemical reactivity of an atom.

The electron configuration of a oxygen atom is

$$\mathrm{O}: \ 1s^2 2s^2 2p^4 \tag{1.1.9B.1}$$

which may be shorted

$$\mathrm{O}: \ [He] 2s^2 2p^4 \tag{1.1.9B.2}$$

where the $[He]$ stands for the configuration of helium ($1s^2$). Similarly, the configuration of calcium with 20 electrons can be written

$$\mathrm{Ca}: \ [Ar] 4s^2 \tag{1.1.9B.3}$$

where the $[Ar]$ stands for the configuration of argon ($1s^2 2s^2 2p^6 3s^2 3p^6$). Electronic configurations that are the same as noble gases are very stable since they have a full octet (except helium with a full 1s orbital).

The $1s$ electrons in oxygen do not participate in bonding (i.e., chemistry) and are called **core electrons**. The valence electrons (i.e., the $2s^2 2p^4$ part) are **valence electrons**, which do participate in the making and breaking of bonds. Similarly, in calcium (Equation 1.1.9B.3), the electrons in the argon-like closed shell are the core electrons and the the two electrons in the 4s orbital are valence electrons.

Example $1.1.9B.1$: Cobalt

What are the core and valence electrons in cobalt?

Solution

Start by writing the electron configuration of cobalt with 27 electrons:

$$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^7$$

However, argon has the electronic structure $1s^2 2s^2 2p^2 3s^2 3p^6$, so we can rewrite the configuration as

$$[Ar] 4s^2 3d^7$$

The two electrons in the $4s$ orbital and the seven electrons in the $3d$ are the valence electrons: all others are core electrons.

The periodicity of valance electrons can be seen in the Periodic Table. Basically, the periodicity is only applied to the main group elements, while in transition metals, rules are complex.

The core electrons remain the same in the increase of group numbers in the main group elements. On the other hand, the valance electrons increase by one from left to right of a main period, and remain the same down the column of a main group. This evolution gives periodical change in property of a period, and similar chemical property of a group, which is called periodical trend. The number of valence electrons in a main period is the same as its group number. The table below shows this rule clearly.

Under construction

Figure 1: 1A + 2A are metals. 3A to 8A are non-metals.

However, this periodicity cannot be applied to the transition group, which is more complicated than that of the main group. Although the outermost electrons can be easily determined, the apparent valence electrons considered in chemical reactivity are complex and fluctuated. Electrons going into d sublevel can play either a role of valence electrons or shielding electrons. So there is not always a certain number of apparent valence electrons. The number of apparent valence electrons for the first transition metal period is shown in the table below.

Under construction

Figure 2: Valence electrons for transition metals.

Relationship with Chemical Reactivity

The chemical reactivity of an atom is mainly determined by valence electrons. Atoms which have a complete shell of valence electrons tend to be chemically inert. Atoms with one or two valence electrons are highly reactive. This phenomenon can be explained by Hund's rule, which states that orbitals that are empty, half-full, or full are more stable than those that are not. For example, Ne is chemically inert because it has two valence electrons that fill its outermost shell which makes it stable compared to atoms such as Al, which has three valence electrons, but its valence electrons does not fill its outermost shell.

Although core electrons do not take part in chemical bonding, they play a role in determining the chemical reactivity of an atom. This influence is generally due to the effect it has on valence electrons. The effect can be observed from the gradual change of chemical reactivity in a group. As you go down a group, more shells are occupied by electrons, which increases the size of the atom. The more core electron shells an atom has, the larger the size of the atom, and the farther the valence electrons are from the nucleus, thus the valence electrons will experience less effective nuclear charge and will be easily lost. For example, Na and K can both react with water, but K has a more radical reaction because it has more shells of core electrons which makes the valence electron in its outermost orbital much easier to lose than the valence electron of Na.

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1.1.9C: Diagrammatic Representations of Electronic Configurations

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1.1.10: Ionization Energies and Electron Affinities

Example of IE_1 of Magnesium: **$Mg(g) \rightarrow Mg^+(g) + e^- \ I_1 = 738$ kJ/mol**

IE_1 stands for the first ionization energy: the energy the atom requires to expel the first electron from its orbital. Similarly, the second ionization energy, will be the energy needed to expel the second electron.

$Mg^+(g) \rightarrow Mg^{2+}(g) + e^- \ I_2 = 1{,}451$ kJ/mol

However, IE_2 of Magnesium will be larger than that of IE_1 because it is not energetically favorable to separate an electron from a positively charged ion.

The general pattern of the ionization energy as they are in regard to the period table is that the IE increases across a period, and decreases down a group. Because it requires more energy to remove an electron from a stable atom, the noble gases are usually associated with the highest IE_1. Because their valence shells are already filled and stablized, they will require much more energy to disrupt that stability. The first electron that is expelled is the most loosely held to the atom.

On the other hand, the group 1 elements are usually associated with the lowest IE_1. Since only one electron occupies the valence shell of these atoms, it will be more energetically favorable for them to lose the electron in order to achieve a full orbital shell.

However, there are few exceptions. The IE1 decreases when crossing from element in group 15 to the element in group 16. The group 15 has half-filled electronic configuration ns^2 np^3. This type of configuration is very stable; it's hard to remove electron from valence shell. Therefore, element in group 15 requires greater value of IE1 than group 16. Another exception is that going from Be (group 2) to B (group 13), the IE1 decreases because Be has the filled shell $2s^2$ which is more stable than the electronic configuration of B $2s^2$ $2p^1$. Hence, Be will require more IE1 than B. Similarly, the IE1 decreases when going from elements in group 12 to group 13

Electron Affinities

Electron affinity, often abbreviated as EA, is the energy released when an electron is added to a valence shell of the atom.

$$F(g) + e^- \rightarrow F^-(g) \ EA = -328 \text{ kJ/mol}$$

[When an electron is added to an atom, energy is given off. This process is exothermic.]

Atoms like the noble gases will not gain an electron because they are already in their most stable state with a full shell. Atoms like F will most likely gain an electron because when a free electron is added to the outer shell of fluorine, it will have obtained a full shell. Generally, atoms increasing across a period will increase in EA also.

Exothermic vs endothermic process

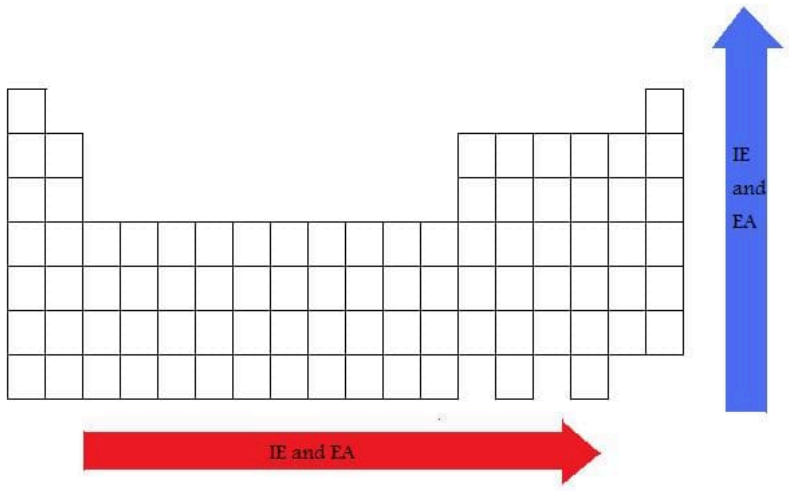
$$O(g) + e^- \rightarrow O^-(g) \ EA_1 = -141.0 \text{ kJ/mol}$$

$$O^-(g) + e^- \rightarrow O^{2-}(g) \ EA_2 = +744 \text{kJ/mol}$$

When an electron is added to an atom, the energy change is exothermic because of the attraction of the electron to the nucleus. However, in the case of EA_2 where the electron is added to an anion, the repulsion between the anion and this newly added electron will overwhelm the attraction of the electron to the nucleus. Therefore, this process will be endothermic, as opposed to EA_1.

Periodic Trend

The general trend of IE and EA along a periodic table.



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- Link to outside sources. Wikipedia entries should probably be referenced here.

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1.2: PERIODIC PROPERTIES OF ATOMS

General periodic trends are specific patterns that are present within the periodic table; these are patterns in properties like electronegativity, ionization energy, electron affinity, atomic radius, melting point, and metallic character. General periodic trends provide chemists with an invaluable tool to quickly predict an element's properties. These trends exist because of the similar atomic structure of the elements within their respective group families or periods, and because of the periodic nature of the elements. Some of the general periodic trends are described in this section.

1.2.1: Ionization energy

1.2.2: Electron Affinity

1.2.3: Covalent and Ionic Radii

References

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1.2.1: Ionization energy

Ionization energy (IE) is the energy required to **remove an electron from a neutral atom or cation in its gaseous phase**. IE is also known as *ionization potential*.

$$A_{(g)}^{n+} \longrightarrow A_{(g)}^{(n+1)+} + e^- \qquad IE = \Delta U$$

Conceptually, ionization energy is the affinity of an element for its outermost electron (an electron it already has in its valence shell).

1st, 2nd, and 3rd Ionization Energies

The symbol I_1 stands for the ***first ionization energy*** (energy required to take away an electron from a neutral atom, where $n = 0$). The symbol I_2 stands for the ***second ionization energy*** (energy required to take away an electron from an atom with a +1 charge, $n = 2$.)

- **First Ionization Energy,** I_1 (general element, A):

$$A_{(g)} \rightarrow A_{(g)}^{1+} + e^-$$

- **Second Ionization Energy,** I_2 (general element, A):

$$A_{(g)}^{1+} \rightarrow A_{(g)}^{2+} + e^-$$

- **Third Ionization Energy,** I_3 (general element, A):

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

Each succeeding ionization energy is larger than the preceding energy. This means that $I_1 < I_2 < I_3 < ... < I_n$ will always be true. For example, ionization energy increases as succeeding electrons are taken away from Mg.

$$Mg_{\,(g)} \rightarrow Mg^{+}{}_{(g)} + e^- \quad I_1 = 738\,kJ/mol$$

$$Mg^{+}{}_{(g)} \rightarrow Mg^{2+}{}_{(g)} + e^- \quad I_2 = 1451\,kJ/mol$$

Ionization energy is correlated with the strength of attraction between the positively-charged nucleus and the negatively-charged valence electrons. The higher the ionization energy, the stronger the attractive force between nucleus and valence electrons, and the more energy is required to remove a valence electron. The lower the ionization energy, the weaker the attractive force between nucleus and valence electrons, and the less energy required to remove a valence electron.

General periodic trends in electron affinity

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. The trends in **first ionization energy** are shown in Figure $1.2.1.1$ and are summarized below.

- **Across a period:** As Z* 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 I_1 of B, Al, Sc)
  - IE energy is especially low where removal of an electron results in a half-filled p or d subshell (examples include I_1 of 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*.
- **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* 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.

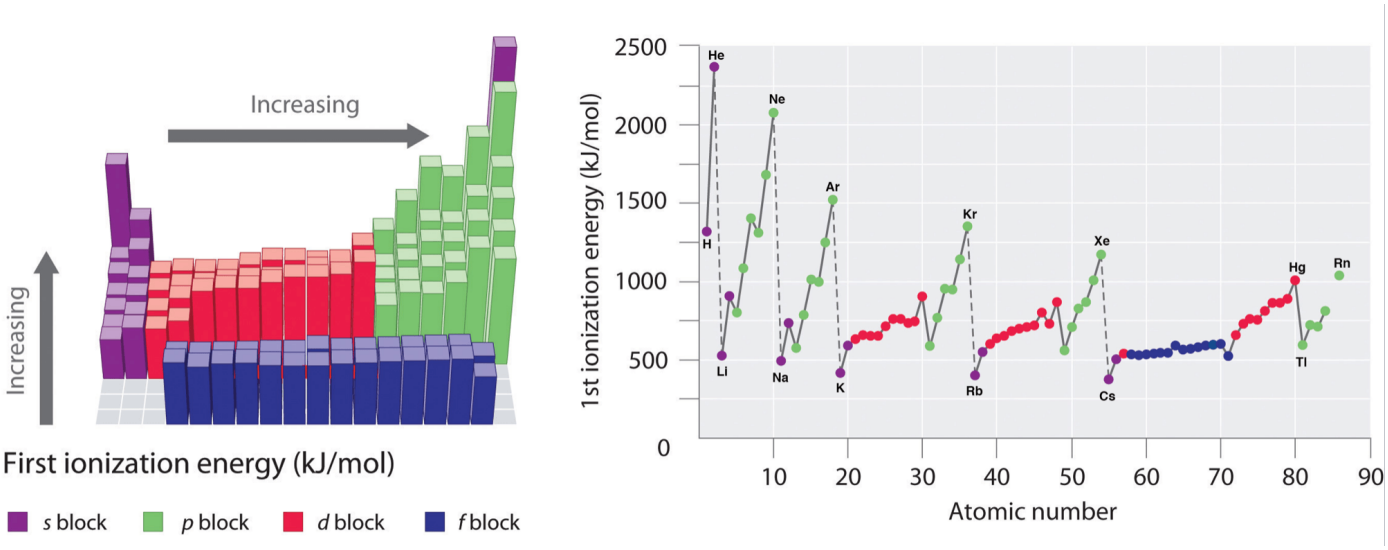


Figure 1.2.1.1: Graph showing the First Ionization Energy of the Elements. Left: ionization energies are mapped onto the periodic table, where the magnitude of ionization energy is depicted as a bar graph. Right: the first ionization energy is plotted against atomic number. In both panels the elements of the s-block are shown in purple, p-block are shown in green, d-block are shown in red, and f-block are shown in blue. (CC BY-NC-SA 3.0; anonymous)

Plots of the I_1, I_2, and I_3 of elements from hydrogen to krypton (first four periods) are shown in Figure 1.2.1.2. Notice that $I_3 > I_2 > I_1$. Also notice that trends mentioned above for I_1 hold true for subsequent ionizations when electron configurations are considered!

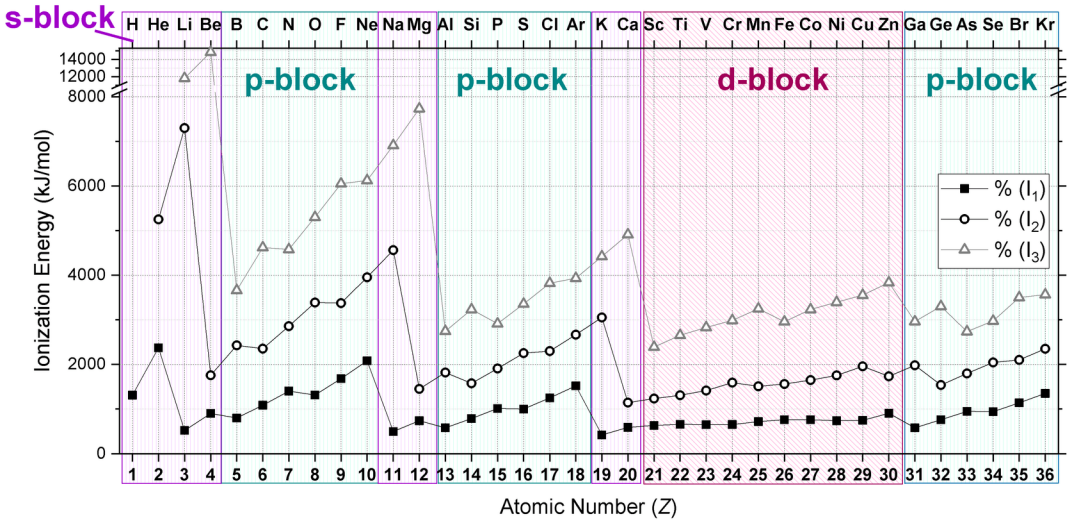


Figure 1.2.1.2. The first (I_1), second (I_2), and third (I_3) ionization energies plotted for elements with Z = 1 to 36 (H to Kr). The position of each element in its atomic form is indicated as s- p- or d-block. (CC-BY-NC-SA; Kathryn Haas)

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1.2.2: Electron Affinity

Definitions of Electron Affinity

According to IUPAC, there are two different, but equivalent, definitions of **electron affinity (EA)**.[1]

Definition: Electron Affinity defined as removal of an electron

Electron affinity can be defined as the energy *required* when an electron is removed from a gaseous anion. The reaction as shown in equation 1.2.2.1 is *endothermic* (positive ΔU) for elements except noble gases and alkaline earth metals. Under this definition, the more positive the EA value, the higher an atom's affinity for electrons.

$$A^-_{(g)} \longrightarrow A_{(g)} + e^- \qquad EA = \Delta U \tag{1.2.2.1}$$

The reaction shown in Equation 1.2.2.1 is similar those that define ionization energy. For this reason, the EA is also described as the *zeroth ionization energy*.

Definition: Electron Affinity defined as addition of an electron

An alternate and more common definition is the microscopic reverse of Equation 1.2.2.1. This more common definition states that electron affinity is the energy *released* when an electron is added to a gaseous atom, as shown in Equation 1.2.2.2. The reaction as shown in equation 1.2.2.2 is *exothermic* (negative ΔU) for elements except noble gases and alkaline earth metals. The more negative this EA value, the higher an atom's affinity for electrons.

$$A_{(g)} + e^- \longrightarrow A^-_{(g)} \qquad EA = \Delta U \tag{1.2.2.2}$$

Conceptually, this second definition is quite similar to the concept of electronegativity; but unlike electronegativity, EA is a well-defined quantitative measurement.

Trends in Electron Affinity

For this discussion, we will use the definition of EA that is consistent with it being a *zeroth ionization energy:* a more positive (larger) value means that the EA is higher (meaning stronger affinity toward an electron).

- **Across a period**: Similar to ionization energy, EA generally increases across a row of the periodic table; this observation is consistent with the increase in effective nuclear charge (Z*) 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^* 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 I_1, two units from I_2, and so on. For example, EA peaks at F, while I_1 peaks at Ne, I_2 peaks at Na, and I_3 peaks at Mg. A plot of EA for the first 13 elements is shown overlaid on plots of I_1, I_2 and I_3 in Figure 1.2.2.1., where the shifts in the peaks and valleys within each zig-zag trend are indicated.

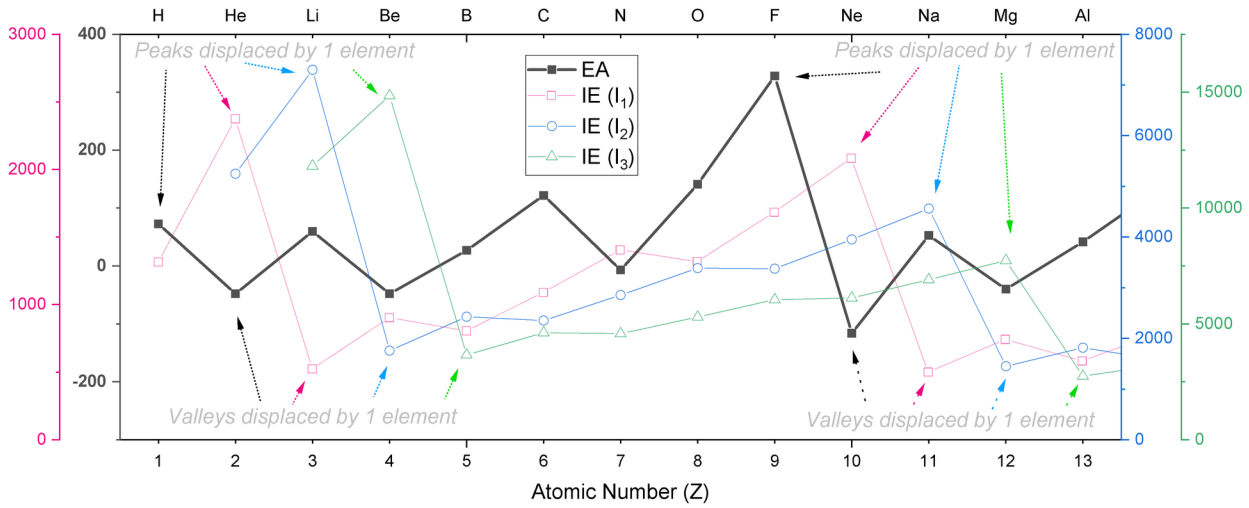


Figure 1.2.2.1. A plot of electron affinity (the zeroth ionization energy) is overlaid on plots of the first (I_1), second (I_2), and third (I_3) ionization energies. Each plot is shown using separate y-axes. Trends in EA are similar to those in ionization energies, except that the peaks and valleys 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)

Sources

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1.2.3: Covalent and Ionic Radii

Measurement of Radius

There are several methods that can be used to determine radii of atoms and ions:

- **Nonpolar atomic radii:** The radius of an atom is derived from the bond lengths within nonpolar molecules; one-half the distance between the nuclei of two atoms within a covalent bond.
- **van der Waals radius:** The radius of an atom is determined by collision with other atoms.
- **Crystal radii**: The atomic or ionic radius is determined using electron density maps from X-ray data.

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.

Regardless, measured atomic and ionic radii reveal obvious trends across the periodic table and between atoms and ions. The relative atomic sizes shown in Figure 1.2.3.1 were derived from crystallographic data.[1]

Trends in Atomic Radius

Atomic size generally decreases gradually from left to right across a period of elements. As nuclear charge (Z) increases, we expect the effective nuclear charge (Z*) of the valence electrons to also increase. Increasing Z pulls electrons closer to the nucleus. However, with each additional unit of Z, there is also an additional electron. The change in size 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.

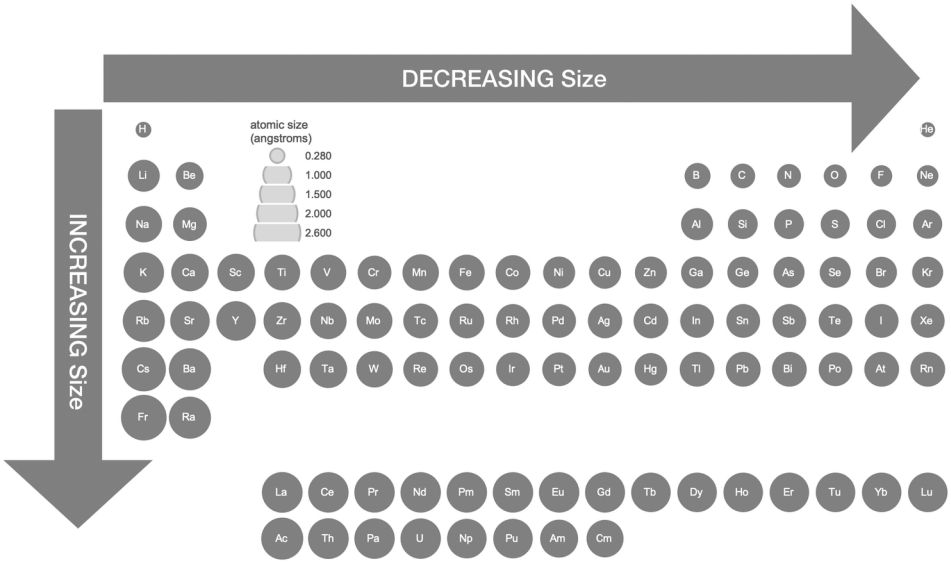


Figure 1.2.3.1. *Atomic Radii Calculated from Crystalographic Data. Data from Cordero, Beatriz, Veronica Gomez, Ana E. Platero-Prats, Marc Reves, Jorge Echeverria, Eduard Cremades, Flavia Barragan, and Santiago Alvarez. "Covalent Radii Revisited." Dalton Transactions, no. 21 (2008): 2832–38. doi:10.1039/b801115j.* (Kathryn Haas; CC-NC-BY-SA)

Trends in Ionic Radius

Trends in ionic radius follow 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 (e.g. high spin or low spin).

Cations

Compared to their atoms, cations have the same Z 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, and having a lower energy level. The result is a contraction in size from the atom to cation. Figure 1.2.3.2 visually illustrates the relative size of atoms and some cations of the first four periods; the data is available in tabular format in Figure 1.2.3.3.

Anions

Compared to their atoms, anions have the same Z 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 1.2.3.2 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 1.2.3.3.

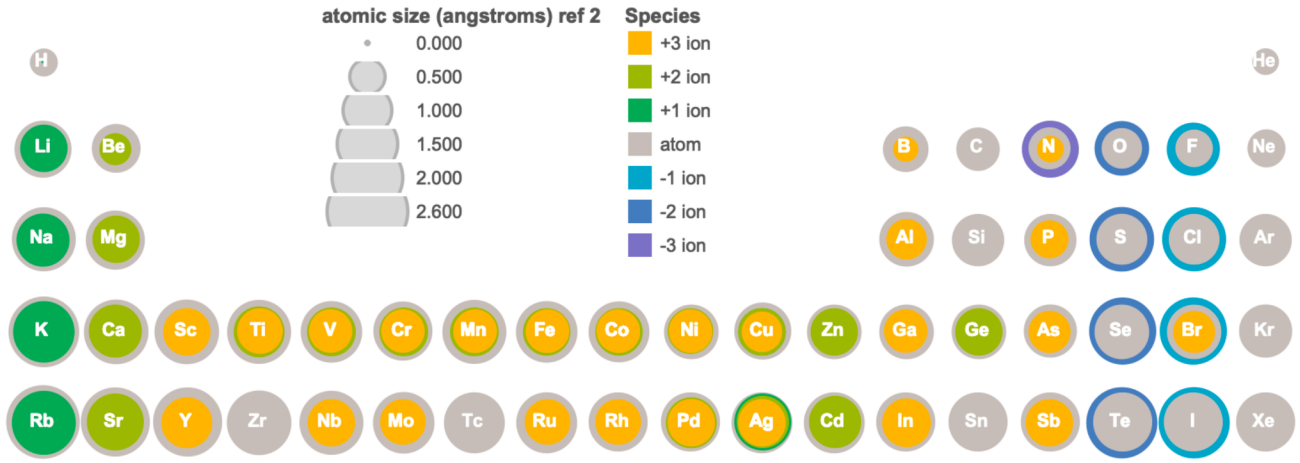


Figure 1.2.3.2. This figure illustrates relative size of atoms and ions of the first four periods of the periodic table. Atomic radius is indicated by grey circles. Radius of cations is shown in green (+1), lime (+2), and yellow (+3) circles. Radius of anions are shown as aqua (-1), blue (-2), and purple (-3) circles. Data from sources 1-3. (Kathryn Haas; CC-NC-BY-SA)

H 0.31 (atom) 0 (+1)																	He 0.28 (atom)
Li 1.28 (atom) 0.9 (+1) - -	Be 0.96 (atom) 0.41 (+2) - -											B 0.84 (atom) 0.25 (+1)	C 0.76 (atom) 0.29 (+4)	N 1.32 (-3) 0.71 (atom) 0.3 (+3) 0.27 (+5)	O 1.21 (-2) 0.66 (atom)	F 1.145 (-1) 0.57 (atom)	Ne 0.58 (atom)
Na 1.66 (atom) 1.16 (+1)	Mg 1.41 (atom) 0.86 (+2)											Al 1.21 (atom) 0.675 (+3)	Si 1.11 (atom) 0.4 (+4)	P 1.07 (atom) 0.58 (+3) 0.31 (+5)	S 1.7 (-2) 1.05 (atom) 0.51 (+4) 0.26 (+6)	Cl 1.67 (-1) 1.02 (atom)	Ar 1.06 (atom)
K 2.03 (atom) 1.52 (+1)	Ca 1.76 (atom) 1.14 (+2)	Sc 1.7 (atom) 0.885 (+3)	Ti 1.6 (atom) 1 (+2) 0.81 (+3) 0.745 (+4)	V 1.53 (atom) 0.93 (+2) 0.78 (+3) 0.72 (+4)	Cr 1.39 (atom) 0.94 (+2 hs) 0.87 (+2 ls) 0.7555 (+3) 0.69 (+4) 0.63 (+5) 0.58 (+6)	Mn 1.61 (atom) 0.97 (+2 hs) 0.81 (+2 ls) 0.785 (+3 hs) 0.72 (+3 ls) 0.67 (+4) 0.47 (+5) 0.395 (+6) 0.39 (+7)	Fe 1.52 (atom) 0.92 (+2 hs) 0.785 (+3 hs) 0.75 (+2 ls) 0.725 (+4) 0.69 (+3 ls) 0.39 (+6)	Co 1.5 (atom) 0.885 (+2 hs) 0.79 (+2 ls) 0.75 (+3 hs) 0.685 (+3 ls) 0.67 (+4 hs)	Ni 1.24 (atom) 0.83 (+2) 0.74 (+3 hs) 0.7 (+3 ls) 0.62 (+4)	Cu 1.32 (atom) 0.91 (+1, cn6) 0.87 (+2, cn6) 0.68 (+3, cn6)	Zn 1.22 (atom) 0.88 (+2)	Ga 1.22 (atom) 0.76 (+3)	Ge 1.2 (atom) 0.87 (+2) 0.67 (+4)	As 1.19 (atom) 0.72 (+3) 0.6 (+5)	Se 1.84 (-2) 1.2 (atom) 0.64 (+4) 0.56 (+6)	Br 1.82 (-1) 1.2 (atom) 0.73 (+3) 0.53 (+7) 0.45 (+5)	Kr 1.16 (atom)
Rb 2.2 (atom) 1.66 (+1)	Sr 1.95 (atom) 1.32 (+2)	Y 1.9 (atom) 1.04 (+3)	Zr 1.75 (atom) 0.86 (+4)	Nb 1.64 (atom) 0.86 (+3) 0.82 (+4) 0.78 (+5)	Mo 1.54 (atom) 0.83 (+3) 0.79 (+4) 0.75 (+5) 0.73 (+6)	Tc 1.47 (atom) 0.785 (+4) 0.74 (+5) 0.7 (+7)	Ru 1.46 (atom) 0.82 (+3) 0.76 (+4) 0.705 (+5) 0.52 (+7) 0.5 (+8)	Rh 1.42 (atom) 0.805 (+3) 0.74 (+4) 0.69 (+5)	Pd 1.39 (atom) 0.73 (+1) 1 (+2) 0.9 (+3) 0.755 (+4)	Ag 1.45 (atom) 1.29 (+1) 1.08 (+2) 0.89 (+3)	Cd 1.44 (atom) 1.09 (+2)	In 1.42 (atom) 0.94 (+3)	Sn 1.39 (atom) 0.83 (+4)	Sb 1.39 (atom) 0.9 (+3) 0.74 (+5)	Te 2.07 (-2) 1.38 (atom) 1.1 (+4) 0.7 (+6)	I 2.06 (-1) 1.39 (atom) 1.09 (+5) 0.67 (+7)	Xe 1.4 (atom) 0.62 (+8)

Figure 1.2.3.3.

This figure shows radii (in Angstroms) of atoms and ions of the first four periods of the periodic table. Radii from each element are listed from largest to smallest, ionic charge indicated in parentheses (); hs = high spin, ls = low spin, cn6 = coordination number is 6. Data from sources 1-3. (Kathryn Haas; CC-NC-BY-SA)

References

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1.3: ELEMENTS AND PERIODICITY

The elements are found in various states of matter and define the independent constituents of atoms, ions, simple substances, and compounds. Isotopes with the same atomic number belong to the same element. When the elements are classified into groups according to the similarity of their properties as atoms or compounds, the periodic table of the elements emerges. Chemistry has accomplished rapid progress in understanding the properties of all of the elements. The periodic table has played a major role in the discovery of new substances, as well as in the classification and arrangement of our accumulated chemical knowledge. The periodic table of the elements is the greatest table in chemistry and holds the key to the development of material science. Inorganic compounds are classified into molecular compounds and solid-state compounds according to the types of atomic arrangements.

1.3.1: The origin of elements and their distribution

1.3.2: Discovery of elements

1.3.3: Electronic Structure of Elements

1.3.4: Block classification of the periodic table and elements

1.3.5: Bonding states of elements

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1.3.1: The origin of elements and their distribution

All substances in the universe are made of elements. According to the current generally accepted theory, hydrogen and helium were generated first immediately after the Big Bang, some 15 billion years ago. Subsequently, after the elements below iron (Z = 26) were formed by nuclear fusion in the incipient stars, heavier elements were produced by the complicated nuclear reactions that accompanied stellar generation and decay.

In the universe, hydrogen (77 wt%) and helium (21 wt%) are overwhelmingly abundant and the other elements combined amount to only 2%. Elements are arranged below in the order of their abundance,

$$ {}^{1}_{1}H > {}^{4}_{2}He >> {}^{16}_{8}O > {}^{12}_{6}C > {}^{20}_{10}Ne > {}^{28}_{14}Si > {}^{27}_{13}Al > {}^{24}_{12}Mg > {}^{56}_{26}Fe $$

The **atomic number** of a given element is written as a left subscript and its **mass numbe**r as a left superscript.

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1.3.2: Discovery of elements

The long-held belief that all materials consist of atoms was only proven recently, although elements, such as carbon, sulfur, iron, copper, silver, gold, mercury, lead, and tin, had long been regarded as being atom-like. Precisely what constituted an element was recognized as modern chemistry grew through the time of alchemy, and about 25 elements were known by the end of the 18th century. About 60 elements had been identified by the middle of the 19th century, and the periodicity of their properties had been observed.

The element technetium (Z = 43), which was missing in the periodic table, was synthesized by nuclear reaction of Mo in 1937, and the last undiscovered element promethium (Z = 61) was found in the fission products of uranium in 1947. Neptunium (Z = 93), an element of atomic number larger than uranium (Z = 92), was synthesized for the first time in 1940. There are 103 named elements. Although the existence of elements Z = 104-111 has been confirmed, they are not significant in inorganic chemistry as they are produced in insufficient quantity.

All trans-uranium elements are radioactive, and among the elements with atomic number smaller than Z = 92, technetium, prometium, and the elements after polonium are also radioactive. The half-lives (refer to Section 7.2) of polonium, astatine, radon, actinium, and protoactinium are very short. Considerable amounts of technetium ^{99}Tc are obtained from fission products. Since it is a radioactive element, handling ^{99}Tc is problematic, as it is for other radioactive isotopes, and their general chemistry is much less developed than those of manganese and rhenium in the same group.

Atoms are equivalent to alphabets in languages, and all materials are made of a combination of elements, just as sentences are written using only 26 letters.

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1.3.3: Electronic Structure of Elements

Wave functions of electrons in an atom are called atomic orbitals. An atomic orbital is expressed using three quantum numbers; the principal quantum number, n; the azimuthal quantum number, l; and the magnetic quantum number, m_{ell}. For a principal quantum number n, there are n azimuthal quantum numbers l ranging from 0 to n-1, and each corresponds to the following orbitals.

$$\ell : 0, 1, 2, 3, 4, \ldots$$
$$s, p, d, f, g, \ldots$$

An atomic orbital is expressed by the combination of n and l. For example, n is 3 and l is 2 for a 3d orbital. There are 2l+1 m $_{ell}$ values, namely l, l-1, l-2,..., -l. Consequently there are one s orbital, three p orbitals, five d orbitals and seven f orbitals. The three aforementioned quantum numbers are used to express the distribution of the electrons in hydrogen-type atom, and another quantum number m_s (1/2, -1/2) which describes the direction of an electron spin is necessary to completely describe an electronic state. Therefore, an electronic state is defined by four quantum numbers (n, l, m_{ell}, m_s).

The wave function ψ which determines the orbital shape can be expressed as the product of a radial wavefunction R and an angular wave function Y as follows.

$$\psi_{n,l,m_l} = R_{n,l}(r)Y_{l,m_l}(\theta, \phi)$$

R is a function of distance from the nucleus, and Y expresses the angular component of the orbital. Orbital shapes are shown in Figure 1.3.3.1. Since the probability of the electron's existence is proportional to the square of the wave function, an electron density map resembles that of a wave function. The following conditions must be satisfied when each orbital is filled with electrons.

[The conditions of electron filling]

Pauli principle

The number of electrons that are allowed to occupy an orbital must be limited to one or two, and, for the latter case, their spins must be anti-parallel (different direction).

Hund's rule

When there are equal-energy orbitals, electrons occupy separate orbitals nd their spins are parallel (same direction).

The order of orbital energy of a neutral atom is

$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p \ldots$$

and the electron configuration is determined as electrons occupy orbitals in this order according to the Pauli principle and Hund's rule. An s orbital with one m_{ell} can accommodate 2 electrons, a p orbital with three m_{ell} 6 electrons, and a d orbital with five m_{ell} 0 electrons.

Exercise 1.3.3.1

Describe the electron configuration of a C atom, an Fe atom, and a Au atom.

Answer available at the end of this section.

Answers

Exercise 1.3.3.1

Electrons equal to the atomic number are arranged in the order of orbital energies. Since the electrons inside the valence shell take the rare gas configuration, they may be denoted by the symbol of a rare gas element in brackets.

$$C : 1s^2 2s^2 2p^2 \quad or \quad [He]2s^2 2p^2$$
$$Fe : 1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2 \quad or \quad [Ar]3d^6 4s^2$$
$$Au : 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^1 \quad or \quad [Xe]4f^{14} 5d^{10} 6s^1$$

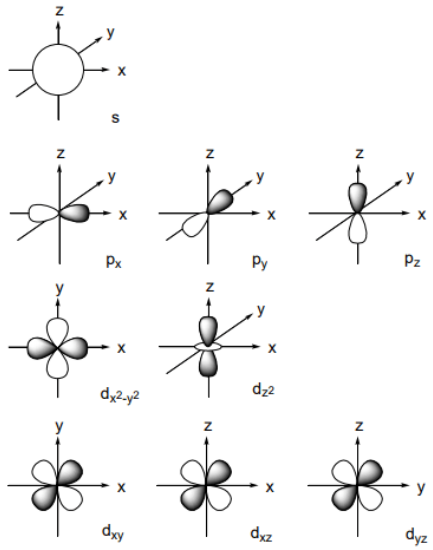


Figure 1.3.3.1: - Shapes of s, p, and d orbitals.

Table 1.3.3.1 *Periodic table of elements. The values are atomic weights*

	1	2	3	4	5	6	7	8	9
1	1.008 $_{1}$H								
2	6.941 $_{3}$Li	9.012 $_{4}$Be							
3	22.99 $_{11}$Na	24.31 $_{12}$Mg							
4	39.10 $_{19}$K	40.08 $_{20}$Ca	44.96 $_{21}$Sc	47.87 $_{22}$Ti	50.94 $_{23}$V	52.00 $_{24}$Cr	54.94 $_{25}$Mn	55.85 $_{26}$Fe	58.93 $_{27}$Co
5	85.47 $_{37}$Rb	87.62 $_{38}$Sr	88.91 $_{39}$Y	91.22 $_{40}$Z	92.91 $_{41}$Nb	95.94 $_{42}$Mo	(99) $_{43}$Tc	101.1 $_{44}$Ru	102.9 $_{45}$Rh
6	132.9 $_{55}$Cs	137.3 $_{56}$Ba	Lanthanoid	178.5 $_{72}$Hf	180.9 $_{73}$Ta	183.8 $_{74}$W	186.2 $_{75}$Re	190.2 $_{76}$Os	192.2 $_{77}$Ir
7	(223) $_{87}$Fr	(226) $_{88}$Ra	Actinoid						
Lanthan-oid			138.9 $_{57}$La	140.1 $_{58}$Ce	140.9 $_{59}$Pr	144.2 $_{60}$Nd	(145) $_{61}$Pm	150.4 $_{62}$Sm	152.0 $_{63}$Eu
Actinoid			(227) $_{89}$Ac	232.0 $_{90}$Th	231.0 $_{91}$Pa	238.0 $_{92}$U	(237) $_{93}$Np	(239) $_{94}$Pu	(243) $_{95}$Am

10	11	12	13	14	15	16	17	18
								4.003 $_{2}$He
			10.81 $_{5}$B	12.01 $_{6}$C	14.01 $_{7}$N	16.00 $_{8}$O	19.00 $_{9}$F	20.18 $_{10}$Ne
			26.98 $_{13}$Al	28.09 $_{14}$Si	30.97 $_{15}$P	32.07 $_{16}$S	35.45 $_{17}$Cl	39.95 $_{18}$Ar
58.69 $_{28}$Ni	63.55 $_{29}$Cu	65.39 $_{30}$Zn	69.72 $_{31}$Ga	72.61 $_{32}$Ge	74.92 $_{33}$As	78.96 $_{34}$Se	79.90 $_{35}$Br	83.80 $_{36}$Kr
106.4 $_{46}$Pd	107.9 $_{47}$Ag	112.4 $_{48}$Cd	114.8 $_{49}$In	118.7 $_{50}$Sn	121.8 $_{51}$Sb	127.6 $_{52}$Te	126.9 $_{53}$I	131.3 $_{54}$Xe
195.1 $_{78}$Pt	197.0 $_{79}$Au	200.3 $_{80}$Hg	204.4 $_{81}$Tl	207.2 $_{82}$Pb	209.0 $_{83}$Bi	(210) $_{84}$Po	(210) $_{85}$At	(222) $_{86}$Rn
157.3 $_{64}$Gd	158.9 $_{65}$Tb	162.5 $_{66}$Dy	164.9 $_{67}$Ho	167.3 $_{68}$Er	168.9 $_{69}$Tm	173.0 $_{70}$Yb	175.0 $_{71}$Lu	
(247) $_{96}$Cm	(247) $_{97}$Bk	(252) $_{98}$Cf	(252) $_{99}$Es	(257) $_{100}$Fm	(258) $_{101}$Md	(259) $_{102}$No	(262) $_{103}$Lr	

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1.3.4: Block classification of the periodic table and elements

Starting from hydrogen, over 100 elements are constituted as electrons are successively accommodated into 1s, 2s, 2p, 3s, 3p, 4s, and 3d orbitals one by one from lower to higher energy levels. When elements with similar properties are arranged in columns, the periodic table of the elements is constructed. The modern periodic table of the elements is based on one published by D. I. Mendeleev in 1892, and a variety of tables have since been devised. The long periodic table recommended by IUPAC is the current standard, and it has the group numbers arranged from Group 1 alkali metals through Group 18 rare gas elements (Table 1.3.4.1).

Based on the composition of electron orbitals, hydrogen, helium and Group 1 elements are classified as s-block elements, Group 13 through Group 18 elements p-block elements, Group 3 through Group 12 elements d-block elements, and lanthanoid and actinoid elements f-block elements. (Figure 1.3.4.2). s-Block, p-block, and Group 12 elements are called main group elements and d-block elements other than Group 12 and f-block elements are called transition elements. The characteristic properties of the elements that belong to these four blocks are described in Chapter 4 and thereafter. Incidentally, periodic tables that denote the groups of s-block and p-block elements with Roman numerals (I, II,..., VIII) are still used, but they will be unified into the IUPAC system in the near future. Since inorganic chemistry covers the chemistry of all the elements, it is important to understand the features of each element through reference to the periodic table.

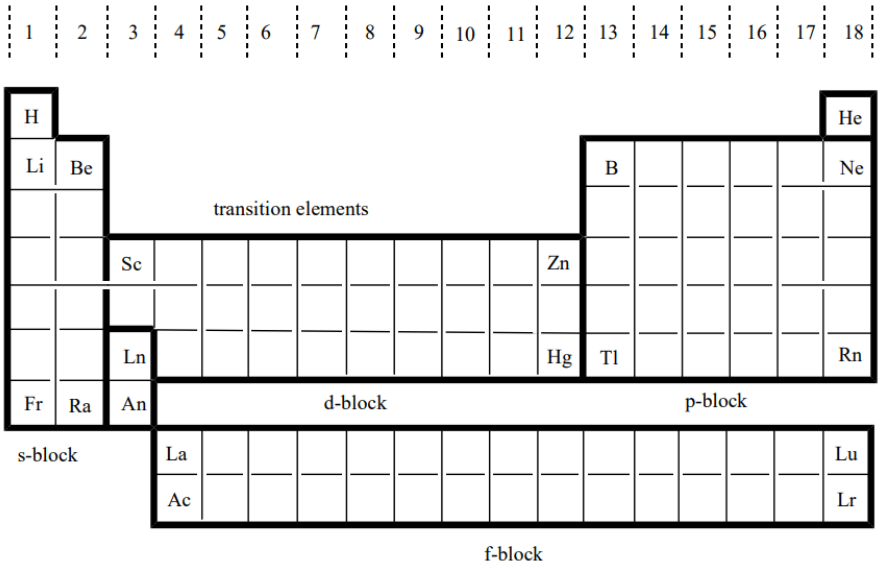


Figure 1.3.4.2: - Block classification of elements in the periodic table.

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1.3.5: Bonding states of elements

Organic compounds are molecular compounds that contain mainly carbon and hydrogen atoms. Since inorganic chemistry deals with all compounds other than organic ones, the scope of inorganic chemistry is vast. Consequently, we have to study the syntheses, structures, bondings, reactions, and physical properties of elements, molecular compounds, and solid-state compounds of 103 elements. In recent years, the structures of crystalline compounds have been determined comparatively easily by use of single crystal X-ray structural analysis, and by through the use of automatic diffractometers. This progress has resulted in rapid development of new areas of inorganic chemistry that were previously inaccessible. Research on higher dimensional compounds, such as multinuclear complexes, cluster compounds, and solid-state inorganic compounds in which many metal atoms and ligands are bonded in a complex manner, is becoming much easier. In this section, research areas in inorganic chemistry will be surveyed on the basis of the classification of the bonding modes of inorganic materials.

Element

Elementary substances exist in various forms. For example, helium and other rare gas elements exist as single-atom molecules; hydrogen, oxygen, and nitrogen as two-atom molecules; carbon, phosphorus, and sulfur as several solid allotropes; and sodium, gold, etc. as bulk metals. A simple substance of a metallic element is usually called bulk metal, and the word “metal” may be used to mean a bulk metal and “metal atom or metal ion” define the state where every particle is discrete. Although elementary substances appear simple because they consist of only one kind of element, they are rarely produced in pure forms in nature. Even after the discovery of new elements, their isolation often presents difficulties. For example, since the manufacture of ultra high purity silicon is becoming very important in science a purification processes have been developed in recent years.

Exercise 1.3.5.2

Give examples of allotropes.

Answer available at the end of this section.

Molecular compounds

Inorganic compounds of nonmetallic elements, such as gaseous carbon dioxide CO_2, liquid sulfuric acid H_2SO_4, or solid phosphorus pentoxide P_2O_5, satisfy the valence requirements of the component atoms and form discrete molecules which are not bonded together. The compounds of main group metals such as liquid tin tetrachloride $SnCl_4$ and solid aluminum trichloride $AlCl_3$ have definite molecular weights and do not form infinite polymers.

Most of the molecular compounds of transition metals are metal complexes and organometallic compounds in which ligands are coordinated to metals. These molecular compounds include not only **mononuclear complexes** with a metal center but also multinuclear complexes containing several metals, or cluster complexes having metal-metal bonds. The number of new compounds with a variety of bonding and structure types is increasing very rapidly, and they represent a major field of study in today' inorganic chemistry (see Chapter 6).

Solid-state compounds

Although solid-state inorganic compounds are huge molecules, it is preferable to define them as being composed of an infinite sequence of 1-dimensional (chain), 2-dimensional (layer), or 3-dimensional arrays of elements and as having no definite molecular weight. The component elements of an inorganic solid bond together by means of ionic, covalent, or metallic bonds to form a solid structure. An ionic bond is one between electronically positive (alkali metals etc.) and negative elements (halogen etc.), and a covalent bond forms between elements with close electronegativities. However, in many compounds there is contribution from both ionic and covalent bonds (see Section 2.1 about bondings).

Exercise 1.3.5.3

Give examples of solid-state inorganic compounds.

Answer available at the end of this section.

The first step in the identification of a compound is to know its elemental composition. Unlike an organic compound, it is sometimes difficult to decide the empirical formula of a solid-state inorganic compound from elemental analyses and to determine its structure by combining information from spectra. Compounds with similar compositions may have different coordination numbers around a central element and different structural dimensions. For example, in the case of binary (consisting of two kinds of elements) metal iodides, gold iodide, AuI, has a chain-like structure, copper iodide, CuI, a zinc blende type structure, sodium iodide, NaI, has a sodium chloride structure, and cesium iodide, CsI, has a cesium chloride structure (refer to Section 2.2 (e)), and the metal atoms are bonded to 2, 4, 6 or 8 iodine atoms, respectively. The minimum repeat unit of a solid structure is called a **unit lattice** and is the most fundamental information in the structural chemistry of crystals. X-ray and neutron diffraction are the most powerful experimental methods for determining a crystal structure, and the bonds between atoms can only be elucidated by using them. **Polymorphism** is the phenomenon in which different kinds of crystals of a solid-state compound are obtained in which the atomic arrangements are not the same. Changes between different polymorphous phases with variations in temperature and/or pressure, or **phase transitions**, are an interesting and important problem in solid-state chemistry or physics.

We should keep in mind that in solid-state inorganic chemistry the elemental composition of a compound are not necessarily integers. There are extensive groups of compounds, called nonstoichiometric compounds, in which the ratios of elements are non-integers, and these non-stoichiometric compounds characteristically display conductivity, magnetism, catalytic nature, color, and other unique solid-state properties. Therefore, even if an inorganic compound exhibits non-integral stoichiometry, unlike an organic compound, the compound may be a thermodynamically stable, orthodox compound. This kind of compound is called a non-stoichiometric compound or Berthollide compound, whereas a stoichiometric compound is referred to as a Daltonide compound. The law of constant composition has enjoyed so much success that there is a tendency to neglect non-stoichiometric compounds. We should point out that groups of compounds in which there are slight and continuous changes of the composition of elements are not rare.

Problem 1.1

Express the isotopes of hydrogen, carbon, and oxygen using the symbols of the elements with atomic and mass numbers and write the number of protons, neutrons, and electrons in parenthesis.

Superheavy elements

The last element in the ordinary periodic table is an actinoid element lawrencium, Lr, (Z = 103). However, elements (Z = 104 – 109) "have already been synthesized" in heavy ion reactions using nuclear accelerators. These are 6d elements which come under the 5d transition elements from hafnium, Hf, to iridium, Ir, and it is likely that their electronic structures and chemical properties are similar. As a matter of fact, only the existence of **nuclides** with very short lives has been confirmed. The trouble of naming the super heavy elements is that the countries of their discoverers, the United States, Russia and Germany, have proposed different names. The tentative names of these elements are: unnilquadium Une (Z = 104), unnilpentium Unp (Z = 105), unnilhexium Unh (Z = 106), unnilseptium Unq (Z = 107), unniloctium Uno (Z = 108) and unnilennium Une (Z = 108). It has recently been settled that they be named: Rutherfordium $_{104}$Rf, Dubnium $_{105}$Db, Seaborgium $_{106}$Sg, Bohrium $_{107}$Bh, Hassium $_{108}$Hs, and Meitnerium $_{109}$Mt.

"Synthesis" of the element (Z = 110), which should come under platinum, was considered the technical limit, but there is a recent report that even the element (Z = 112) "was synthesized". In any case, the superheavy elements will run out shortly. It is natural that complications are caused by naming of a new element a scientist to have a new element named after him or her.

Answers

Exercise 1.3.5.2

- Carbon: graphite, diamond.
- Phosphorus: white phosphorus, red phosphorus.

Exercise 1.3.5.3

- Sodium chloride NaCl
- Silicon dioxide, SiO_2
- Molybdenum disulfide, MoS_2

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2: CHEM 2101 TOPIC 2- BONDING

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2.1.1.2: Breaking the octet rule with higher electron counts (hypervalent atoms)

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2.1: SIMPLE BONDING THEORY

2.1.1: Lewis Electron-Dot Diagrams

2.1.1.1: Resonance

2.1.1.2: Breaking the octet rule with higher electron counts (hypervalent atoms)

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2.1.5.P: Problems

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2.1.1: 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.

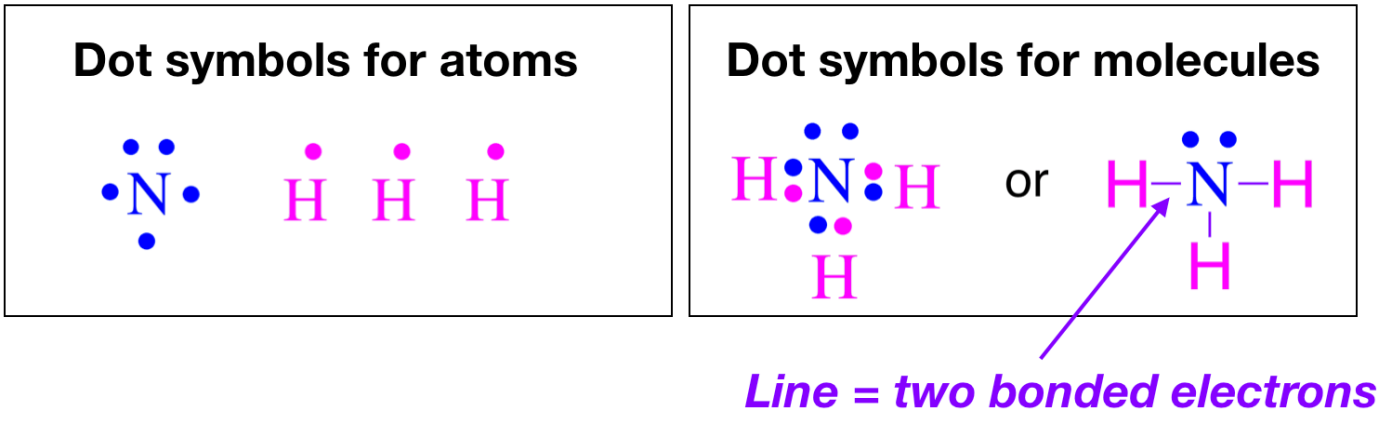


Figure 2.1.1.1: Lewis dot structure of atoms comprising ammonia and the dot structure of the molecule. (Kathryn Haas; CC-NC-BY-SA)

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 3.1.1. 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. You should get out an actual piece of paper (I know...just do it. It's good for you.) and a writing tool and try to complete each problem before checking the answer.

Exercise 2.1.1.1

Draw the Lewis structures for H_2O, CO_2, and N_2.

Answer available at the end of this section.

Exercise 2.1.1.2

Draw the Lewis structures for H_2, BH_3 and BF_3.

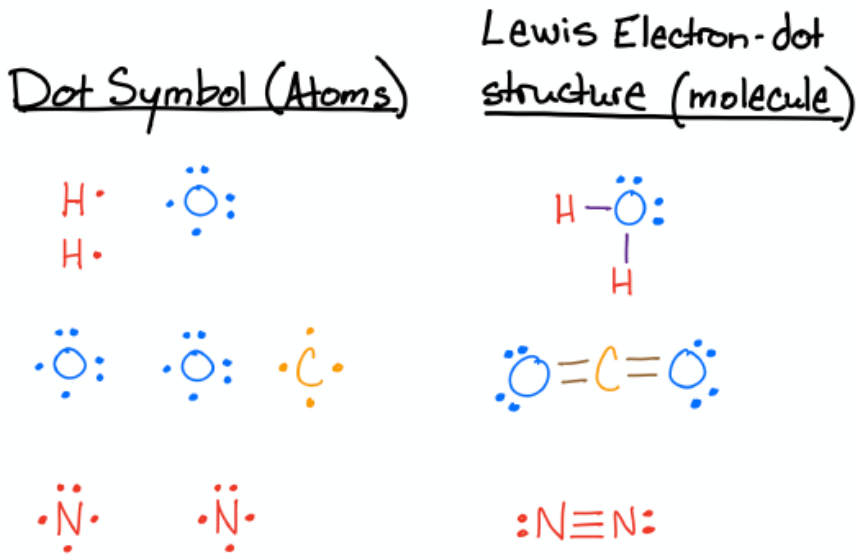
Answer available at the end of this section.

Outside Links

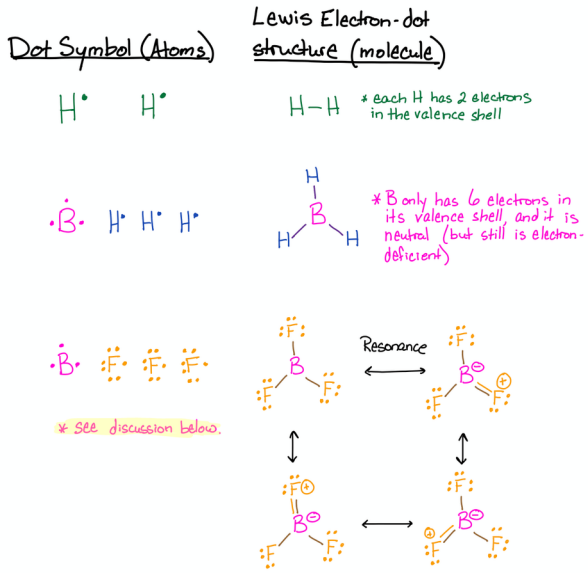
- en.Wikipedia.org/wiki/Lewis_structures
- http://www.ausetute.com.au/lewisstr.html
- cost.georgiasouthern.edu/chem...cule/lewis.htm

Answers

Exercise 2.1.1.1



Exercise 2.1.1.2



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).

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- 2.1B: Lewis Structures by Andrew Iskandar is licensed CC BY 4.0.

2.1.1.1: Resonance

Learning Objectives

- To understand the concept of resonance.

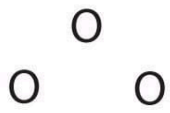
Resonance structures are a set of two or more Lewis Structures that collectively describe the electronic bonding of a single polyatomic species including fractional bonds and fractional charges. Resonance structures are capable of describing delocalized electrons that cannot be expressed by a single 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 (O_3), an allotrope of oxygen with a V-shaped structure and an O–O–O angle of 117.5°.

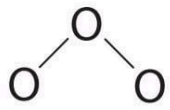
Ozone (O_3)

1. We know that ozone has a V-shaped structure, so one O atom is central:



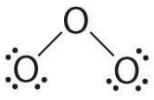
2. Each O atom has 6 valence electrons, for a total of 18 valence electrons.

3. Assigning one bonding pair of electrons to each oxygen–oxygen bond gives



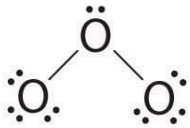
with 14 electrons left over.

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:

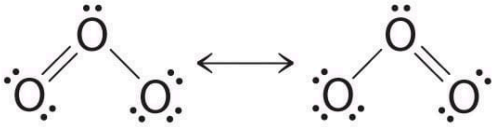


6. The central oxygen has only 6 electrons. We must convert one lone pair on a terminal oxygen atom to a bonding pair of electrons—but which one? Depending on which one we choose, we obtain either



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:



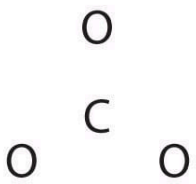
The double-headed arrow indicates that the actual electronic structure is an *average* of those shown, not that the molecule oscillates between the two structures.

> 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.

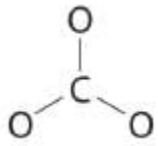
1. Because carbon is the least electronegative element, we place it in the central position:



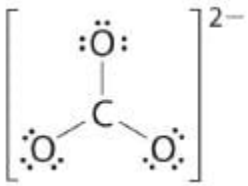
The three oxygens are drawn in the shape of a triangle with the carbon at the center of the triangle.

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:



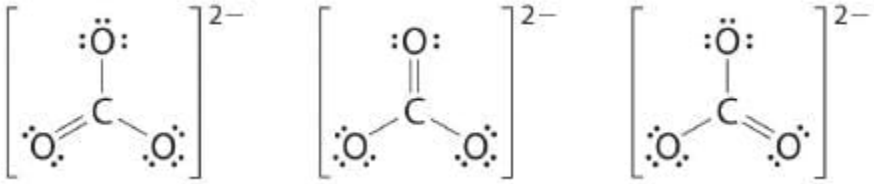
4. We divide the remaining 18 electrons equally among the three oxygen atoms by placing three lone pairs on each and indicating the –2 charge:



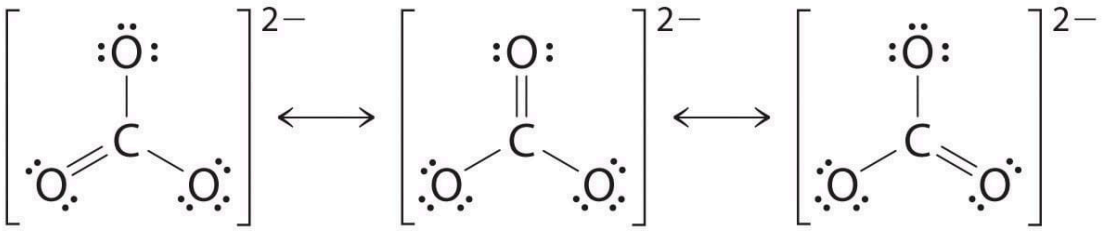
The Lewis dot structure has a central carbon that is bonded to 3 oxygens. Each oxygen has 3 lone pairs. The molecule is inside square brackets and has a charge of minus 2.

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:



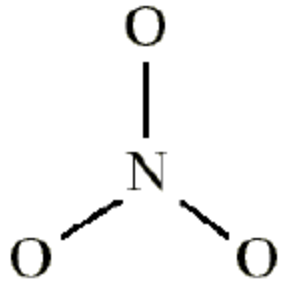
The resonance structure includes all three Lewis dot structures with double headed arrows between them.

The actual structure is an average of these three resonance structures.

The Nitrate (NO_3^-) ion

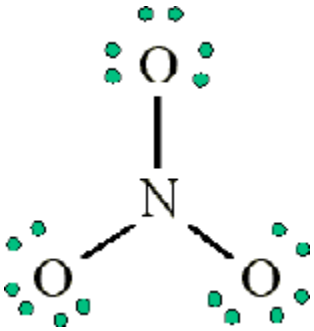
1. Count up the valence electrons: (1*5) + (3*6) + 1(ion) = **24** electrons

2. Draw the bond connectivities:

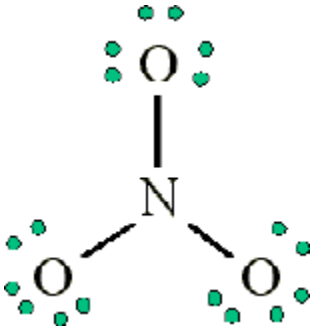


The three oxygens are drawn in the shape of a triangle with the nitrogen at the center of the triangle.

3. Add octet electrons to the atoms bonded to the center atom:

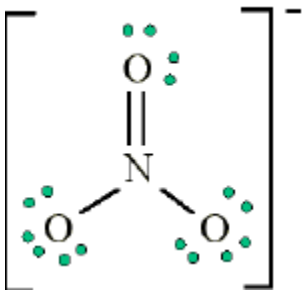


4. Place any leftover electrons (24-24 = **0**) on the center atom:



5. Does the central atom have an octet?

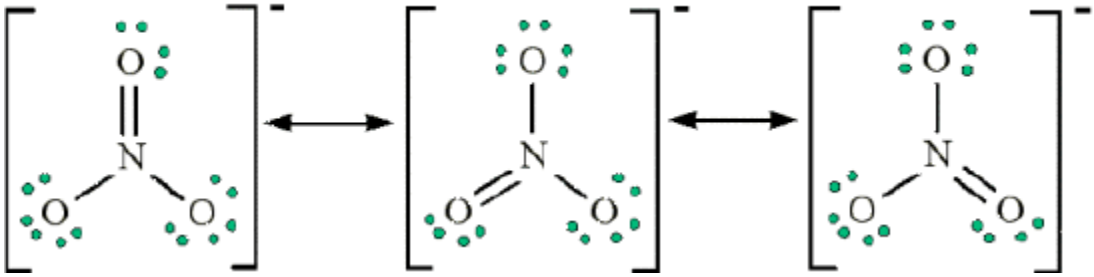
- **NO**, it has 6 electrons
- Add a multiple bond (first try a double bond) to see if the central atom can achieve an octet:



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 NO_3^- ion to be somewhat shorter than a single bond.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

View this YouTube Video online

Example 2.1.1.1.1: 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

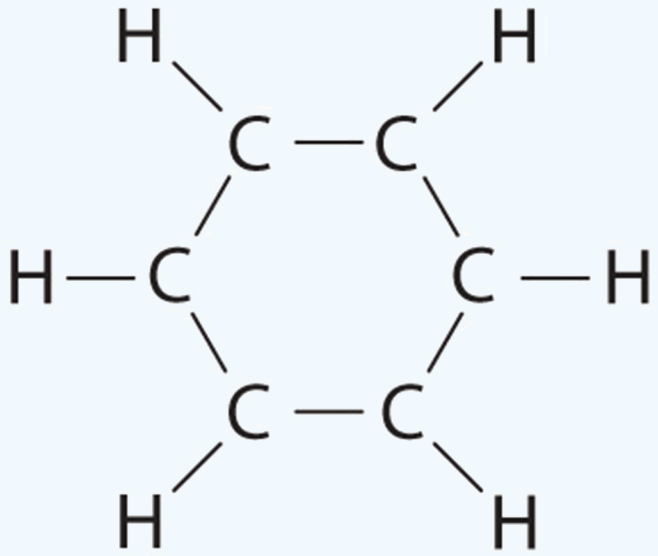
Asked for: resonance structures

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.

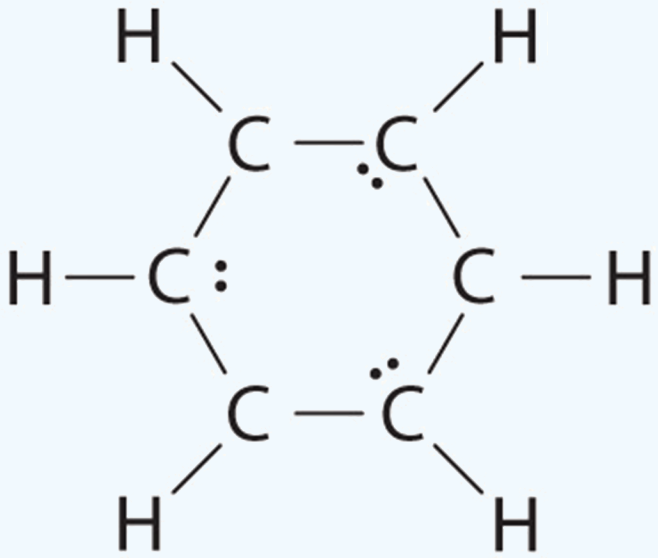
Solution:

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:



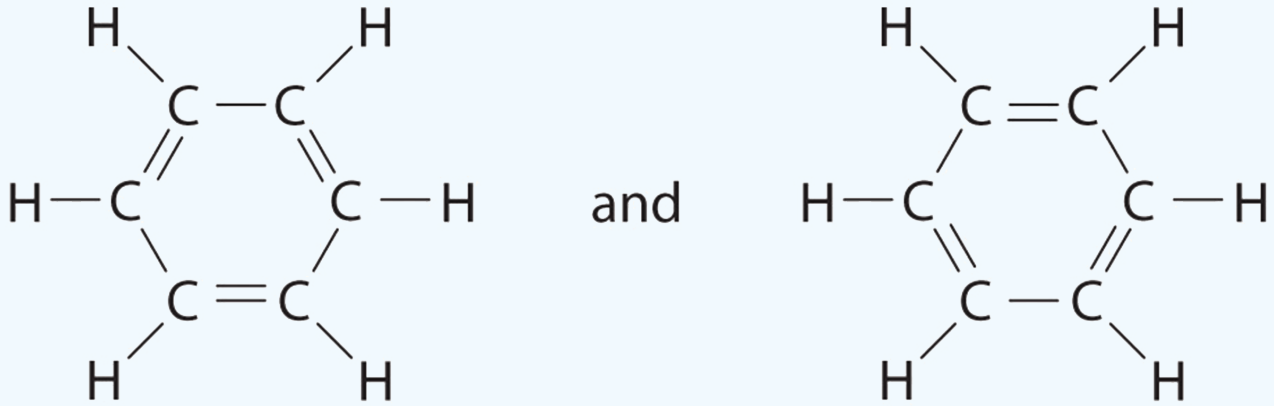
Each carbon atom in this structure has only 6 electrons and has a formal charge of +1, but we have used only 24 of the 30 valence electrons.

B If the 6 remaining electrons are uniformly distributed pairwise on alternate carbon atoms, we obtain the following:

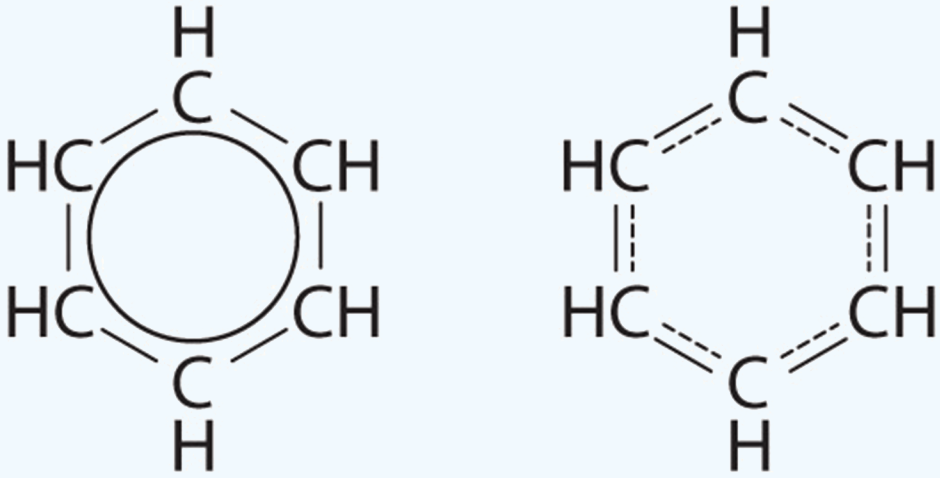


Three carbon atoms now have an octet configuration and a formal charge of –1, while three carbon atoms have only 6 electrons and a formal charge of +1. We can convert each lone pair to a bonding electron pair, which gives each atom an octet of electrons and a formal charge of 0, by making three C=C double 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

Exercise 2.1.1.1.1: Nitrite Ion

The sodium salt of nitrite is used to relieve muscle spasms. Draw two resonance structures for the nitrite ion (NO_2^-).

Answer available at the end of this section.

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 2.1.1.1.1. 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.

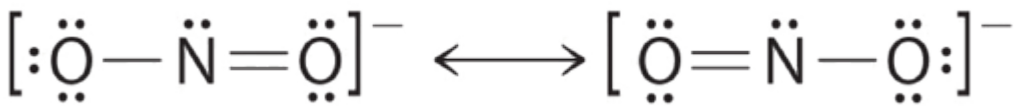
Resonance structures is a mechanism that allows us to use all of the possible resonance structures to try to predict what the actual form of the molecule would be. Single bonds, double bonds, triple bonds, +1 charges, -1 charges, these are our limitations in explaining the structures, and the true forms 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.

Answers

Exercise 2.1.1.1.1**: Nitrite Ion**



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.

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2.1.1.2: 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 2.1.1.2.1

Draw the Lewis structures for sulfur hexafluoride ($\mathrm{SF_6}$).

Answer available at the end of this section.

Exercise 2.1.1.2.1

Draw the Lewis structure for chlorine trifluoride ($\mathrm{ClF_3}$.

Answer available at the end of this section.

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.

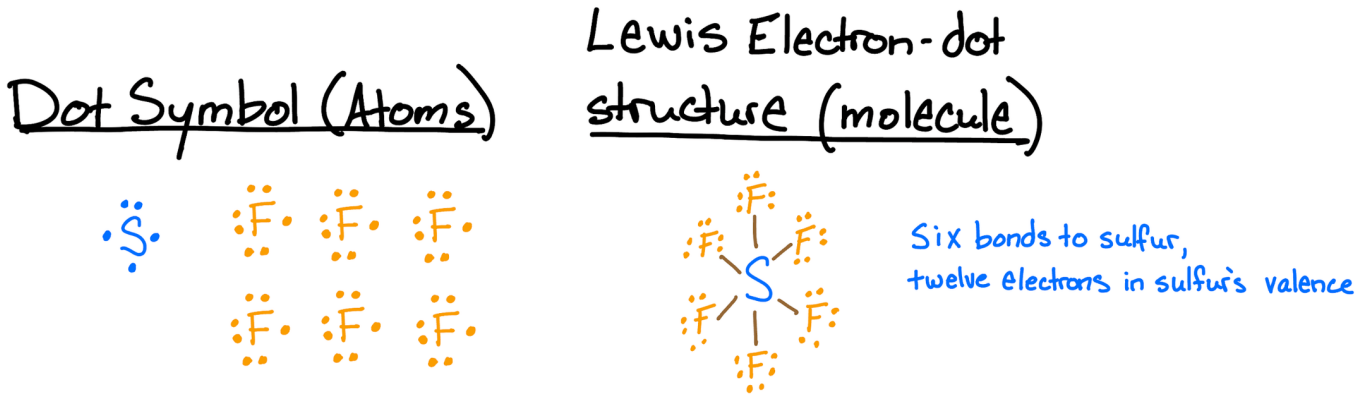
> Bonding theories can only be judged by their predictions.

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.

Answers

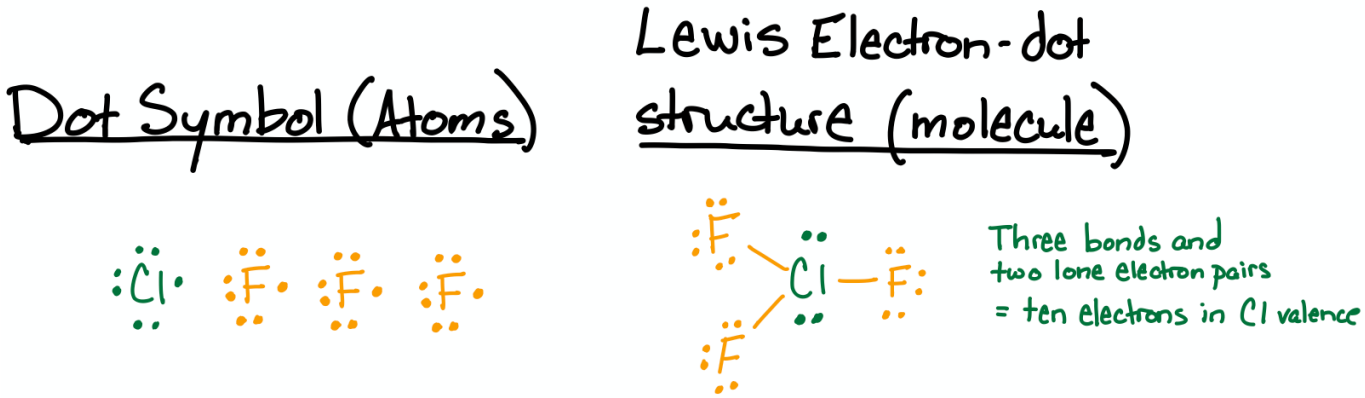
Exercise 2.1.1.2.1

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 2.1.1.2.1

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.



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2.1.1.3: 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) - (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.

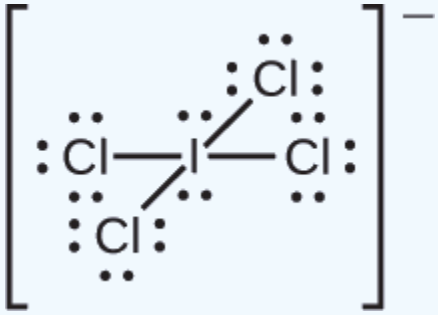
We must remember that the formal charge calculated for an atom is not the *actual* charge of the atom in the molecule. Formal charge is only a useful bookkeeping procedure; it does not indicate the presence of actual charges.

Calculating Formal Charge from Lewis Structures

Assign formal charges to each atom in the interhalogen ion $\mathrm{ICl_4^-}$.

Solution

We divide the bonding electron pairs equally for all $\mathrm{I{-}Cl}$ 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).

Exercise 2.1.1.3.1

Calculate the formal charge for each atom in the carbon monoxide molecule:



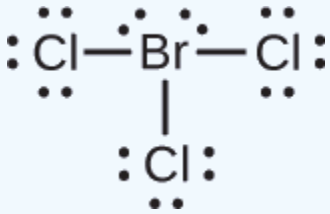
Answer available at the end of this section.

Example: Calculating Formal Charge from Lewis Structures

Assign formal charges to each atom in the interhalogen molecule $\mathrm{BrCl_3}$.

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 $\mathrm{BrCl_3}$ have a formal charge of zero, and the sum of the formal charges totals zero, as it must in a neutral molecule.

Exercise 2.1.1.3.2

Determine the formal charge for each atom in $\mathrm{NCl_3}$.

Answer available at the end of this section.

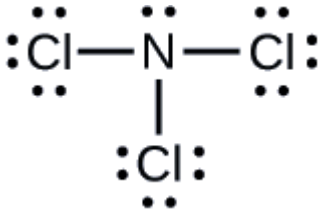
Answers

Exercise 2.1.1.3.1

C –1, O +1

Exercise 2.1.1.3.2

N: 0; all three Cl atoms: 0



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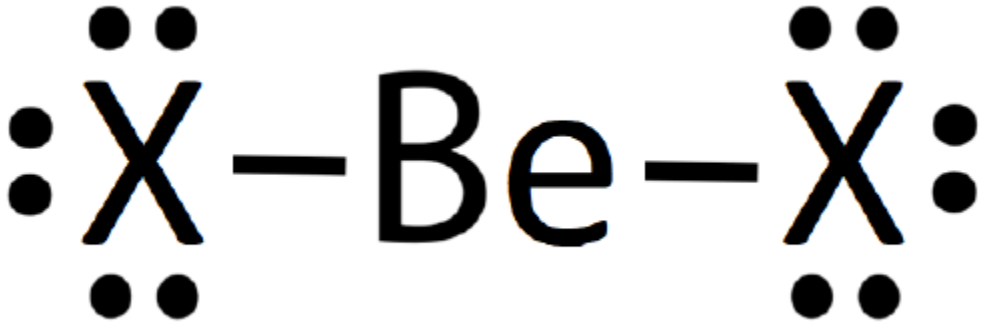
- 7.5: Formal Charges and Resonance by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

2.1.1.4: 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 $\mathrm{BeX_2}$, where X is one of the halogens, F or Cl.



Each of the structures above would predict a linear geometry for the $\mathrm{BeX_2}$ 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 $\mathrm{BeCl_2}$ at very high temperatures).

It turns out that the monomer of $\mathrm{BeX_2}$ 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 $2.1.1.4.1$) 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 $2.1.1.4.1$.

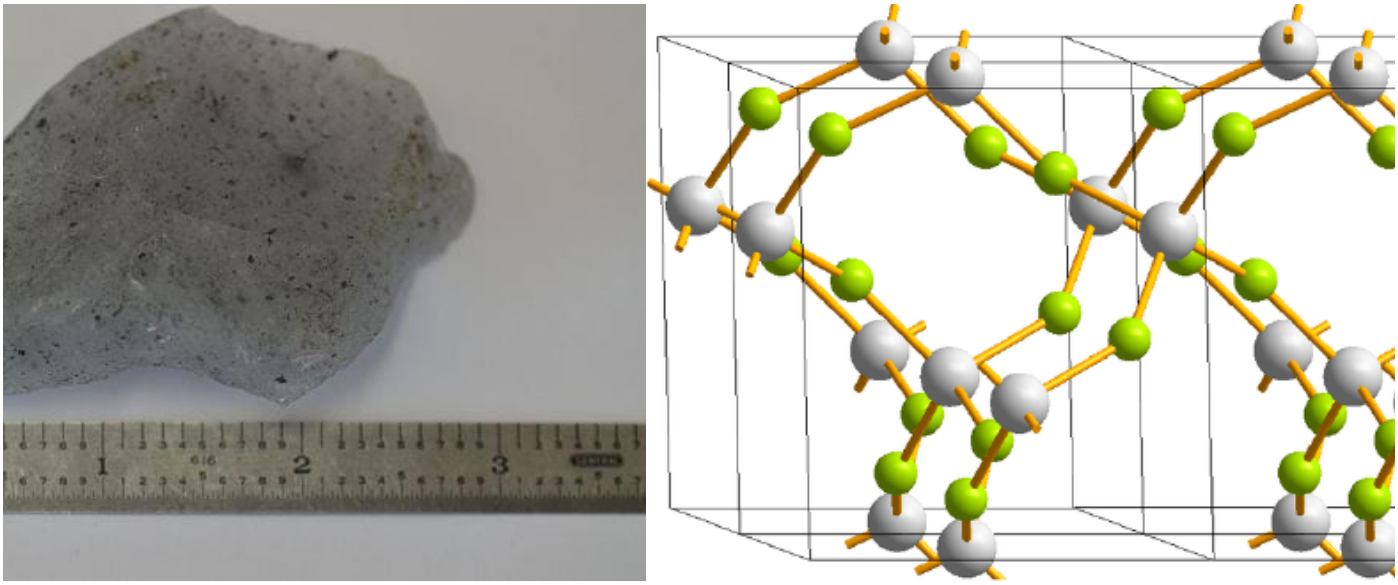


Figure 2.1.1.4.1: (left) A nugget of beryllium fluoride obtained from Materion. Black spots are carbon (CC BY-SA 3.0; Bckelleher via Wikipedia). (right) BeF2 structure (CC BY-SA 3.0 Unported; Materialscientist via Wikipedia)

In the liquid phase, $\mathrm{BeF_2}$ 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, $\mathrm{BeF_2}$ exists as a monomer with linear geometry and a bond length of 1.43 Å, consistent with a double bond between Be and F.

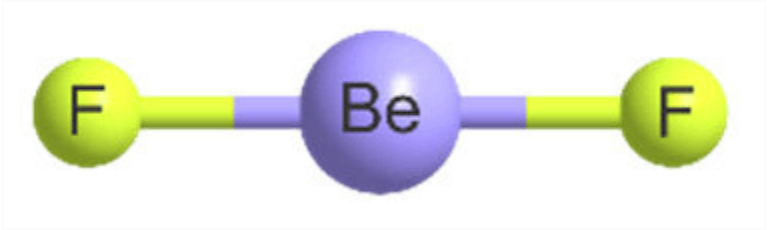


Figure 2.1.1.4.2: Geometries of $\mathrm{BeF_2}$. (CC BY; Ibon Alkorta and Anthony C. Legoe via Inorganics)

$\mathrm{BeCl_2}$

At ambient temperature and pressure, $\mathrm{BeCl_2}$ is a solid. As in $\mathrm{BeF_2}$ described above, $\mathrm{BeCl_2}$ has four-coordinate, tetrahedral Be and two-coordinate Cl. In contrast to $\mathrm{BeF_2}$, solid $\mathrm{BeCl_2}$ is a 1-dimensional polymer consisting of edge-shared tetrahedral.

In the gas phase, $\mathrm{BeCl_2}$ 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 $\mathrm{BH_3}$ and $\mathrm{BF_3}$ were described in Exercise 3.1.2, and are drawn again below for convenience.

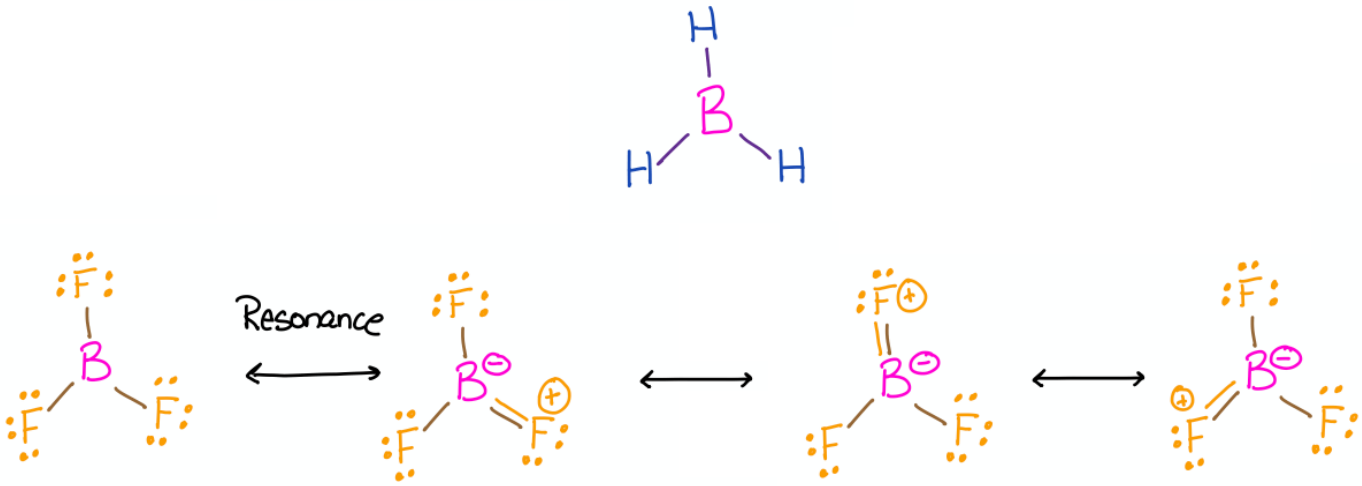


Figure 2.1.1.4.2: Lewis structures of $\mathrm{BH_3}$ and $\mathrm{BF_3}$. (Kathryn Haas; CC-NC-BY-SA)

Boron trihalides

Boron trihalides, like $\mathrm{BF_3}$, have properties that are largely predicted by Lewis structures and VSEPR theory. The Lewis structure for $\mathrm{BF_3}$ 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 $\mathrm{BF_3}$ 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 $\mathrm{BF_3}$ 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 $(\mathrm{BH_3})$ 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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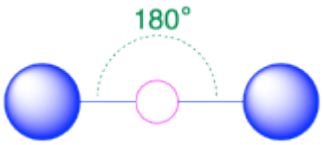
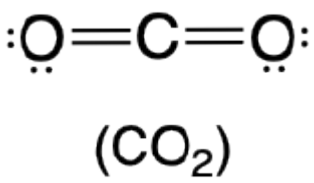
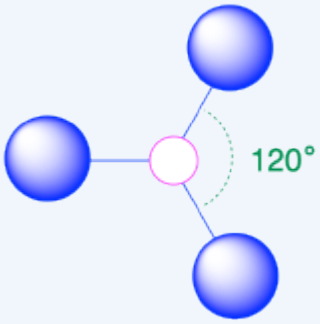
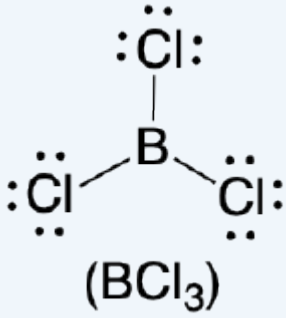
2.1.2: Valence Shell Electron-Pair Repulsion

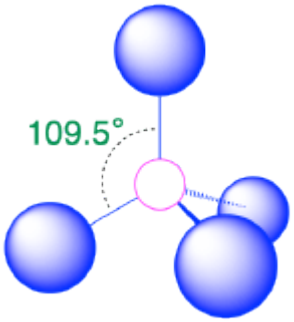
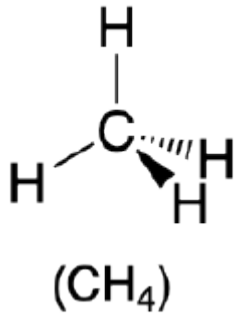
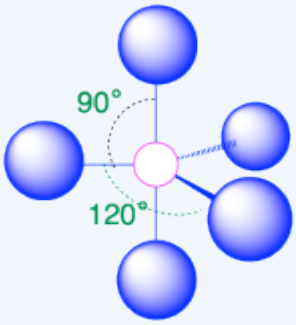
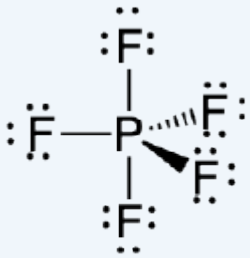
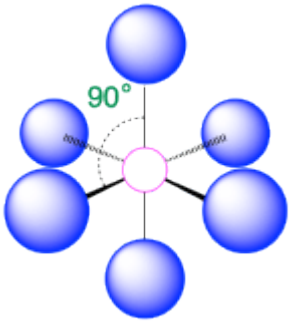
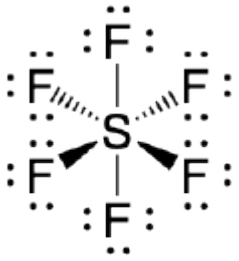
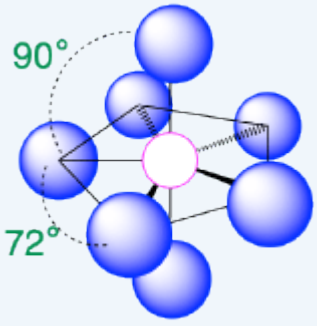
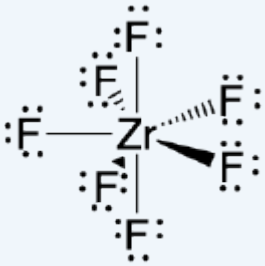
Introduction to VSEPR

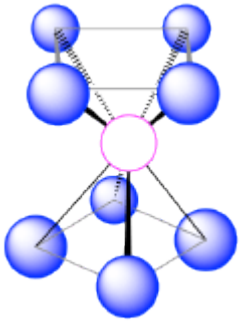
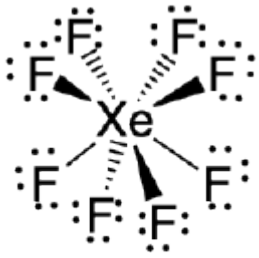
The **Valence Shell Electron Repulsion (VSEPR)** model can predict the structure of most molecules and polyatomic ions in which the central atom is a nonmetal; it also works for some structures in which the central atom is a metal. VSEPR builds on Lewis electron dot structures (discussed in Section 3.1); 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 $\mathbf{AX}_{\boldsymbol{m}}\mathbf{E}_{\boldsymbol{n}}$ 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 $\boldsymbol{m}$ and $\boldsymbol{n}$ are integers. The number of groups is equal to the sum of $\boldsymbol{m}$ and $\boldsymbol{n}$. 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 2.1.2.1. The cases where lone pairs contribute to the total groups ($n \geq 1$) are discussed in the next section about lone pair repulsion.

Table 2.1.2.1. 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°	

Groups around central atom (*m* + *n*)	Geometry Name	Geometry Sketch	Predicted bond Angle	Example
4	tetrahedron		109.5°	 (CH_4)
5	trigonal bipyramid		90° and 120°	 (PF_5)
6	octahedron		90°	 (SF_6)
7	pentagonal bipyramid		90° and 72°	 ($[ZrF_7]^{3-}$)

Groups around central atom ($m + n$)	Geometry Name	Geometry Sketch	Predicted bond Angle	Example
8	square antiprism		70.5°, 99.6° and 109.5°	 ($[XeF_8]^{2-}$)

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

Exercise 2.1.2.1

Predict the geometry around the central atom in BeH_2 and CO_2.

Answer BeH2 available at the end of this section.

Answer CO2 available at the end of this section.

2. The carbon atom forms two double bonds. Each double bond is counted as one group, so there are two groups around the central atom. Once again, both groups around the central atom are bonds, so CO_2 is designated as AX_2.

3. Like BeH_2, the arrangement that minimizes repulsions places the groups 180° apart.

4. VSEPR only recognizes groups around the *central* atom (the carbon). Thus the lone pairs on the oxygen atoms do not influence the molecular geometry. With two bonded groups on the central atom and no lone pairs, the molecular geometry of CO_2 is linear (Table 2.1.2.1). The structure of CO_2 is shown in Table 2.1.2.1.

Exercise 2.1.2.2

Predict the geometry around the central atom in BCl_3 and CO_3^{2-}.

Answer BCl3 available at the end of this section.

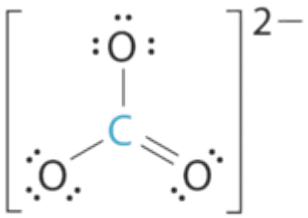
2. There are three groups around the central atom and all are single bonds. The structure is designated as AX_3.

3. To minimize repulsions, the groups are placed 120° apart (Table 2.1.2.1).

4. From Table 2.1.2.1 we see that with three bonding pairs around the central atom, the molecular geometry of BCl_3 is *trigonal planar*.

Answer CO_3^{2-}

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

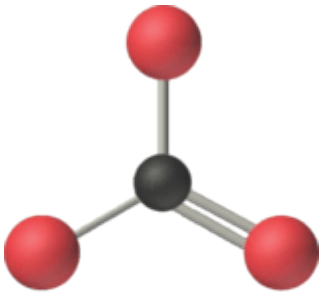


Lewis structure

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 2.1.2.1).

4. We see from Table 2.1.2.1 that the molecular geometry of CO_3^{2-} is trigonal planar with bond angles of 120°.



Molecular geometry
(trigonal planar)

In our next example we encounter the effects of lone pairs and multiple bonds on molecular geometry for the first time.

Exercise 2.1.2.3

Predict the geometry around the central atom in CH_4, PCl_5 and SF_6.

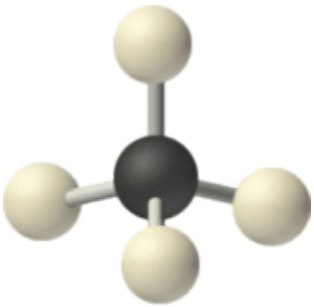
Answer CH4 available at the end of this section.

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 2.1.2.1, repulsions are minimized by placing the groups in the corners of a tetrahedron with bond angles of 109.5°.

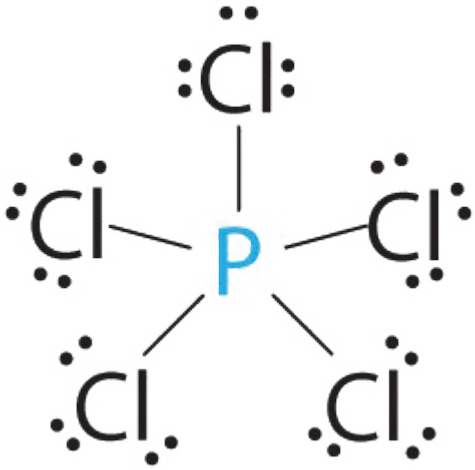
4. With four bonding pairs, the molecular geometry of methane is *tetrahedral* (Table 2.1.2.1).



Molecular geometry
(tetrahedral)

Answer PCl_5

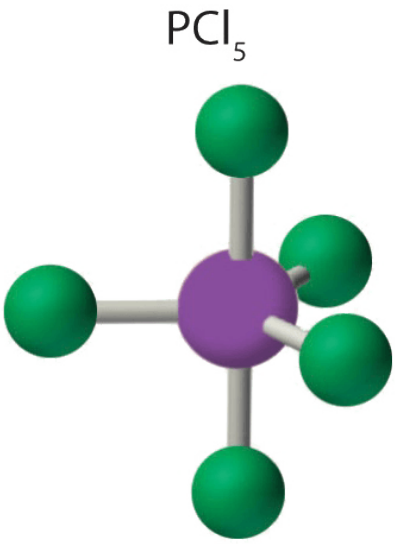
1. Phosphorus has five valence electrons and each chlorine has seven valence electrons, so the Lewis electron structure of PCl_5 is



2. There are five bonding groups around phosphorus, the central atom. All electron groups are bonds, so the structure is designated as AX_5.

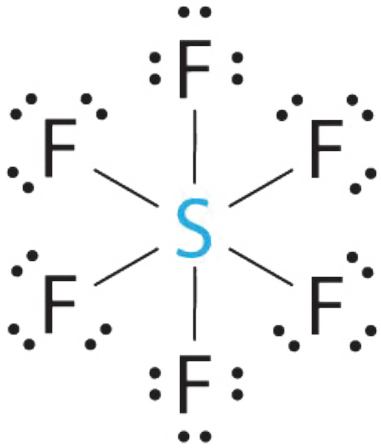
3. The structure that minimizes repulsions is a *trigonal bipyramid*, which consists of two trigonal pyramids that share a base (Table 2.1.2.1).

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.



Answer SF_6

1. The central atom, sulfur, contributes six valence electrons, and each fluorine atom has seven valence electrons, so the Lewis electron structure is



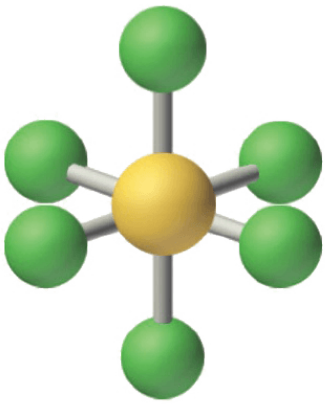
Lewis structure

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 2.1.2.2 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.

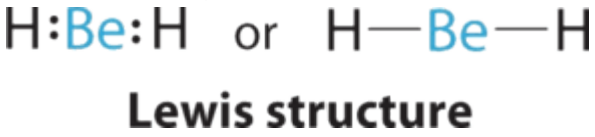


Molecular geometry
(octahedral)

Answers

Exercise 2.1.2.1

1. The central atom, beryllium, contributes two valence electrons, and each hydrogen atom contributes one. The Lewis electron structure is

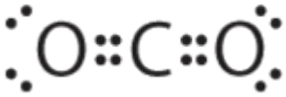


Lewis structure

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 2.1.2.1 that the arrangement that minimizes repulsions places the groups 180° apart.
4. From Table 2.1.2.1 we see that with two bonding pairs, the molecular geometry that minimizes repulsions in BeH_2 is *linear*.

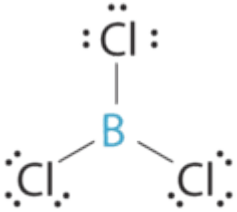
Exercise 2.1.2.1

1. The central atom, carbon, contributes four valence electrons, and each oxygen atom contributes six. The Lewis electron structure is



Exercise 2.1.2.2

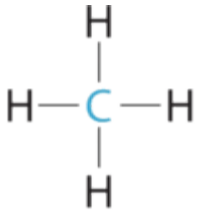
1. The central atom, boron, contributes three valence electrons, and each chlorine atom contributes seven valence electrons. The Lewis electron structure is



Lewis structure

Exercise 2.1.2.3

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

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2.1.2.1: 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 $\mathbf{AX_mE_n}$, 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.

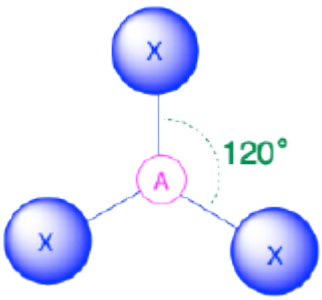
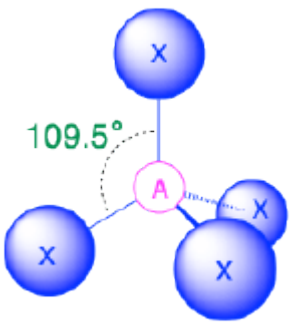
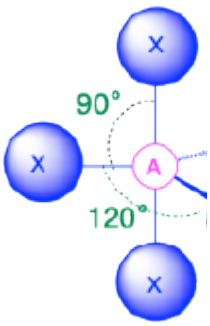
When one or more of the groups is a lone pair of electrons (non-bonded electrons), the experimentally-observed geometry around an atom is slightly different than in the case where all groups are bonds. The actual bond angles are similar, but not exactly the same, as those predicted based on the *total 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:

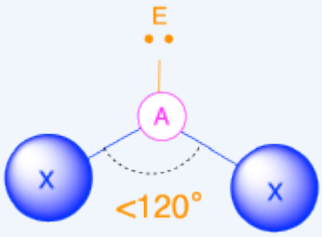
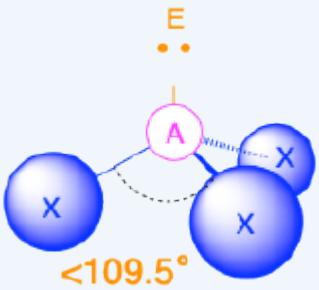
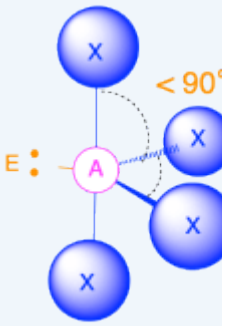
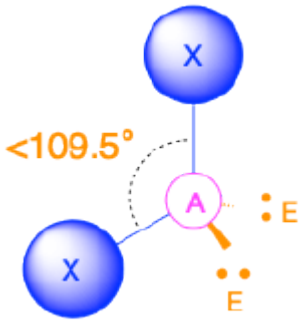
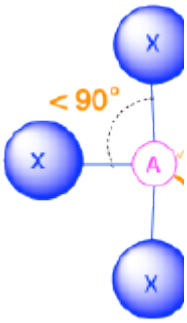
Trend in bond angles:

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 2.1.2.1.1.

Table 2.1.2.1.1: Predictions of molecular geometry and bond angles around atoms with a mixture of bonded (X) and unbonded (E) ele

	Electron Groups (m + n)			
	2 **(steric number = 2)**	**3** **(steric number = 3)**	**4** **(steric number = 4)**	**5** **(steric number**
Parent Geometry **(0 lone pairs)** $\mathbf{AX_m}$	 $\mathbf{AX_2}$, linear 180°	 $\mathbf{AX_3}$, trig. plane 120°	 $\mathbf{AX4}$, tetrahedron 109.5°	 $\mathbf{AX_5}$, trig. bipyra 90°, 120°

	Electron Groups (m + n)			
	2 (steric number = 2)	3 (steric number = 3)	4 (steric number = 4)	5 (steric number
1 lone pair **AX_mE_1**		 **AX_2E_1**, bent <120°	 **AX_3E_1**, trig. pyramid <109.5°	 **AX_4E_1**, see-s <90°, <120°
2 lone pairs **AX_mE_2**			 **AX_2E_2**, bent <109.5°	 **AX_3E_2**, T-sha <90°

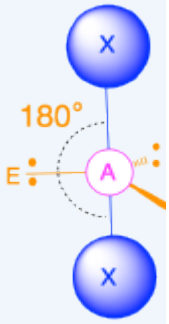
	Electron Groups (*m* + *n*)			
	2 (steric number = 2)	3 (steric number = 3)	4 (steric number = 4)	5 (steric number
3 lone pairs **AX_mE_3**				 **AX_2E_3**, linea 180°

Table 2.1.2.1.1 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.

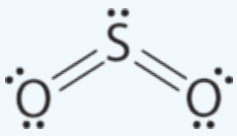
Three Electron Groups (m + n = 3)

(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°**.

AX_2E Molecules: Example SO_2

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 2.1.2.1.1).

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)

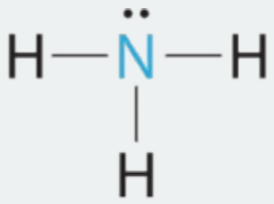
(Steric number = 4) In the case that there are four electron groups around a central atom, those groups will lie approximately 109.5° from one another in space. This results in an electronic geometry that is approximately **tetrahedral**. There are three different molecular geometries that are possible 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°**.

AX_3E Molecules: Example NH_3

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.

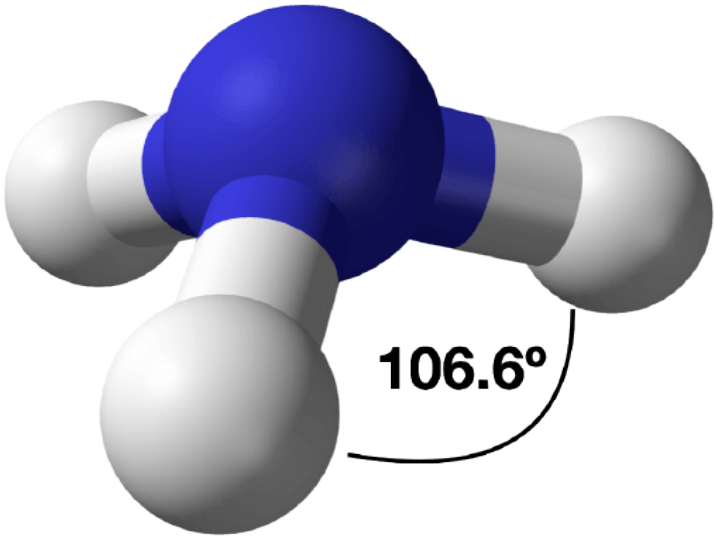
1. In ammonia, the central atom, nitrogen, has five valence electrons and each hydrogen donates one valence electron, producing the Lewis electron structure



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°.

AX_2E_2 Molecules: Example H_2O

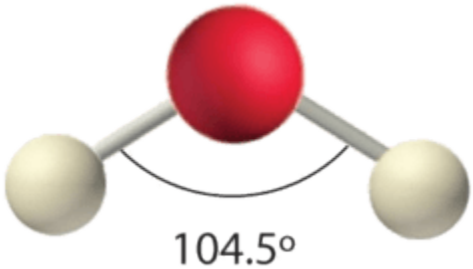
1. Oxygen has six valence electrons and each hydrogen has one valence electron, producing the Lewis electron structure



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)

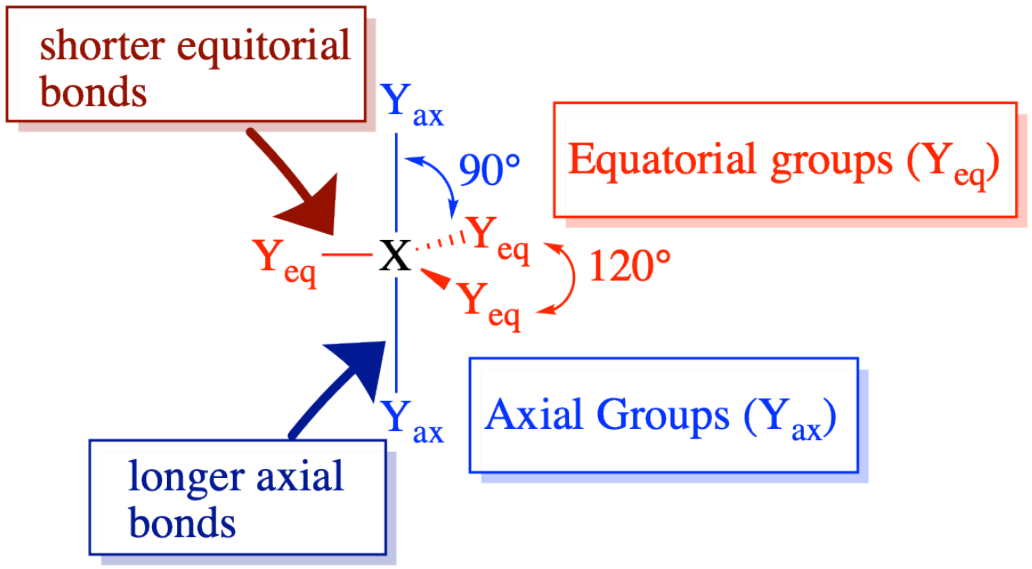


Figure: Trigonal pyramidal molecules (steric number 5) possess different bond angles and lengths for axial (ax) and equatorial (eq) pendant atoms. (CC-BY-NC-SA; Kathryn Haas).

(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°**.

AX_4E Molecules: SF_4

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.

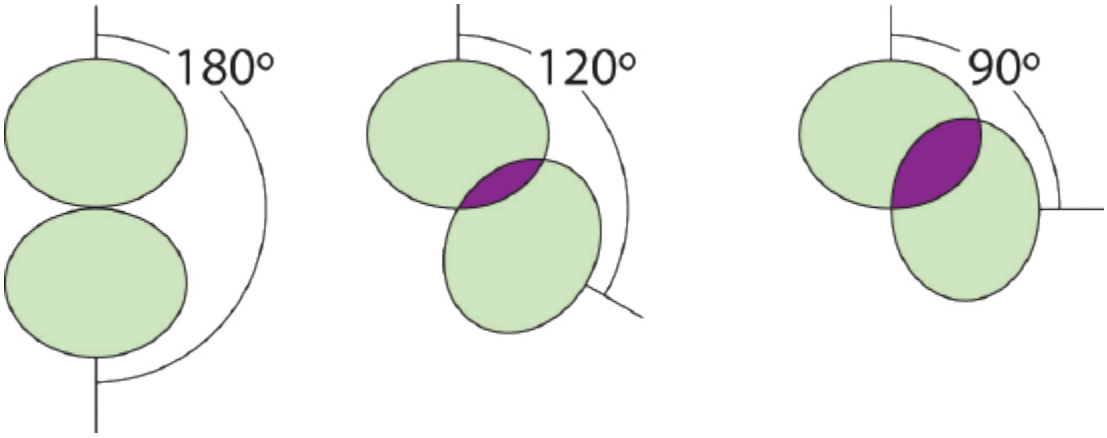
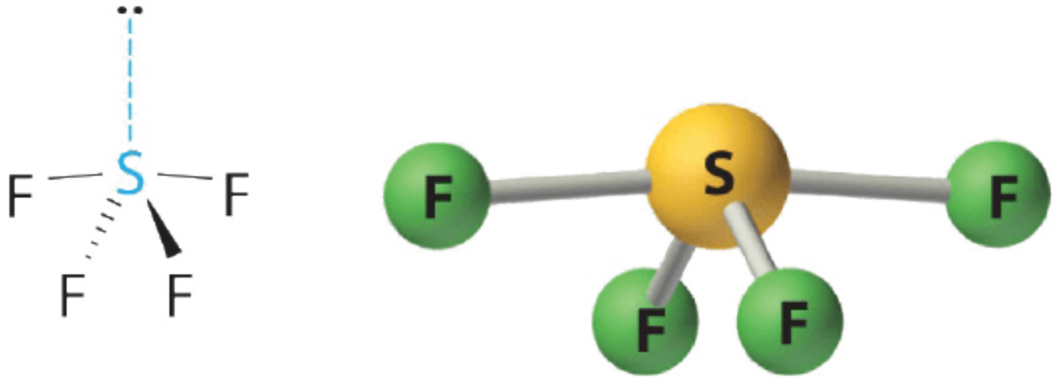


Illustration of the Area Shared by Two Electron Pairs versus the Angle between Them

At 90°, the two electron pairs share a relatively large region of space, which leads to strong repulsive electron–electron interactions.

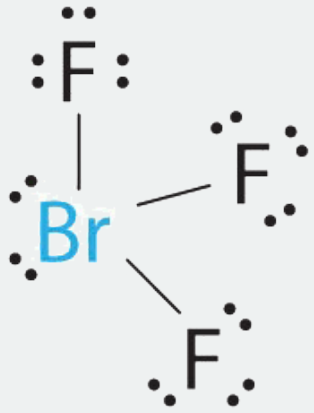
4. With four nuclei and one lone pair of electrons, the molecular structure is based on a trigonal bipyramid with a missing equatorial vertex; it is described as a *seesaw*. The F_{axial}–S–F_{axial} angle is 173° rather than 180° because of the lone pair of electrons in the equatorial plane.



Molecular geometry (seesaw)

AX_3E_2 Molecules: BrF_3

1. The bromine atom has seven valence electrons, and each fluorine has seven valence electrons, so the Lewis electron structure is

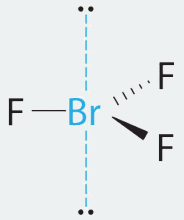


Lewis structure

Once again, we have a compound that is an exception to the octet rule.

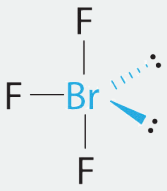
2. There are five groups around the central atom, three bonding pairs and two lone pairs. We again direct the groups toward the vertices of a trigonal bipyramid.

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°:



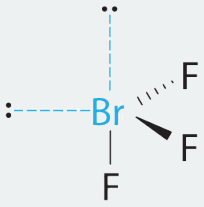
Lone pairs axial

(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.

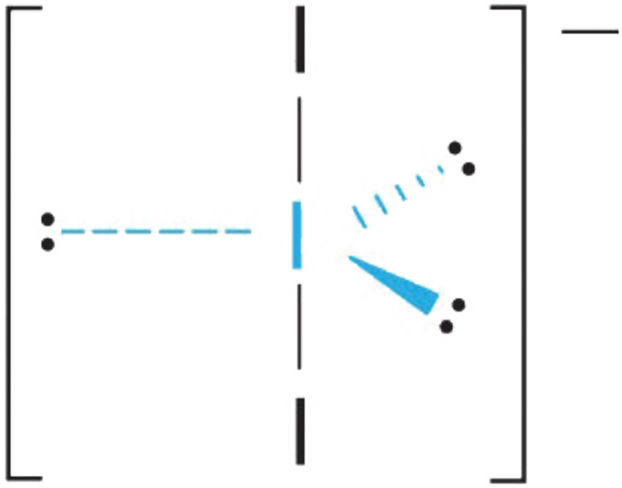
AX_2E_3 Molecules: I_3^-

1. Each iodine atom contributes seven electrons and the negative charge one, so the Lewis electron structure is



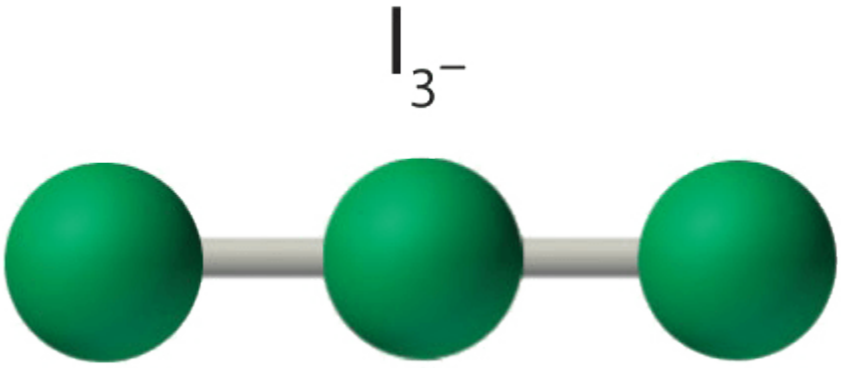
2. There are five electron groups about the central atom in I_3^-, two bonding pairs and three lone pairs. To minimize repulsions, the groups are directed to the corners of a trigonal bipyramid.

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.



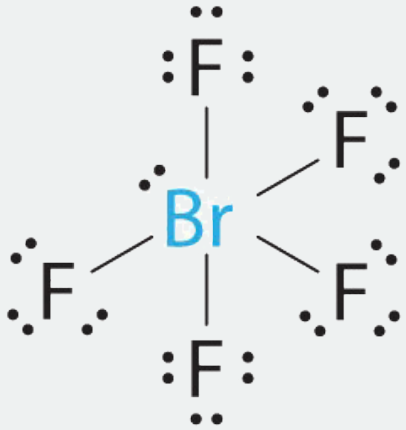
Six Electron Groups (m + n = 6)

(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°**.

AX_5E Molecules: BrF_5

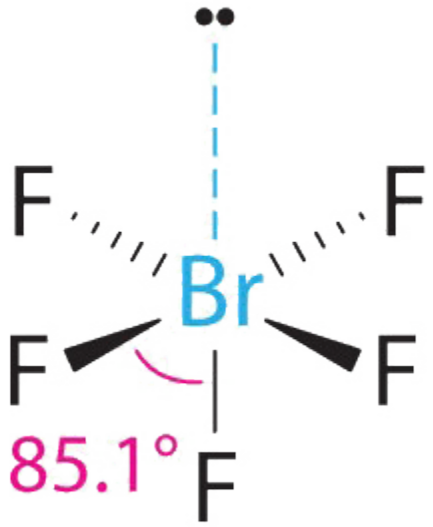
1. The central atom, bromine, has seven valence electrons, as does each fluorine, so the Lewis electron structure is



Lewis structure

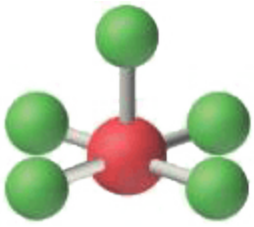
With its expanded valence, this species is an exception to the octet rule.

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.

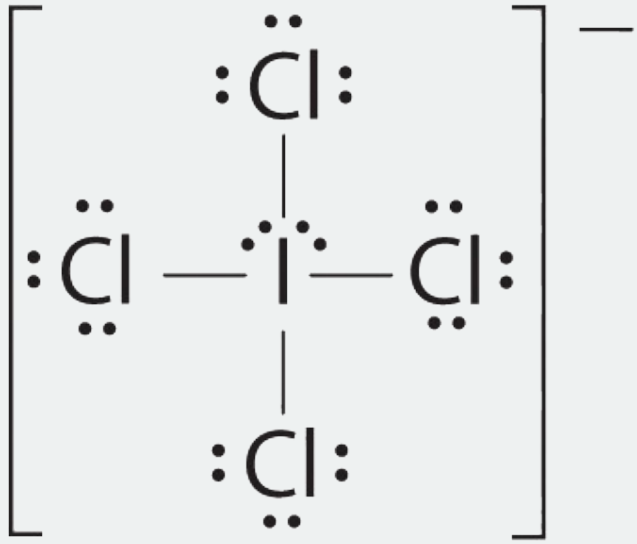
4. With five nuclei surrounding the central atom, the molecular structure is based on an octahedron with a vertex missing. This molecular structure is *square pyramidal*. The F_{axial}–B–$F_{equatorial}$ angles are 85.1°, less than 90° because of LP–BP repulsions.



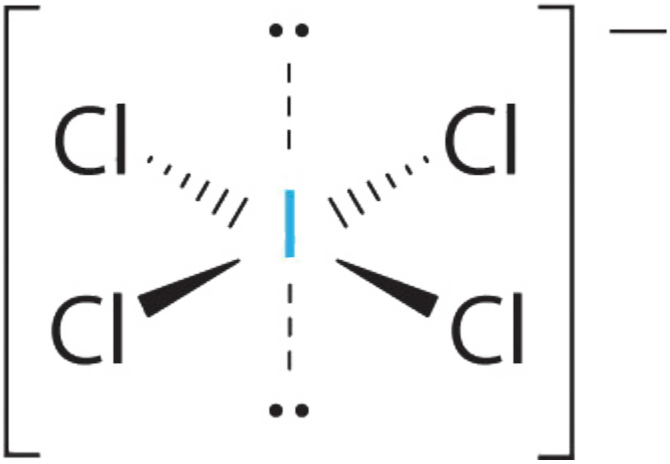
Molecular geometry
(square pyramidal)

AX_4E_2 Molecules: ICl_4^-

1. The central atom, iodine, contributes seven electrons. Each chlorine contributes seven, and there is a single negative charge. The Lewis electron structure is



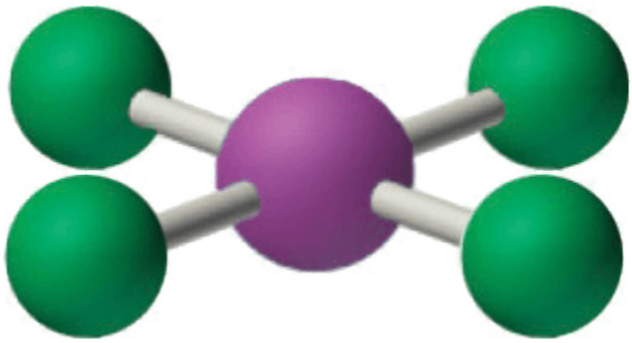
2. There are six electron groups around the central atom, four bonding pairs and two lone pairs. The structure that minimizes LP–LP, LP–BP, and BP–BP repulsions is



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 2.1.2.1.1.

Example Excercises

Example 2.1.2.1.1

Using the VSEPR model, predict the molecular geometry of each molecule or ion.

1. PF_5 (phosphorus pentafluoride, a catalyst used in certain organic reactions)
2. H_3O^+ (hydronium ion)

Given: two chemical species

Asked for: molecular geometry

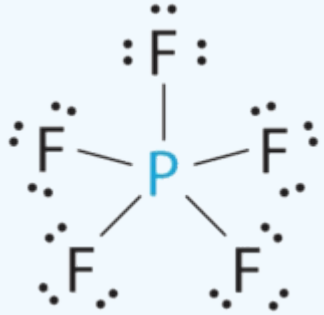
Strategy:

A. Draw the Lewis electron structure of the molecule or polyatomic ion.
B. Determine the electron group arrangement around the central atom that minimizes repulsions.
C. Assign an AX_mE_n designation; then identify the LP–LP, LP–BP, or BP–BP interactions and predict deviations in bond angles.

D. Describe the molecular geometry.

Solution:

1. **A** The central atom, P, has five valence electrons and each fluorine has seven valence electrons, so the Lewis structure of PF_5 is



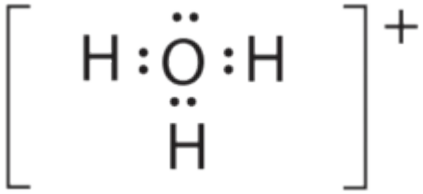
B There are five bonding groups about phosphorus. The structure that minimizes repulsions is a trigonal bipyramid.

C 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.

D The PF_5 molecule has five nuclei and no lone pairs of electrons, so its molecular geometry is trigonal bipyramidal.



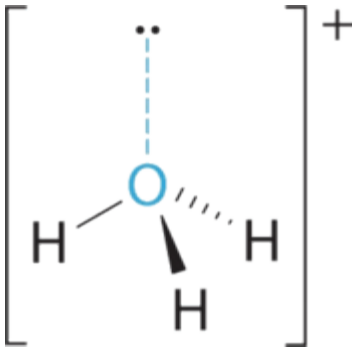
- **A** The central atom, O, has six valence electrons, and each H atom contributes one valence electron. Subtracting one electron for the positive charge gives a total of eight valence electrons, so the Lewis electron structure is



B 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.

C 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.

D 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 2.1.2.1.1

Using the VSEPR model, predict the molecular geometry of each molecule or ion.

a. XeO_3
b. PF_6^-
c. NO_2^+

Answer a available at the end of this section.

Example 2.1.2.1.2

Predict the molecular geometry of each molecule.

1. XeF_2
2. $SnCl_2$

Given: two chemical compounds

Asked for: molecular geometry

Strategy:

Use the strategy given in Example2.1.2.1.1.

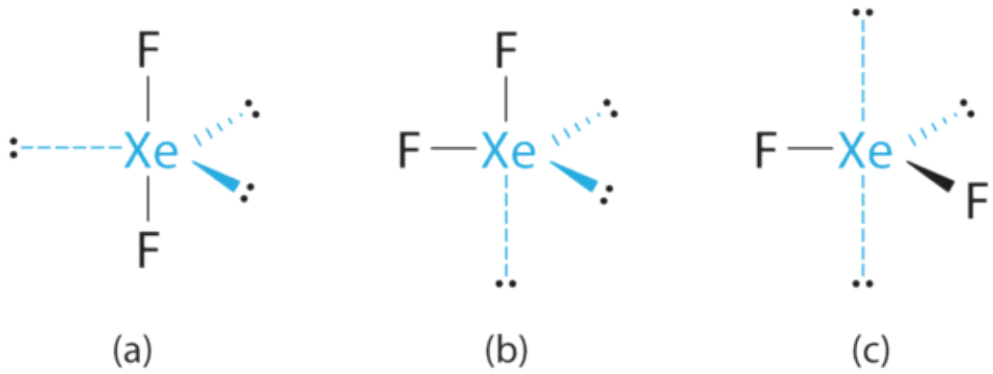
Solution:

1. **A** Xenon contributes eight electrons and each fluorine seven valence electrons, so the Lewis electron structure is



B 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.

C 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:



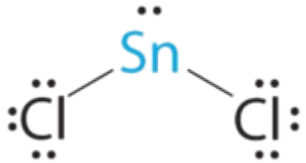
Interactions

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.

D 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.

- **A** The tin atom donates 4 valence electrons and each chlorine atom donates 7 valence electrons. With 18 valence electrons, the Lewis electron structure is



B 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.

C 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.

D 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 2.1.2.1.2

Predict the molecular geometry of each molecule.

a. SO_3
b. XeF_4

Answer a available at the end of this section.

Answers

Exercise 2.1.2.1.1

trigonal pyramidal

octahedral

linear

Exercise 2.1.2.1.2

trigonal planar

square planar

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2.1.2.2: 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.

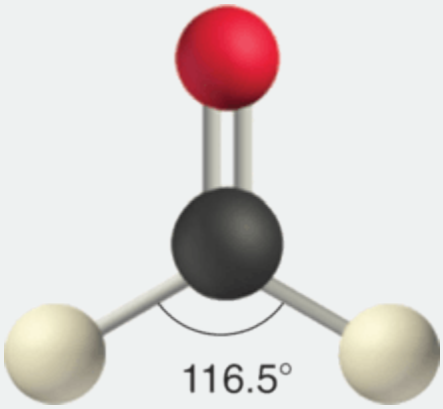
Double and triple bonds are more repulsive than single bonds

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.

Examples 2.1.2.2.1

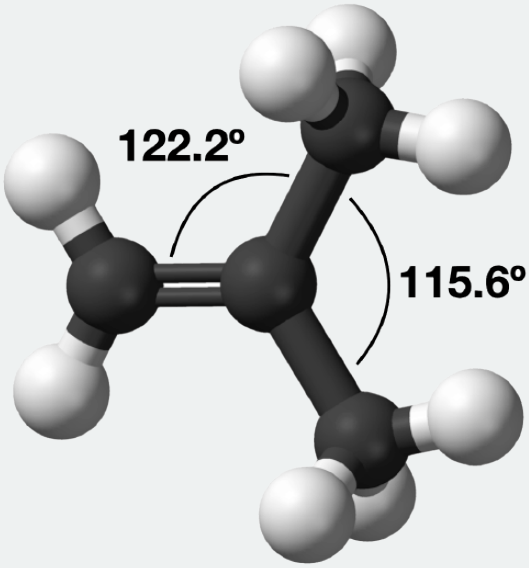
CH_2O

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°).



2-methybutene

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

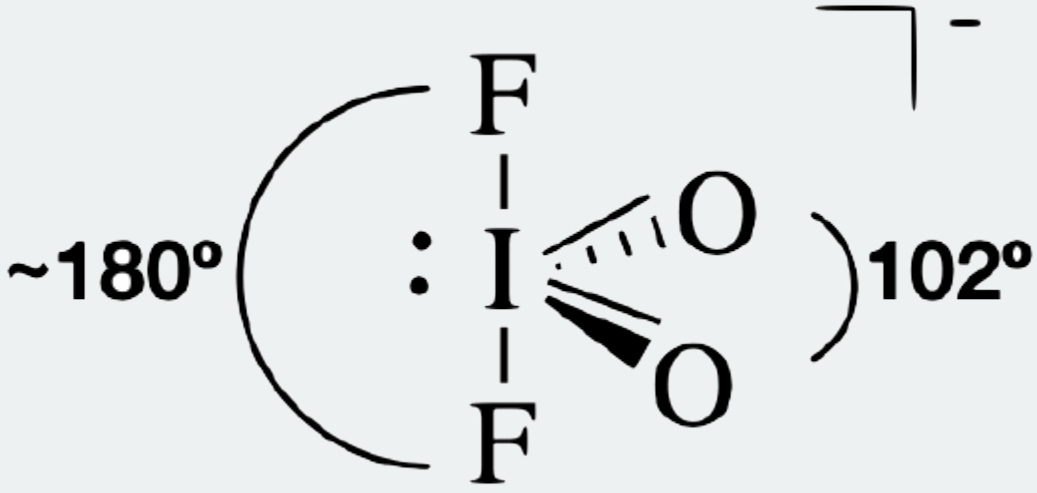
In general, we expect that a lone pair has slightly greater repulsive force than a multiple bond, and that a multiple bond has slightly greater repulsive force than a single bond. The **order of expected repulsive force** is:

$$\text{lone pair} > \text{double or triple bond} > \text{single bond}$$

Examples2.1.2.2.1

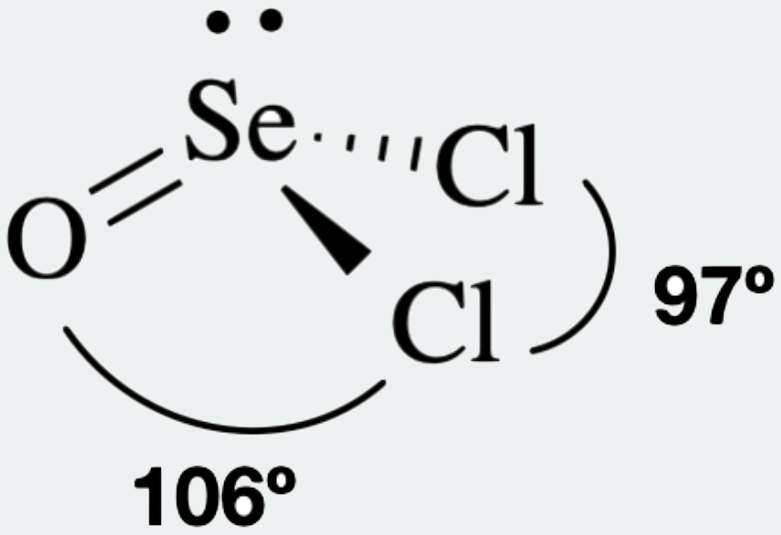
$IO_2F_2^-$

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.



$SeOCl_2$

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.



Practice

Exercise 2.1.2.2.1

Use VSEPR theory to predict the geometries and draw the structures of the following.

a. $XeOF_4$
b. NO_2^-
c. $SOCl_2$
d. IOF_3^-

Answer a available at the end of this section.

Answer b available at the end of this section.

Answer c available at the end of this section.

Answer d available at the end of this section.

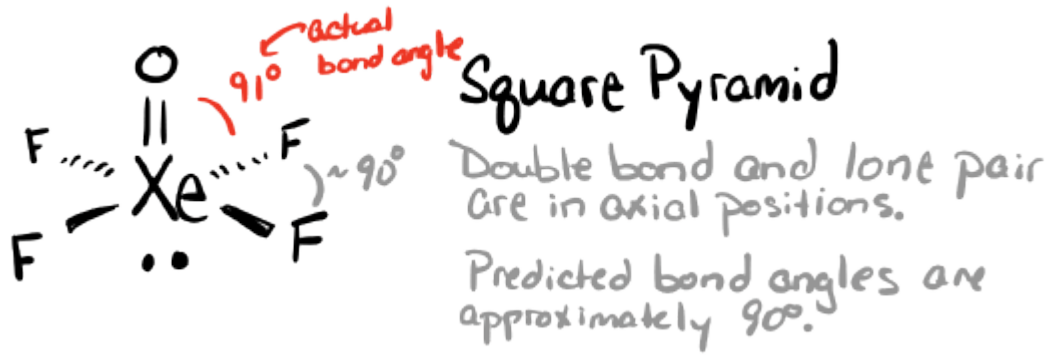
References

- Miessler, G.; Fischer, P.J.; Tarr, D. (2014). Inorganic Chemistry. New Jersey: Prentice-Hall. pp. 55

Answers

Exercise 2.1.2.2.1

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).



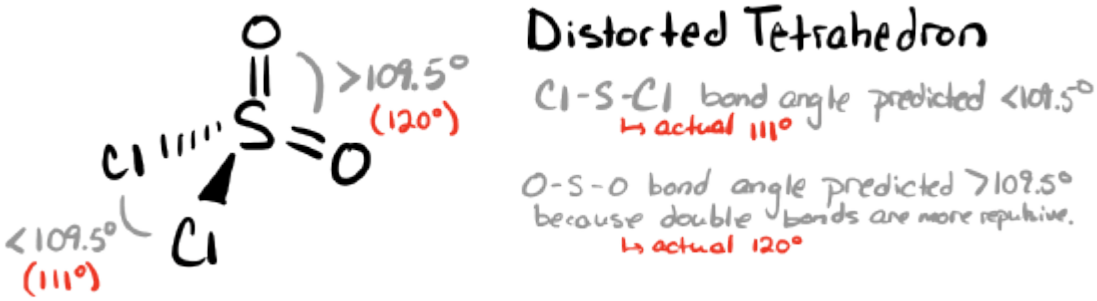
Exercise 2.1.2.2.1

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°.*



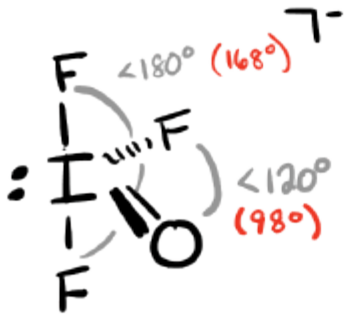
Exercise 2.1.2.2.1

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 2.1.2.2.1

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°

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2.1.2.3: Electronegativity and Atomic Size Effects

Introduction

We saw in previous sections how lone pairs of electrons and multiple bonds distort bond angles between non-central atoms (ligands) around a central atom. This section describes how ligand **electronegativity and size also influence bond angles and molecular geometry**. Electronegativity is generally correlated with atomic size going down any group of the periodic table. There are some cases where bond angles can be predicted by these correlations. However, size and electronegativity can also work as competing factors in determining bond angles.

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:

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

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 2.1.2.3.1: Table of Pauling electronegativities from Wikipedia's Electronegativity page (click).

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 the table below. More thorough descriptions of how values in each scale are calculated are described on Wikipedia's Electronegativity page (click) and a concise history of electronegativity scales is summarized in ref 4.

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) $$\mathrm{CE} = \frac{n\varepsilon_s + m\varepsilon_p}{n+m}$$ $n = \text{number of s electrons}$ $m = \text{number of p electrons}$ $\varepsilon_s, \varepsilon_p = \text{experimental 1-electron s and p energies}$

The primary advantage to this 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. We will see below that both electronegativity and atomic size influence bond angles and absolute molecular geometry around a central atom. In some cases, the size and electronegativity affects are aligned; in some cases these effects compete.

Electronegativity and Size Influence Bond Angles

Let's begin by examining the bond angles of several trigonal pyramidal molecules. The molecules shown in Figure 2.1.2.3.2 each have three identical "pendant groups" on the central atom (Figure 2.1.2.3.2). *Pendant atoms* or *pendant groups* are the atoms, or groups of atoms, that are bonded directly to the central atom. The molecules shown here are arranged according to the size of the central and pendant atoms. Central atoms increase in size going down this figure, and pendant atoms increase in size going across from left to right. The bond angles and bond lengths are labeled in each case.

What trends can you identify?

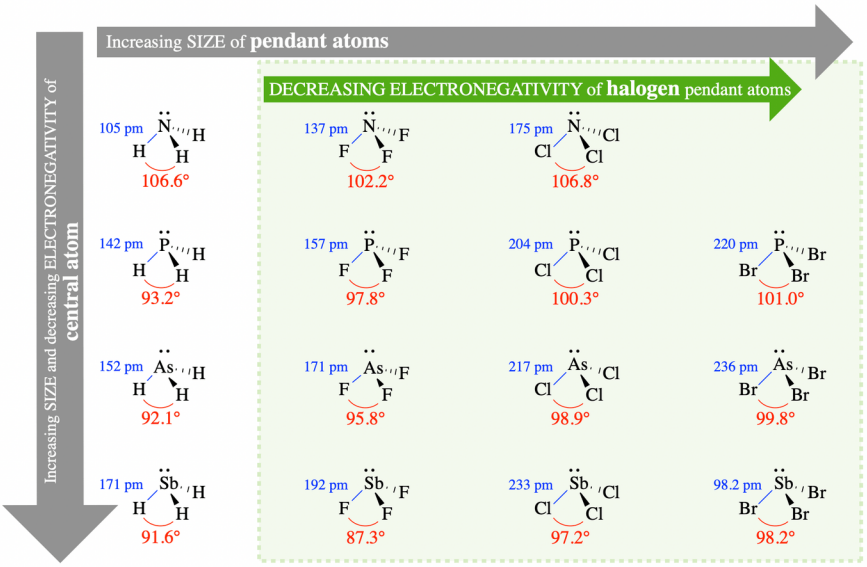


Figure 2.1.2.3.2: Several molecules with trigonal pyramidal electronic geometry are shown arranged according to size of the central atom (increasing size of central atom from top to bottom) and pendant atom (increasing size of pendant atoms from left to right). Bond angles and bond lengths are indicated. (Kathryn Haas; CC-NC-BY-SA)

Trends in Size

First, let's examine how the size of the central and pendant groups might influence bond angle. In VSEPR theory, **the size of atoms (or groups of atoms) will affect bond angles due to changes in steric interactions between pendant groups.**

Size of the central atom

Examine the relationship between the size of the central atom and the bond angles in Figure 2.1.2.3.2 (go down any column in the figure). For example, compare NH_3, PH_3, AsH_3, and SbH_3, with bond angles 106.6°, 93.2°, 92.1°, and 91.6°, respectively. In this series, the size of the central atom increases from N to Sb while the size of the pendant atom (hydrogen) remains constant. *As the size of the central atom increases, the bond angles decrease; thus, we observe a negative relationship between size of the central atom and the bond angle in these molecules*. This relationship is explained by sterics. As the central atom increases in size, the bond lengths also increase and the pendant atoms are farther from each other in space. In VSEPR theory, this will reduce steric interactions between the pendant groups. Since the lone pair on these molecules is more repulsive than bonded groups, the decrease in steric interactions between bonded groups results in a decrease in bond angles.

Size of the pendant atoms (or groups)

Examine the relationships between size of the halogen pendant atoms and bond angle in Figure 2.1.2.3.2 (go across any row within the shaded region). For example, compare PF_3, PCl_3, and PBr_3, with bond angles 97.8°, 100.3°, and 101.0°, respectively. In this series, the size of the pendant atom increases from F to Br while the central atom remains constant (phosphorous). *As the size of pendant atoms increases, the bond angle increases; thus, we observe a direct relationship between size of the pendant group and the bond angle in these molecules*. Again, we can explain this using sterics. As the size of the pendant atoms increases, sterics between the pendant groups will increase (despite small changes in bond length). Increased steric interactions between pendant groups will prefer larger bond angles between the groups.

This trend fails, however, if we consider the molecules with hydrogen as the pendant atoms. Notice, for example, that H is the smallest pendant atom. If we consider the trend described above, we should assume that XH_3 (where X is a variable atom) would have the smallest bond angle in the series of XH_3, XF_3, XCl_3, and XBr_3. However this is not the case of NH_3, NF_3, and NCl_3, with bond angles 106.6°, 102.2°, and 106.8°, respectively. To explain the variation in these bond angles, we need to consider electronegativity.

Trends in Electronegativity

Now let's examine how electronegativity influences bond angles around a central atom. In VSEPR theory, **electronegativity of atoms/groups will affect bond angles due to changes in the distribution of electron pairs around the central atom (and thus changes in the severity of electron pair repulsion).** This really comes down to bond polarity caused by the difference in electronegativity between the central atom and pendant groups (bond polarity in the context of valence bond theory). In a polar bond, the more electronegative atom will pull electron density towards itself. When a pendant atom is more electronegative, it will pull the bonded electron pair towards itself and away from the central atom; this will reduce the electron pair repulsion between bonded electron pairs on the central atom. A decrease in electron pair repulsion on the central atom should decrease bond angles between the groups (Figure 2.1.2.3.3).

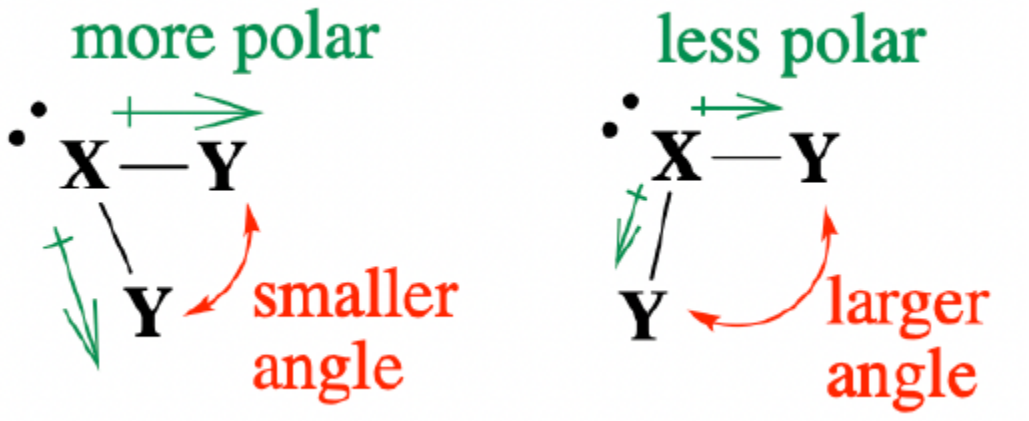


Figure 2.1.2.3.3. When electron pairs are distributed away from the central atom, repulsions are decreased, allowing smaller bond angles. (Kathryn Haas; CC-NC-BY-SA)

Electronegativity is an alternative explanation to the trends we already examined above in Figure 2.1.2.3.2 . For example, when we compare the halogen pendant atoms (shaded region in Figure 2.1.2.3.2) , the electronegativity of pendant groups decreases, bond polarity of the bonds decreases, and bond angles increase going from left to right and from F to Br. As more electron density remains on the central atom, electron repulsion between the bonded pairs increases and bond angles increase.

The electronegativity argument can also be used to explain the fact that NH_3 (106.6°) has a larger bond angle than NF_3 (102.2°). This particular case illustrates how electronegativity and size can be competing factors. While electronegativity differences seem to dominate in the case of NH_3 (106.6°) compared to NF_3 (102.2°), size differences still dominate in the cases of other XH_3 and XF_3 examples in Figure 2.1.2.3.2).

Exercise 2.1.2.3.1

Predict the geometry and approximate bond angles. Then put the molecules in each series in order of smallest to largest bond angle. Defend your answer.

a. The X-S-X bond angle in OSF_2, $OSCl_2$, $OSBr_2$
b. H_2O, H_2S, H_2Se, H_2Te
c. H_2O, OF_2, OCl_2

Answer (a) available at the end of this section.

Group Electronegativities

You probably heard the terms "electron donating group" and "electron withdrawing group" from your coursework in Organic Chemistry. For example, the acid trifluoroacetic acid (TFA) is more acidic than acetic acid due to the electron withdrawing effects of the CF_3 group compared to CH_3. CF_3 is an electron withdrawing group, while CH_3 is an electron donating group. In other words,

CF_3 is more electronegative than CH_3.

The electron withdrawing ability (electronegativity) of groups can be estimated and compared, just as they are with atoms. Although there is no one scale that is used for group electronegativities, and published values even for the same groups vary widely, there are reliable trends within similar groups. The same size and electronegativity factors discussed above that affect bond angles for *pendant atoms*, also can be used to rationalize distorted bond angles for *pendant groups* around a central atom.

Exercise 2.1.2.3.2

Consider the relative electronegativities and sizes of the pendant atoms/groups in the following examples. Is the trend in bond angles what you would expect from the relative group electronegativities and relative sizes? What, if any, is the more dominant factor in determining the trend?

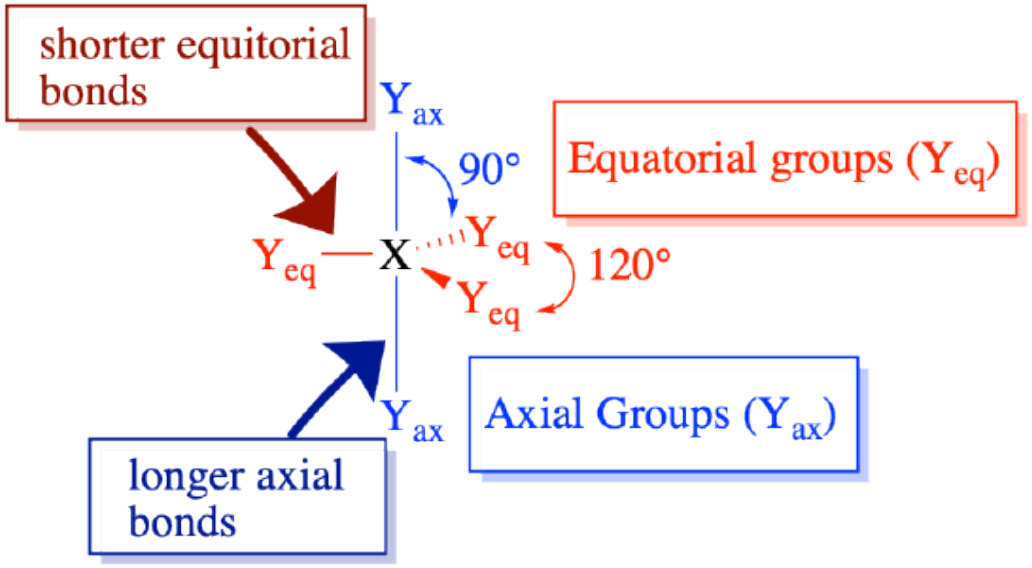
a. $N(CH_3)_3$ has an C-N-C bond angle of 110.9°, while $N(CF_3)_3$ has a bond angle of 117.9°.
b. The X-S-X bond angles in molecules of the form $SO_2(X)_2$ are: $SO_2(OH)_2$ 101.3°; $SO_2(CF_3)_2$ 102.0°; $SO_2(CH_3)_2$ 102.6°.

Answer (a) available at the end of this section.

Answer (b) available at the end of this section.

Special case of electronegativity and size in steric number 5 (trigonal bypyramid)

Molecules with steric number 5 are interesting because they posses two different types of positions (equatorial and axial). These positions have unique bond angles and bond lengths. Pendant atoms/groups have different preferences for the axial and equatorial positions that depend somewhat on their electronegativity.



Molecules with steric number 5 possess different bond angles and lengths for axial (ax) and equatorial (eq) pendant atoms. (CC-BY-NC-SA; Kathryn Haas)

In a previous section, we discussed the preference of lone pairs and multiple bonds for the equatorial positions in trigonal bipyramidal molecules. VSEPR theory rationalizes this by assuming that lone pairs and multiple bonds are more repulsive than the electron pairs in single bonds. Equatorial positions are less crowded (with only two closest neighbors at 90°, and two farther neighbors at 120°) compared to axial positions (with three closest neighbors at 90°), thus the more repulsive groups prefer the less crowded equatorial positions.

Pendant groups that are more electronegative result in weaker electron pair repulsion around the central atom, while groups that

are less electronegative result in stronger electron-pair repulsion around the central atom (as described above). The result for steric number 5: **bonding pairs to *less electronegative elements* are *more repulsive*, and *generally prefer equatorial* positions.** Still, lone pairs and multiple bonds are more repulsive than single bonds and would show a stronger preference for equatorial positions.

Examples and Nuances

Exercise 2.1.2.3.3

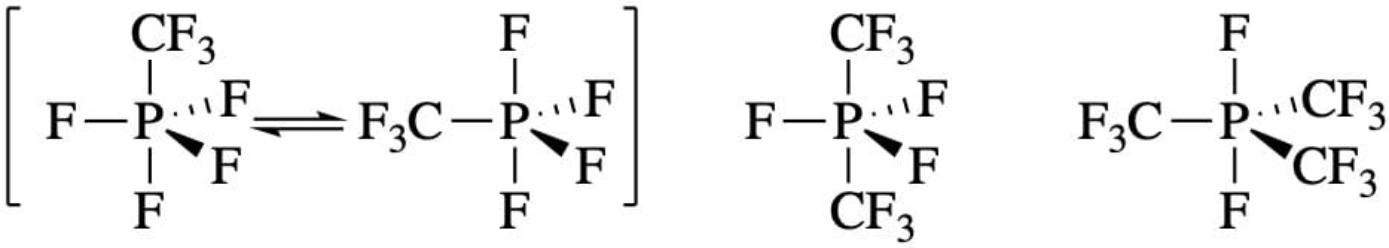
Some examples of molecule that demonstrate the equatorial preference of less electronegative groups are below. Predict (draw) their structures.

a. PF_4Cl, PF_3Cl_2, and PF_2Cl_3
b. $PF_4(CH_3)$ $PF_3(CH_3)_2$, and $PF_2(CH_3)_3$

Answer (a) available at the end of this section.

Answer (b) available at the end of this section.

In the exercise above, the structures can be explained by the electronegativity of the pendant groups; less electronegative groups prefer the equatorial positions. There are other similar molecules for which explanations (or predictions) are difficult. For example, the series of molecules below seems to have completely random placement of F and CF_3 groups. **These structures could not be predicted based on VSEPR theory.** It seems that in this case, the more symmetrical arrangements of pendant groups is preferred.



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Acknowledgment

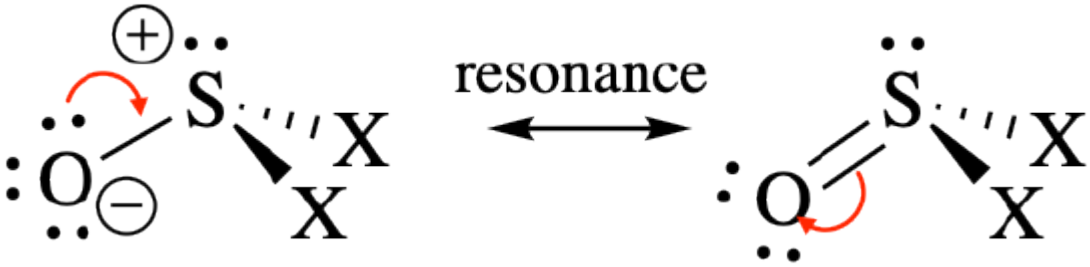
- Matthew Salem (UC Davis) (Pauling Electronegativity)
- Introduction to Inorganic Chemistry Wikibook (https://chem.libretexts.org/Bookshel..._Bond_Strength)

- Curated or created by Kathryn Haas

Answers

Exercise 2.1.2.3.1

Geometry and predicted bond angles: These are molecules with steric number 4. They can be written as two different resonance structures, and the resonance hybrid would have double bond character between S and O.



We would expect a trigonal pyramidal geometry with all bond angles <109.5° because the lone pair is more repulsive than bonds. Because the double bond is more repulsive than single bonds, we should also expect the O-S-X bond angles to be greater than the X-S-X bond angles.

Trend: This is a series of molecules that varies in the identity of the pendant atoms; the variation is within the halogens. The size of the halogens increases, and the electronegativity decreases in the order F, Cl, Br. Both size and electronegativity would lead us to conclude that the X-S-X bond angles would increase in the order $OSF_2 < OSCl_2 < OSBr_2$

Explanation: (1) Increasing electonegativity of the pendant atom (F > Cl > Br) increases the polarity of the bond and reduces the electron density of the bonded pair on the central atom. This reduces the e-e repulsions of adjacent bonded electron pairs on S, allowing the halogens to become closer. The more electronegative pendant atoms can have smaller bond angles. (2) Increasing size of pendant atoms (F < Cl < Br) increases steric repulsions and increases bond angle. Both explanations lead to the same predicted trend.

The actual measured X-S-X bond angles are OSF_2 (92.3°) / $OSCl_2$ (96.2°) / $OSBr_2$ (98.2°). The trend in these bond angles is consistent with the prediction.

Geometry and predicted bond angles: These are molecules with steric number 4, bent molecular geometry, with predicted bond angles <109.5° because the two lone pairs are each more repulsive than the bonds. There are two lone pairs and two single bonds to H around each central atom.

Trend: This is a series of molecules that varies in the identity of the central atom. The central atom increases in the order O < S < Se < Te, where Te is the largest element and O is the smallest. Arguments based on size would lead us to predict that the pendant groups of H_2Te would be less sterically crowded and thus have a smaller bond angle than the pendant groups of H_2O. The electronegativity decreases in the order O > S > Se > Te, where O is the most electronegative element and Te is the least. Thus, we expect the bonding electro pairs to be closer to the central atom on O than they would be on Te; we should expect H_2Te to have the least electron pair repulsions and thus smallest bond angle in this series, while H_2O would have the strongest electron pair repulsions and largest bond angles.

Both arguments lead to the same conclusion, that the order of increasing bond angle is $H_2Te < H_2Se < H_2S < H_2O$.

The actual measured bond angles are H_2Te (90.2°) / H_2Se (90.6°) / H_2S (92.1°) / H_2O (104.5). The trend in these bond angles is consistent with prediction.

Geometry and predicted bond angles: These are molecules with steric number 4, bent molecular geometry, with predicted bond angles <109.5° because the two lone pairs are each more repulsive than the bonds. There are two lone pairs and two single bonds to H around each central atom. (This is similar to the case in (b)).

Trend: This is a series of molecules that varies in the identity of the pendant atoms; two of the molecules have halogens, and the other has hydrogen pendant atoms. This is a case where size and electronegativity will be conflicting factors because trends in electronegativity do not mirror the trend in size.

- *Size:* The size of pendant atoms increases in the order H < F < Cl where H is smallest and Cl is largest. Prediction of bond angles based on size alone would lead to the predicted order of increasing bond angle $H_2O < OF_2 < OCl_2$.
- *Electronegativity*: The electronegativity decreases in the order F > Cl > H where F has the greatest electronegativity and H has the least. Since we expect the most electronegative pendant atoms to have the smallest bond angles, prediction based on electronegativity alone would lead to the predicted order of increasing bond angle $OF_2 < OCl_2 < H_2O$.

The points above illustrate how the two different arguments would lead to different predictions about the trend in bond angle. This makes it difficult to predict the actual order of increasing bond angle. However, we saw above in the example of NH_3 vs NF_3 that electronegativity is more important than size; yet in the case of NH_3 vs NCl_3, the much larger size of the pendant atom is more important. If we apply this lesson to the current problem, we might predict the order $OF_2 < H_2O < OCl_2$, and in fact this more nuanced prediction, based on a similar case, matches the actual order for measured bond angles: OF_2 (103.3°) < H_2O (104.5°) < OCl_2 (110.9°).

Exercise 2.1.2.3.2

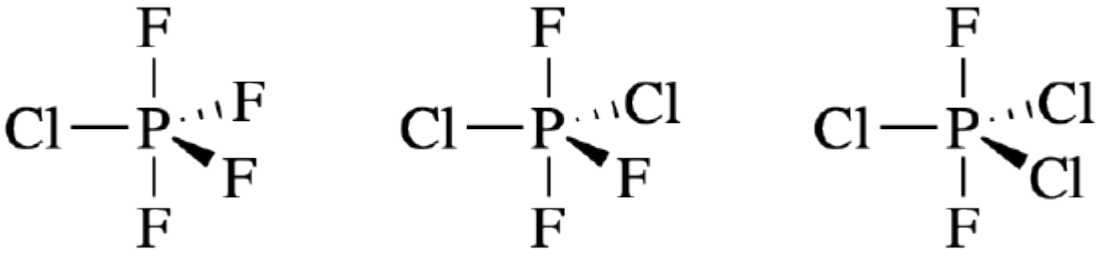
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Exercise 2.1.2.3.2

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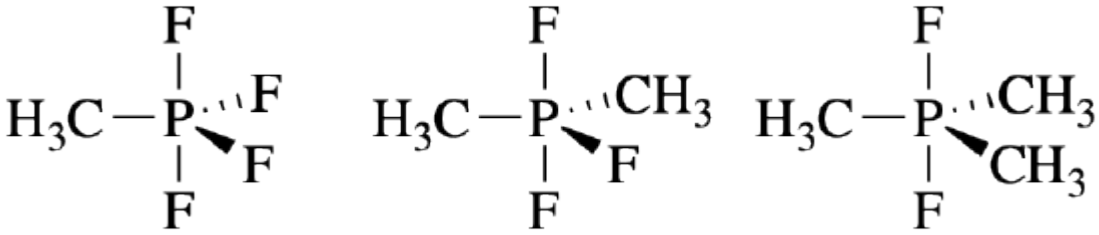
Exercise 2.1.2.3.3

Cl is less electronegative than F; thus we expect Cl to have stronger preference for the equatorial positions.



Exercise 2.1.2.3.3

CH_3, an electron donating group, is less electronegative than F. We expect CH_3 to have a stronger preference for the equatorial positions.



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2.1.2.4: Ligand Close Packing

Introduction

Ligand Close Packing (LCP) theory is complimentary to VSEPR, except that LCP focuses on repulsions between pendant *atoms* ("outer" atoms that are not directly bonded to one another), rather than focusing on the chemical environment around the central atom in a molecule. Both LCP and the VSEPR models were developed by Robert Gillespie.

The LCP model assumes that ligands (or pendant atoms) "pack" as closely as possible around a central atom. A given ligand will have a specific atomic radius when bound to a central atom. The distance between two ligands around the same central atom is simply the sum of the atomic radii of the pendant atoms. Therefore for a specific set of ligands around a specific central atom, the ligand-ligand distances are constant despite the coordination number or bond angles. In other words, for a series of similar molecules with the same central atom, while bond angles and bond distances of pendant atoms may change, the distances between two pendant atoms remain the same.

Ligand Close Packing Theory

According to LCP, distances between two pendant atoms are similar...

- even when steric number changes
- even when bond angles change
- Reason: pendant atoms "pack" around the central atom.

Ligand Close Packing and Bond Distances

If the distance between non-bonded atoms remains constant even while bond angles change, then the bond length between the pendant and central atom must change to accommodate. For example, PF_4^+ and PF_3O have almost identical $F-F$ distances of 238 and 237 pm, respectively. As expected from VSEPR, the $F-P-F$ bond angle in PF_4^+ is 109.5°. The $F-P-F$ bond angle in PF_3O (101.1°) is smaller due to the increased repulsion of the oxygen double bond. Therefore the P-F bond lengths must be different. In fact, the P-F bond distances are 145.7 pm in PF_4^+ and 154 pm in PF_3O.

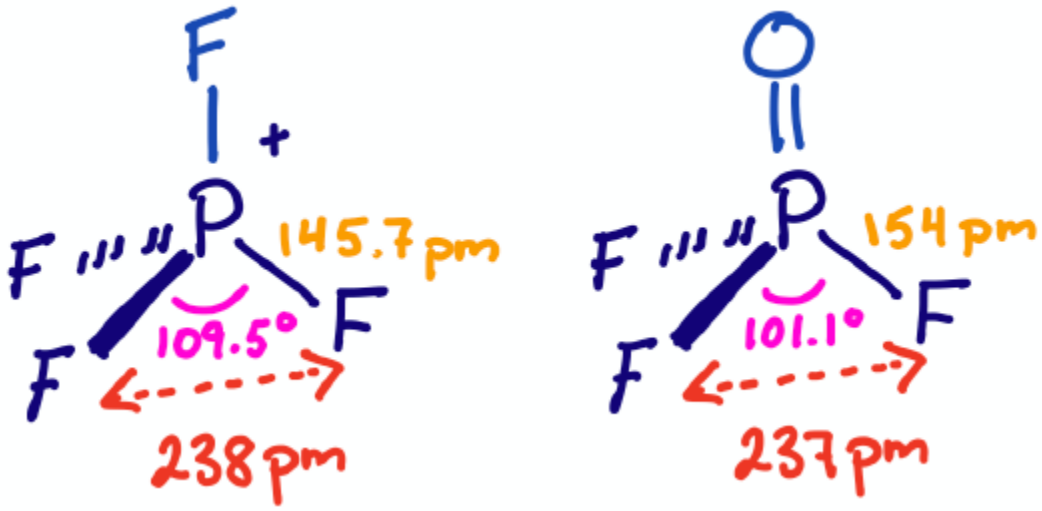


Figure 2.1.2.4.1: The molecular structures of PF_4^+ and PF_3O. The distances between neighboring F atoms are similar in the two molecules, while bond lengths and angles differ. The PF_4^+ ion has a $P-F$ bond length of 145.7 pm, an $F-P-F$ bond angle of 109.5°, and a distance of 238 pm between neighboring F atoms. The PF_3O molecule has a $P-F$ bond length of 154 pm, an $F-P-F$ bond angle of 101.1°, and a distance of 237 pm between neighboring F atoms. (CC-BY-NC-SA; Kathryn Haas)

The relationship between bond angles, bond lengths, and close-packing distance is described by right angle trigonometry (recall SOA-CAH-TOA). In a right triangle, the hypotenuse is the longest side, opposite to the right angle. For either of the other two angles in the triangle, the angle (θ) and lengths of the sides (*opposite* and *adjacent* to θ) are related by the trigometric functions shown in Figure 2.1.2.4.2 .

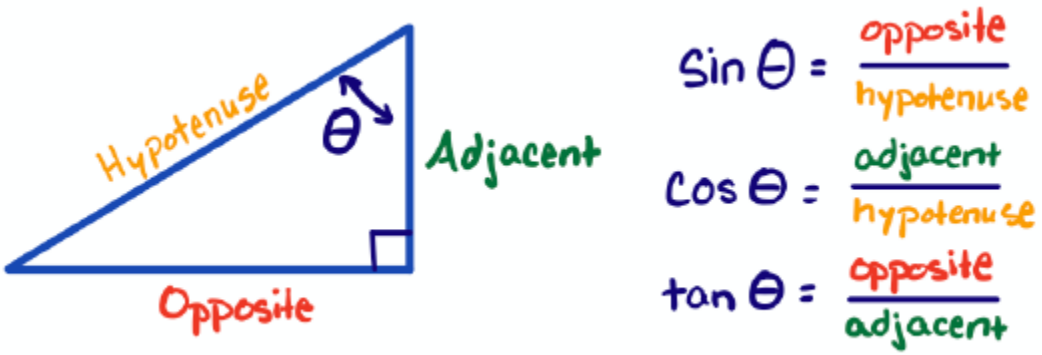


Figure 2.1.2.4.2: Visual depiction of SOA-CAH-TOA. (CC-BY-NC-SA; Kathryn Haas)

In the case of a molecule, we can apply right angle trigonometry by imagining that the bond angle is divided into two right angles, as illustrated in Figure 2.1.2.4.2. The hypotenuse of the triangles is the bond length, the opposite side is one half of the close-packing distance, and θ is one half the bond angle.

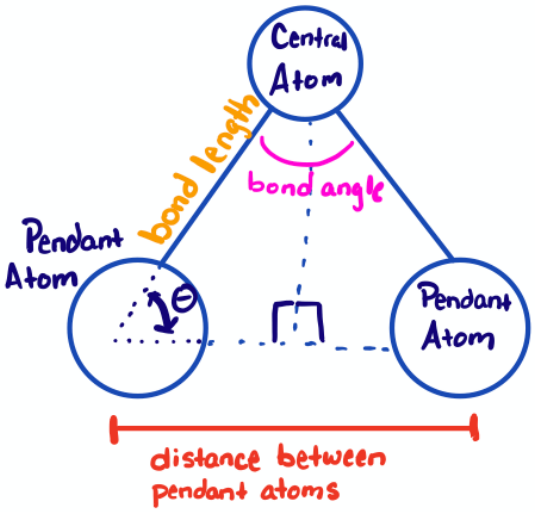


Figure 2.1.2.4.1: Illustration of how right angle trigonometry can be applied to determine bond angle, bond length, or distance between neighboring atoms: any bond angle can be divided into two right angles where the bond length is the hypotenuse, the distance between neighbors is twice the opposite side, and the bond angle is twice θ. (CC-BY-NC-SA; Kathryn Haas)

Exercise 2.1.2.4.1

The distance between F atoms is 212 pm in both NF_4^+ and NF_3. The bond angles are 109.5° and 102.3°, respectively. What are the expected $N-F$ bond lengths?

Answer available at the end of this section.

Sources and Resources

- https://en.Wikipedia.org/wiki/LCP_th...ieNyholm1957-3

Answers

Exercise 2.1.2.4.1



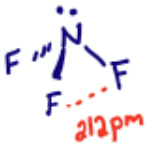
$$\sin\theta = \frac{\text{opposite}}{\text{hypotenuse}}$$

$$\sin\left(\frac{1}{2}\cdot 109.5^\circ\right) = \frac{106\,\text{pm}}{x}$$

$$x = 130\ \text{pm}$$

Triangle:





$$\sin\theta = \frac{\text{opposite}}{\text{hypotenuse}}$$

$$\sin\left(\frac{1}{2}\cdot 102.3\right) = \frac{106\,\text{pm}}{x}$$

$$x = 136\ \text{pm}$$

The actual measured bond lengths are 130 pm for NF_4^+ and 136.5 pm for NF_3.

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2.1.3: Molecular Polarity

Dipole moments occur when there is a separation of charge. They can occur between two ions in an ionic bond or between atoms in a covalent bond; dipole moments arise from differences in electronegativity. The larger the difference in electronegativity, the larger the dipole moment. The distance between the charge separation is also a deciding factor in the size of the dipole moment. The dipole moment is a measure of the polarity of the molecule.

Introduction

When atoms in a molecule share electrons unequally, they create what is called a dipole moment. This occurs when one atom is more electronegative than another, resulting in that atom pulling more tightly on the shared pair of electrons, or when one atom has a lone pair of electrons and the difference of electronegativity vector points in the same way. One of the most common examples is the water molecule, made up of one oxygen atom and two hydrogen atoms. The differences in electronegativity and lone electrons give oxygen a partial negative charge and each hydrogen a partial positive charge.

Dipole Moment

When two electrical charges, of opposite sign and equal magnitude, are separated by a distance, an electric dipole is established. The size of a dipole is measured by its dipole moment (μ). Dipole moment is measured in Debye units, which is equal to the distance between the charges multiplied by the charge (1 Debye equals $3.34 \times 10^{-30}\ C\ m$). The dipole moment of a molecule can be calculated by Equation 2.1.3.1:

$$\vec{\mu} = \sum_i q_i \vec{r}_i \tag{2.1.3.1}$$

where

- $\vec{\mu}$ is the dipole moment vector
- q_i is the magnitude of the i^{th} charge, and
- $\vec{r}_i$ is the vector representing the position of i^{th} charge.

The dipole moment acts in the direction of the vector quantity. An example of a polar molecule is $\mathrm{H_2O}$. Because of the lone pair on oxygen, the structure of $\mathrm{H_2O}$ is bent (via VSEPR theory), which means that the vectors representing the dipole moment of each bond do not cancel each other out. Hence, water is polar.

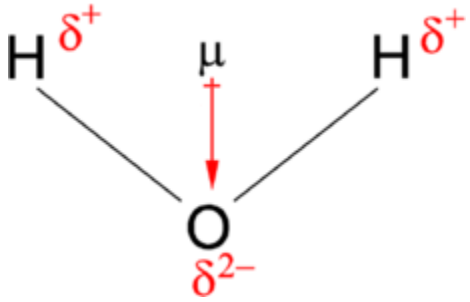


Figure 2.1.3.1: Dipole moment of water. The convention in chemistry is that the arrow representing the dipole moment goes from positive to negative. Physicist tend to use the opposite orientation.

The vector points from positive to negative, on both the molecular (net) dipole moment and the individual bond dipoles. Table A2 shows the electronegativity of some of the common elements. The larger the difference in electronegativity between the two atoms, the more electronegative that bond is. To be considered a polar bond, the difference in electronegativity must be large. The dipole moment points in the direction of the vector quantity of each of the bond electronegativities added together.

It is relatively easy to measure dipole moments: just place a substance between charged plates (Figure 2.1.3.2); polar molecules increase the charge stored on the plates, and the dipole moment can be obtained (i.e., via the capacitance of the system).

Nonpolar CCl_4 is not deflected; moderately polar acetone deflects slightly; highly polar water deflects strongly. In general, polar molecules will align themselves: (1) in an electric field, (2) with respect to one another, or (3) with respect to ions (Figure 2.1.3.2).

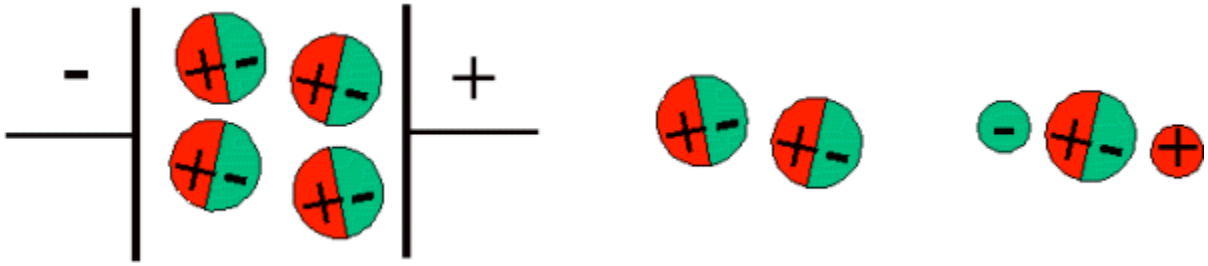


Figure 2.1.3.2: Polar molecules align themselves in an electric field (left), with respect to one another (middle), and with respect to ions (right)

Equation 2.1.3.1 can be simplified for a simple separated two-charge system like diatomic molecules or when considering a bond dipole within a molecule

$$\mu_{diatomic} = Q \times r \tag{2.1.3.2}$$

This bond dipole is interpreted as the dipole from a charge separation over a distance r between the partial charges Q^+ and Q^- (or the more commonly used terms δ^+ - δ^-); the orientation of the dipole is along the axis of the bond. Consider a simple system of a single electron and proton separated by a fixed distance. When the proton and electron are close together, the dipole moment (degree of polarity) decreases. However, as the proton and electron get farther apart, the dipole moment increases. In this case, the dipole moment is calculated as (via Equation 2.1.3.2):

$$\begin{aligned} \mu &= Qr \\ &= (1.60 \times 10^{-19}\, C)(1.00 \times 10^{-10}\, m) \\ &= 1.60 \times 10^{-29}\, C \cdot m \end{aligned}$$

The Debye characterizes the size of the dipole moment. When a proton and electron are 100 pm apart, the dipole moment is $4.80\ D$:

$$\begin{aligned} \mu &= (1.60 \times 10^{-29}\, C \cdot m)\left(\frac{1\ D}{3.336 \times 10^{-30}\, C \cdot m}\right) \\ &= 4.80\ D \end{aligned}$$

$4.80\ \ D$ is a key reference value and represents a pure charge of +1 and -1 separated by 100 pm. If the charge separation is increased then the dipole moment increases (linearly):

- If the proton and electron are separated by 120 pm:

$$\mu = \frac{120}{100}(4.80\ D) = 5.76\, D \tag{2.1.3.3}$$

- If the proton and electron are separated by 150 pm:

$$\mu = \frac{150}{100}(4.80\ D) = 7.20\, D \tag{2.1.3.4}$$

- If the proton and electron are separated by 200 pm:

$$\mu = \frac{200}{100}(4.80\ D) = 9.60\, D \tag{2.1.3.5}$$

Example 2.1.3.1: Water

The water molecule in Figure 2.1.3.1 can be used to determine the direction and magnitude of the dipole moment. From the electronegativities of oxygen and hydrogen, the difference in electronegativity is 1.2e for each of the hydrogen-oxygen bonds. Next, because the oxygen is the more electronegative atom, it exerts a greater pull on the shared electrons; it also has two lone pairs of electrons. From this, it can be concluded that the dipole moment points from between the two hydrogen atoms

toward the oxygen atom. Using the equation above, the dipole moment is calculated to be 1.85 D by multiplying the distance between the oxygen and hydrogen atoms by the charge difference between them and then finding the components of each that point in the direction of the net dipole moment (the angle of the molecule is 104.5˚).

The bond moment of the O-H bond =1.5 D, so the net dipole moment is

$$\mu = 2(1.5)\cos\left(\frac{104.5^\circ}{2}\right) = 1.84\ D$$

Polarity and Structure of Molecules

The shape of a molecule and the polarity of its bonds determine the OVERALL POLARITY of that molecule. A molecule that contains polar bonds might not have any overall polarity, depending upon its shape. The simple definition of whether a complex molecule is polar or not depends upon whether its overall centers of positive and negative charges overlap. If these centers lie at the same point in space, then the molecule has no overall polarity (and is non polar). If a molecule is completely symmetric, then the dipole moment vectors on each molecule will cancel each other out, making the molecule nonpolar. A molecule can only be polar if the structure of that molecule is not symmetric.

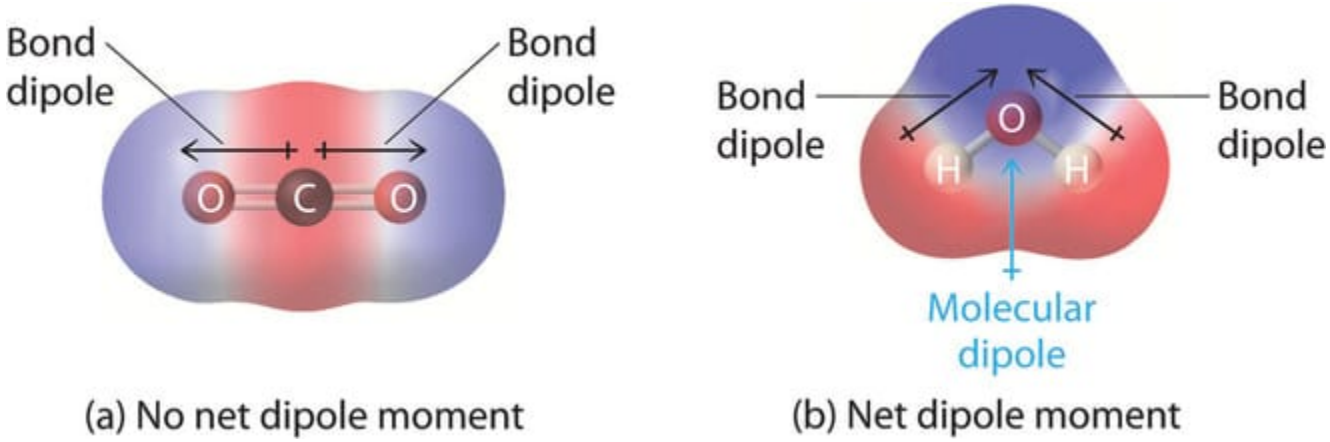


Figure 2.1.3.3: Charge distributions of CO_2 and H_2O\). Blue and red colored regions are negatively and positively signed regions, respectively. (CC BY-SA-NC 3.0; anonymous)

A good example of a nonpolar molecule that contains polar bonds is carbon dioxide (Figure $2.1.3.3a$). This is a linear molecule and each C=O bond is, in fact, polar. The central carbon will have a net positive charge, and the two outer oxygen atoms a net negative charge. However, since the molecule is linear, these two bond dipoles cancel each other out (i.e. the vector addition of the dipoles equals zero) and the overall molecule has a zero dipole moment ($\mu = 0$).

> Although a polar bond is a prerequisite for a molecule to have a dipole, not all molecules with polar bonds exhibit dipoles

For AB_n molecules, where A is the central atom and B are all the same types of atoms, there are certain molecular geometries which are symmetric. Therefore, they will have no dipole even if the bonds are polar. These geometries include linear, trigonal planar, tetrahedral, octahedral and trigonal bipyramid.

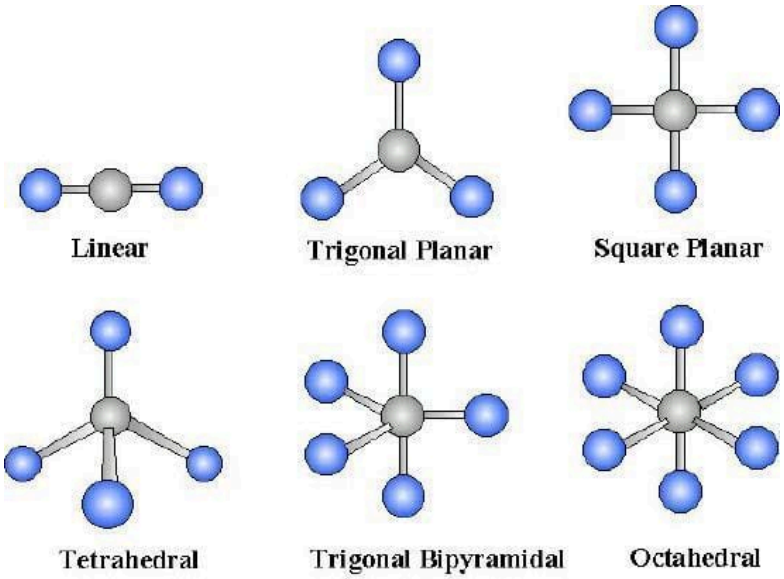
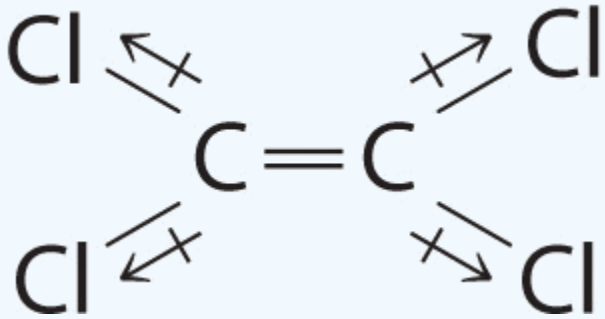


Figure 2.1.3.4: Molecular geometries with exact cancellation of polar bonding to generate a non-polar molecule ($\mu = 0$)

Example 2.1.3.3: C_2Cl_4

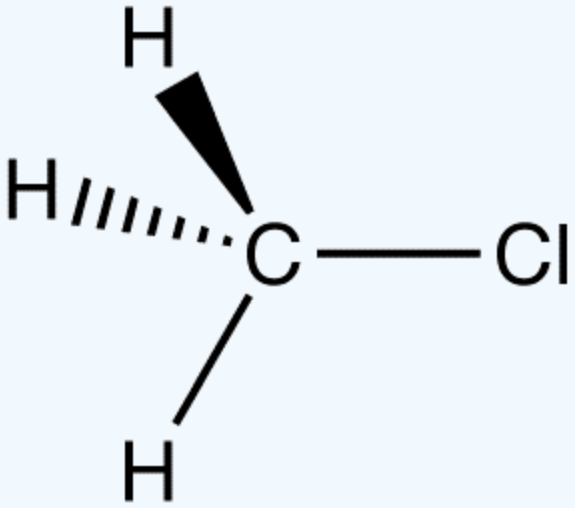
Although the C–Cl bonds are rather polar, the individual bond dipoles cancel one another in this symmetrical structure, and $Cl_2C{=}CCl_2$ does not have a net dipole moment.



Example 2.1.3.3: CH_3Cl

C-Cl, the key polar bond, is 178 pm. Measurement reveals 1.87 D. From this data, % ionic character can be computed. If this bond were 100% ionic (based on proton & electron),

$$\mu = \frac{178}{100}(4.80\ D)$$
$$= 8.54\ D$$



Although the bond length is ***increasing***, the dipole is ***decreasing*** as you move down the halogen group. The electronegativity decreases as we move down the group. Thus, the greater influence is the electronegativity of the two atoms (which influences the ***charge*** at the ends of the dipole).

Table 2.1.3.1: Relationship between Bond length, Electronegativity and Dipole moments in simple Diatomics

Compound	Bond Length (Å)	Electronegativity Difference	Dipole Moment (D)
HF	0.92	1.9	1.82
HCl	1.27	0.9	1.08
HBr	1.41	0.7	0.82
HI	1.61	0.4	0.44

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2.1.4: Hydrogen Bonding

A hydrogen bond is an intermolecular force (IMF) that forms a special type of dipole-dipole attraction when a hydrogen atom bonded to a strongly electronegative atom exists in the vicinity of another electronegative atom with a lone pair of electrons. Intermolecular forces (IMFs) occur between molecules. Other examples include ordinary dipole-dipole interactions and dispersion forces. Hydrogen bonds are are generally stronger than ordinary dipole-dipole and dispersion forces, but weaker than true covalent and ionic bonds.

The evidence for hydrogen bonding

Many elements form compounds with hydrogen. If you plot the boiling points of the compounds of the group 14 elements with hydrogen, you find that the boiling points increase as you go down the group.

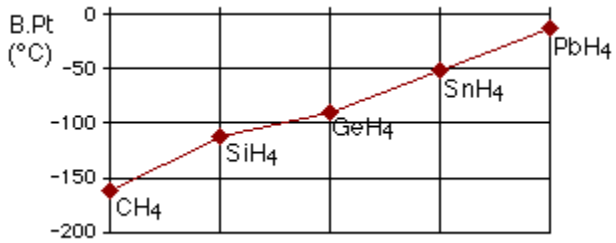


Figure 1: Boiling points of group 14 elemental halides.

The increase in boiling point happens because the molecules are getting larger with more electrons, and so van der Waals dispersion forces become greater. If you repeat this exercise with the compounds of the elements in groups 15, 16, and 17 with hydrogen, something odd happens.

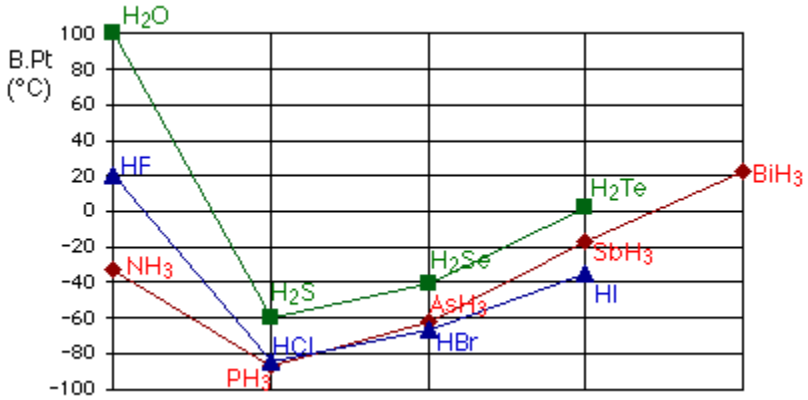


Figure 2: Boiling points of group 15-17 elemental halides.

Although the same reasoning applies for group 4 of the periodic table, the boiling point of the compound of hydrogen with the first element in each group is abnormally high. In the cases of NH_3, H_2O and HF there must be some additional intermolecular forces of attraction, requiring significantly more heat energy to break the IMFs. These relatively powerful intermolecular forces are described as hydrogen bonds.

Origin of Hydrogen Bonding

The molecules capable of hydrogen bonding include the following:

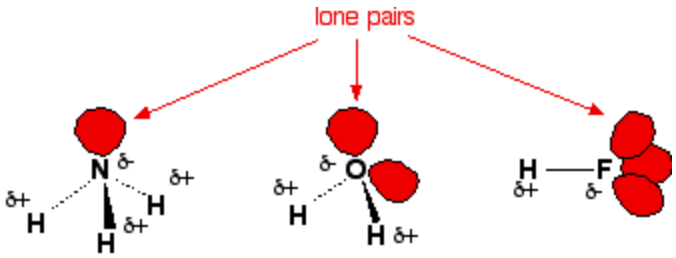


Figure 3: The lone pairs responsible for hydrogen bonding in NH_3, H_2O, and HF. The solid line represents a bond in the plane of the screen or paper. Dotted bonds are going back into the screen or paper away from you, and wedge-shaped ones are coming out towards you.

Notice that in each of these molecules:

- The hydrogen is attached directly to a highly electronegative atoms, causing the hydrogen to acquire a highly positive charge.
- Each of the highly electronegative atoms attains a high negative charge and has at least one "active" lone pair. Lone pairs at the 2-level have electrons contained in a relatively small volume of space, resulting in a high negative charge density. Lone pairs at higher levels are more diffuse and, resulting in a lower charge density and lower affinity for positive charge.

If you are not familiar with electronegativity, you should follow this link before you go on.

Consider two water molecules coming close together.

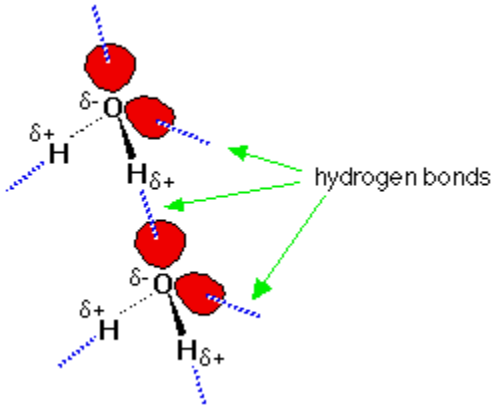


Figure 4: Hydrogen bonding in water

The δ^+ hydrogen is so strongly attracted to the lone pair that it is almost as if you were beginning to form a co-ordinate (dative covalent) bond. It doesn't go that far, but the attraction is significantly stronger than an ordinary dipole-dipole interaction. Hydrogen bonds have about a tenth of the strength of an average covalent bond, and are constantly broken and reformed in liquid water. If you liken the covalent bond between the oxygen and hydrogen to a stable marriage, the hydrogen bond has "just good friends" status.

Water is an ideal example of hydrogen bonding. Notice that each water molecule can potentially form four hydrogen bonds with surrounding water molecules: two with the hydrogen atoms and two with the with the oxygen atoms. There are exactly the right numbers of δ^+ hydrogens and lone pairs for every one of them to be involved in hydrogen bonding.

This is why the boiling point of water is higher than that of ammonia or hydrogen fluoride. In the case of ammonia, the amount of hydrogen bonding is limited by the fact that each nitrogen only has one lone pair. In a group of ammonia molecules, there are not enough lone pairs to go around to satisfy all the hydrogens. In hydrogen fluoride, the problem is a shortage of hydrogens. In water, two hydrogen bonds and two lone pairs allow formation of hydrogen bond interactions in a lattice of water molecules. Water is thus considered an ideal hydrogen bonded system.

More complex examples of hydrogen bonding

The hydration of negative ions

When an ionic substance dissolves in water, water molecules cluster around the separated ions. This process is called hydration. Water frequently attaches to positive ions by co-ordinate (dative covalent) bonds. It bonds to negative ions using hydrogen bonds.

> If you are interested in the bonding in hydrated positive ions, you could follow this link to co-ordinate (dative covalent) bonding.

The diagram shows the potential hydrogen bonds formed with a chloride ion, Cl-. Although the lone pairs in the chloride ion are at the 3-level and would not normally be active enough to form hydrogen bonds, they are made more attractive by the full negative charge on the chlorine in this case.

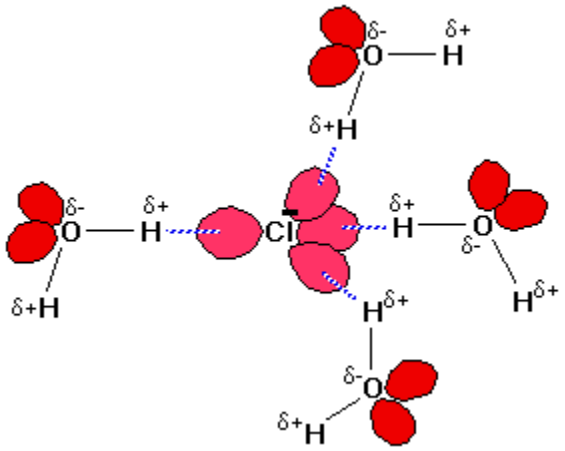


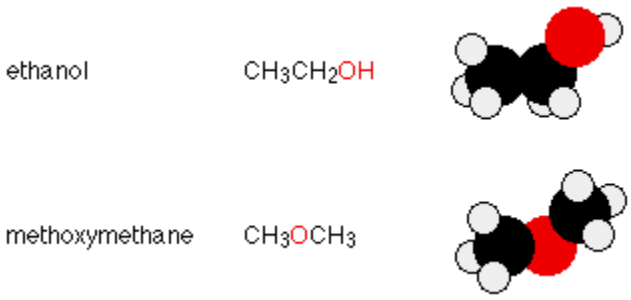
Figure 5: Hydrogen bonding between chloride ions and water.

However complicated the negative ion, there will always be lone pairs that the hydrogen atoms from the water molecules can hydrogen bond to.

Hydrogen bonding in alcohols

An alcohol is an organic molecule containing an -OH group. Any molecule which has a hydrogen atom attached directly to an oxygen or a nitrogen is capable of hydrogen bonding. Hydrogen bonds also occur when hydrogen is bonded to fluorine, but the HF group does not appear in other molecules. Molecules with hydrogen bonds will always have higher boiling points than similarly sized molecules which don't have an -O-H or an -N-H group. The hydrogen bonding makes the molecules "stickier," such that more heat (energy) is required to separate them. This phenomenon can be used to analyze boiling point of different molecules, defined as the temperature at which a phase change from liquid to gas occurs.

Ethanol, CH_3CH_2-O-H, and methoxymethane, CH_3-O-CH_3, both have the same molecular formula, C_2H_6O.



They have the same number of electrons, and a similar length. The van der Waals attractions (both dispersion forces and dipole-

dipole attractions) in each will be similar. However, ethanol has a hydrogen atom attached directly to an oxygen; here the oxygen still has two lone pairs like a water molecule. Hydrogen bonding can occur between ethanol molecules, although not as effectively as in water. The hydrogen bonding is limited by the fact that there is only one hydrogen in each ethanol molecule with sufficient $\delta+$ charge.

In methoxymethane, the lone pairs on the oxygen are still there, but the hydrogens are not sufficiently $\delta+$ for hydrogen bonds to form. Except in some rather unusual cases, the hydrogen atom has to be attached directly to the very electronegative element for hydrogen bonding to occur. The boiling points of ethanol and methoxymethane show the dramatic effect that the hydrogen bonding has on the stickiness of the ethanol molecules:

ethanol (with hydrogen bonding)	78.5°C
methoxymethane (without hydrogen bonding)	-24.8°C

The hydrogen bonding in the ethanol has lifted its boiling point about 100°C. It is important to realize that hydrogen bonding exists in addition to van der Waals attractions. For example, all the following molecules contain the same number of electrons, and the first two have similar chain lengths. The higher boiling point of the butan-1-ol is due to the additional hydrogen bonding.

pentane	$CH_3CH_2CH_2CH_2CH_3$	B.Pt: 36.3°C
butan-1-ol	$CH_3CH_2CH_2CH_2OH$	B.Pt: 117°C
2-methylpropan-1-ol	$CH_3CH(CH_3)CH_2OH$	B.Pt: 108°C

Comparing the two alcohols (containing -OH groups), both boiling points are high because of the additional hydrogen bonding; however, the values are not the same. The boiling point of the 2-methylpropan-1-ol isn't as high as the butan-1-ol because the branching in the molecule makes the van der Waals attractions less effective than in the longer butan-1-ol.

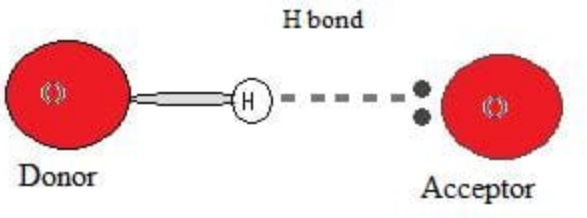
Hydrogen bonding in organic molecules containing nitrogen

Hydrogen bonding also occurs in organic molecules containing N-H groups; recall the hydrogen bonds that occur with ammonia. Examples range from simple molecules like CH_3NH_2 (methylamine) to large molecules like proteins and DNA. The two strands of the famous double helix in DNA are held together by hydrogen bonds between hydrogen atoms attached to nitrogen on one strand, and lone pairs on another nitrogen or an oxygen on the other one.

Donors and Acceptors

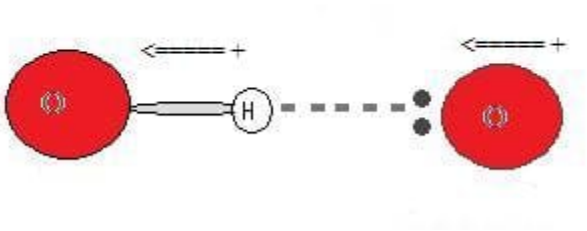
In order for a hydrogen bond to occur there must be both a hydrogen donor and an acceptor present. The donor in a hydrogen bond is usually a strongly electronegative atom such as N, O, or F that is covalently bonded to a hydrogen bond.

The hydrogen acceptor is an electronegative atom of a neighboring molecule or ion that contains a lone pair that participates in the hydrogen bond.



Why does a hydrogen bond occur?

Since the hydrogen donor (N, O, or F) is strongly electronegative, it pulls the covalently bonded electron pair closer to its nucleus, and away from the hydrogen atom. The hydrogen atom is then left with a partial positive charge, creating a dipole-dipole attraction between the hydrogen atom bonded to the donor and the lone electron pair of the acceptor. This results in a hydrogen bond.(see Interactions Between Molecules With Permanent Dipoles)

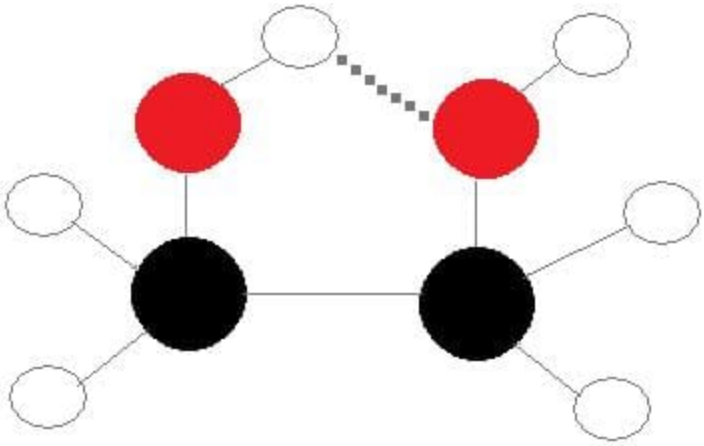


Types of hydrogen bonds

Although hydrogen bonds are well-known as a type of IMF, these bonds can also occur within a single molecule, between two identical molecules, or between two dissimilar molecules.

Intramolecular hydrogen bonds

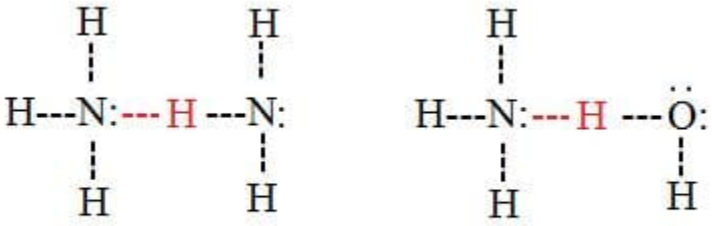
Intramolecular hydrogen bonds are those which occur *within* one single molecule. This occurs when two functional groups of a molecule can form hydrogen bonds with each other. In order for this to happen, both a hydrogen donor a hydrogen acceptor must be present within one molecule, and they must be within close proximity of each other in the molecule. For example, intramolecular hydrogen bonding occurs in ethylene glycol ($C_2H_4(OH)_2$) between its two hydroxyl groups due to the molecular geometry.



Intramolecular h-bonding in Ethylene Glycol molecule

Intermolecular hydrogen bonds

Intermolecular hydrogen bonds occur *between* separate molecules in a substance. They can occur between any number of like or unlike molecules as long as hydrogen donors and acceptors are present in positions where they can interact with one another. For example, intermolecular hydrogen bonds can occur between NH_3 molecules alone, between H_2O molecules alone, or between NH_3 and H_2O molecules.



Properties and effects of hydrogen bonds

On Boiling Point

When we consider the boiling points of molecules, we usually expect molecules with larger molar masses to have higher normal boiling points than molecules with smaller molar masses. This, without taking hydrogen bonds into account, is due to greater dispersion forces (see Interactions Between Nonpolar Molecules). Larger molecules have more space for electron distribution and thus more possibilities for an instantaneous dipole moment. However, when we consider the table below, we see that this is not always the case.

Compound	Molar Mass	Normal Boiling Point
H_2O	18 g/mol	373 K
HF	20 g/mol	292.5 K
NH_3	17 g/mol	239.8 K
H_2S	34 g/mol	212.9 K

Compound	Molar Mass	Normal Boiling Point
HCl	36.4 g/mol	197.9 K
PH_3	34 g/mol	185.2 K

We see that H_2O, HF, and NH_3 each have higher boiling points than the same compound formed between hydrogen and the next element moving down its respective group, indicating that the former have greater intermolecular forces. This is because H_2O, HF, and NH_3 all exhibit hydrogen bonding, whereas the others do not. Furthermore, H_2O has a smaller molar mass than HF but partakes in more hydrogen bonds per molecule, so its boiling point is higher.

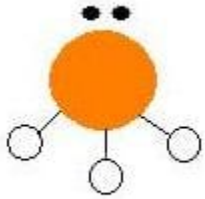
On Viscosity

The same effect that is seen on boiling point as a result of hydrogen bonding can also be observed in the viscosity of certain substances. Substances capable of forming hydrogen bonds tend to have a higher viscosity than those that do not form hydrogen bonds. Generally, substances that have the possibility for multiple hydrogen bonds exhibit even higher viscosities.

Factors preventing Hydrogen bonding

Electronegativity

Hydrogen bonding cannot occur without significant electronegativity differences between hydrogen and the atom it is bonded to. Thus, we see molecules such as PH_3, which do not participate in hydrogen bonding. PH_3 exhibits a trigonal pyramidal molecular geometry like that of ammonia, but unlike NH_3 it cannot hydrogen bond. This is due to the similarity in the electronegativities of phosphorous and hydrogen. Both atoms have an electronegativity of 2.1, and thus, there is no dipole moment. This prevents the hydrogen atom from acquiring the partial positive charge needed to hydrogen bond with the lone electron pair in another molecule. (see Polarizability)



Atom Size

The size of donors and acceptors can also affect the ability to hydrogen bond. This can account for the relatively low ability of Cl to form hydrogen bonds. When the radii of two atoms differ greatly or are large, their nuclei cannot achieve close proximity when they interact, resulting in a weak interaction.

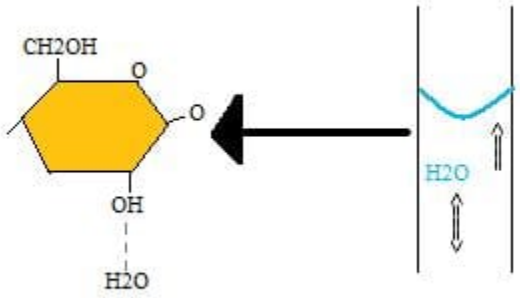


Hydrogen Bonding in Nature

Hydrogen bonding plays a crucial role in many biological processes and can account for many natural phenomena such as the Unusual properties of Water. In addition to being present in water, hydrogen bonding is also important in the water transport system of plants, secondary and tertiary protein structure, and DNA base pairing.

Plants

The cohesion-adhesion theory of transport in vascular plants uses hydrogen bonding to explain many key components of water movement through the plant's xylem and other vessels. Within a vessel, water molecules hydrogen bond not only to each other, but also to the cellulose chain that comprises the wall of plant cells. Since the vessel is relatively small, the attraction of the water to the cellulose wall creates a sort of capillary tube that allows for capillary action. This mechanism allows plants to pull water up into their roots. Furthermore, hydrogen bonding can create a long chain of water molecules, which can overcome the force of gravity and travel up to the high altitudes of leaves.



Proteins

Hydrogen bonding is present abundantly in the secondary structure of proteins, and also sparingly in tertiary conformation. The secondary structure of a protein involves interactions (mainly hydrogen bonds) between neighboring polypeptide backbones which contain nitrogen-hydrogen bonded pairs and oxygen atoms. Since both N and O are strongly electronegative, the hydrogen atoms bonded to nitrogen in one polypeptide backbone can hydrogen bond to the oxygen atoms in another chain and vice-versa. Though they are relatively weak, these bonds offer substantial stability to secondary protein structure because they repeat many times and work collectively.

In tertiary protein structure, interactions are primarily between functional R groups of a polypeptide chain; one such interaction is called a hydrophobic interaction. These interactions occur because of hydrogen bonding between water molecules around the hydrophobe that further reinforces protein conformation.

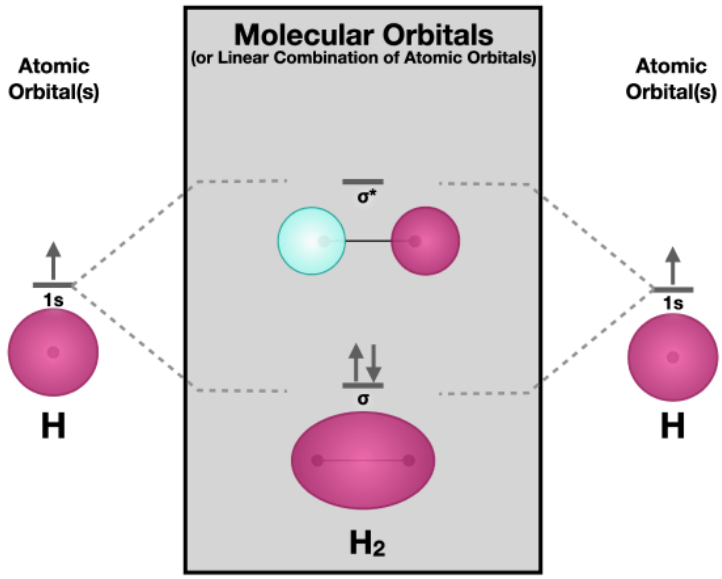
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2.1.5: MOLECULAR ORBITALS



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).

2.1.5.1: Formation of Molecular Orbitals from Atomic Orbitals

- 2.1.5.1.1: Molecular Orbitals from s Orbitals
- 2.1.5.1.2: Molecular Orbitals from p Orbitals
- 2.1.5.1.3: Molecular orbitals from d orbitals
- 2.1.5.1.4: Nonbonding Orbitals and Other Factors

2.1.5.2: Homonuclear Diatomic Molecules

- 2.1.5.2.1: Molecular Orbitals
- 2.1.5.2.2: Orbital Mixing
- 2.1.5.2.3: Diatomic Molecules of the First and Second Periods
- 2.1.5.2.4: Photoelectron Spectroscopy

2.1.5.3: Heteronuclear Diatomic Molecules

- 2.1.5.3.1: Orbital ionization energies
- 2.1.5.3.2: Polar bonds
- 2.1.5.3.3: Ionic Compounds and Molecular Orbitals

2.1.5.P: Problems

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2.1.5.1: 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 Ψ for electrons in individual atoms, we can approximate the molecular wavefunction (what Ψ would look like if we combined the ψ 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 ψ to the molecular Ψ.

$$\Psi = c_a\psi_a + c_b\psi_b$$

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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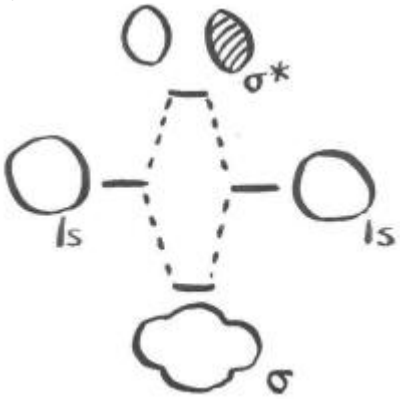
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2.1.5.1.1: Molecular Orbitals from s Orbitals

In the case of the hydrogen molecule, we took two atomic orbitals and combined them to form two molecular orbitals. These new molecular orbitals had different wavelengths than the two atomic orbitals: one had a longer wavelength and was a little lower in energy, while the other had a shorter wavelength and was 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. Both of these ideas are useful in considering the formation of more complex molecules from individual atoms.

- ◦ The average energy of the orbitals has remained almost constant.
  ◦ Also, the number of wavefunctions has remained constant.



◦

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.

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. There would be a different electronic energy, however. That difference would affect the prospects of helium-helium bond formation.

- The electrons have lower kinetic energy in the bond than they had before bonding.
- Electronic energy has decreased. A stable bond has formed.

Exercise 2.1.5.1.1.1

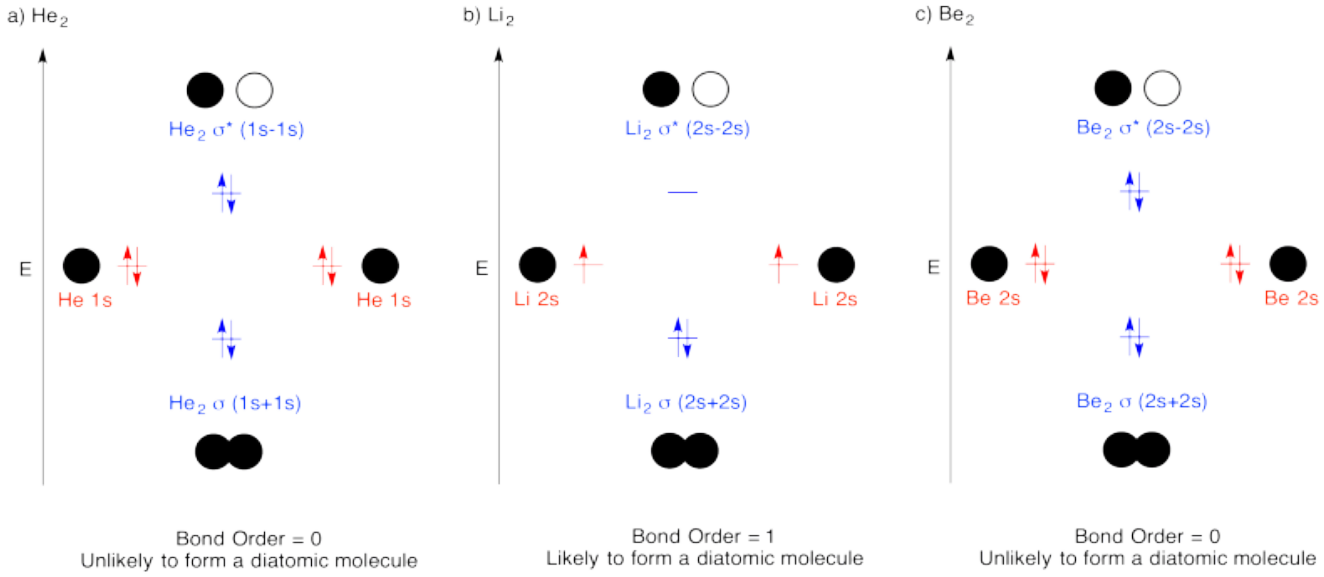
Construct molecular orbital diagrams for the following diatomic species and discuss the likelihood of bond formation in each case.

a. He_2.
b. Li_2.
c. Be_2.

Answer available at the end of this section.

Answers

Exercise 2.1.5.1.1.1



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2.1.5.1.2: Molecular Orbitals from p Orbitals

Bonding with P-orbitals

Sigma bonding with p-orbitals

Other diatomic molecules in the upper right corner of the periodic table can be constructed in a similar way. Look at dinitrogen, N_2.

We can think about how dinitrogen would form if two nitrogen atoms were placed close enough together to share electrons. Nitrogen has more electrons than hydrogen, so this interaction is more complicated.

In our qualitative examination of bonding in main group diatomics, we will take the approach used in Lewis structures and just look at the valence electrons. A quantitative molecular orbital calculation with a computer would not take this shortcut, but would include all of the electrons in the atoms that are bonding together.

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:

- Orbital interactions are governed by symmetry.

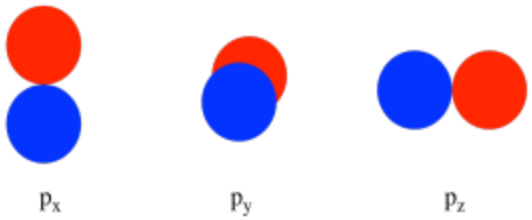
Orbitals interact most easily with other orbitals that have the same element of symmetry. For now, we can simplify and say that orbitals on one atom only interact with the same type of orbitals on the other atom.

- 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.

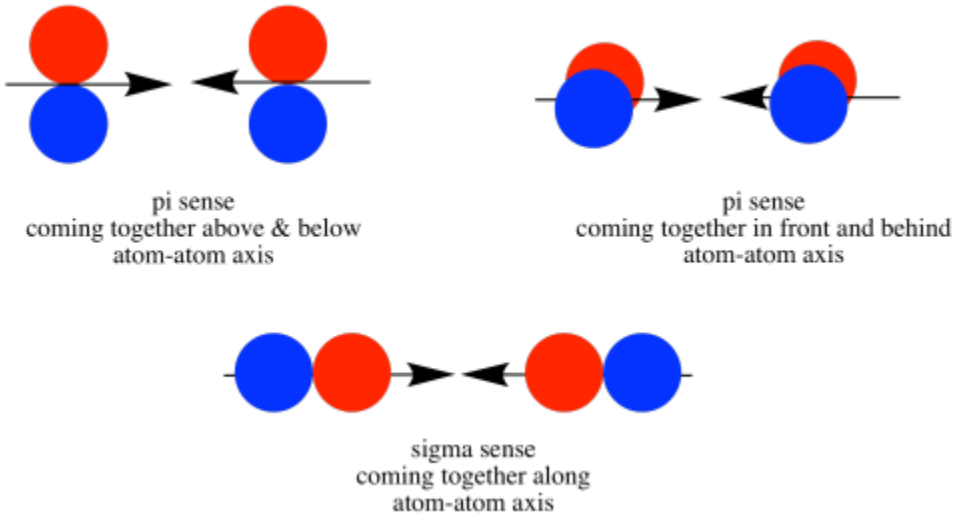
Another complication here is that the s and p orbitals do not start out at the same energy level. When the orbitals mix, one combination goes up in energy and one goes down. Does the s antibonding combination go higher in energy than the combinations from p orbitals? Do the p bonding combinations go 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.

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.

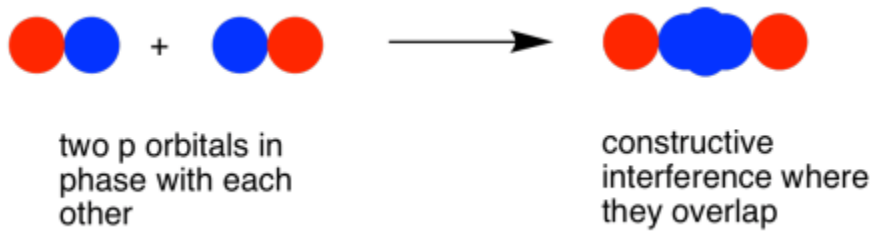


We first need to define one axis as lying along the N-N bond. It does not really matter which one. We arbitrarily say the N-N bond lies along the z axis. The p_z orbitals have a different spatial relationship to each other compared to the p_y and p_x. The p_z orbitals lie along the bond axis, whereas the p_y and p_x are orthogonal to it.

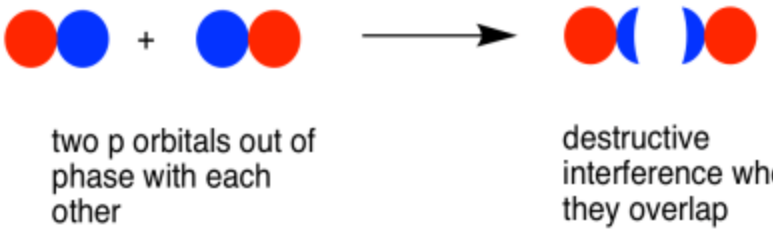


As the nitrogen atoms are brought together, one lobe on one p_z orbital overlaps strongly with one lobe on the other p_z orbital. The other lobes point away from each other and do not interact in any obvious way.

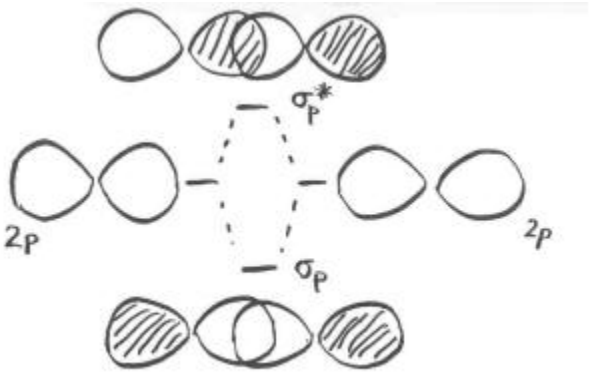
As with the s orbital, the p_z orbitals can be in-phase or out-of-phase. The in-phase combination results in constructive interference. (Here, "in-phase" means the lobes that overlap are in-phase; for that to happen the two p orbitals are actually completely out-of-phase with each other mathematically, 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.



What about those other p orbitals, the ones that do not lie along the bond axis? We'll take a look at that problem on the next page.

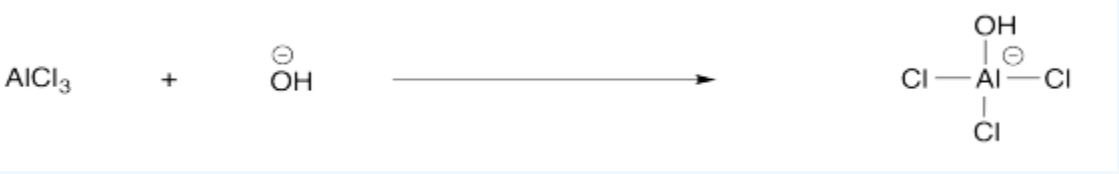
Exercise 2.1.5.1.2.2

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 available at the end of this section.

Exercise 2.1.5.1.2.3

Chemical reactions can be described by MO diagrams too! Consider the following reaction in which a new sigma bond is formed.



Draw an MO diagram for the reaction above. In other words, start from the one frontier MO on each reactant to build the MO's of the new sigma bond in the product.

- Draw the orbital from the base (hydroxide) that is likely to donate its electrons.
- Draw the orbital from the acid (aluminum chloride) that is likely to accept electrons.
- Complete the MO mixing diagram of these two orbitals:

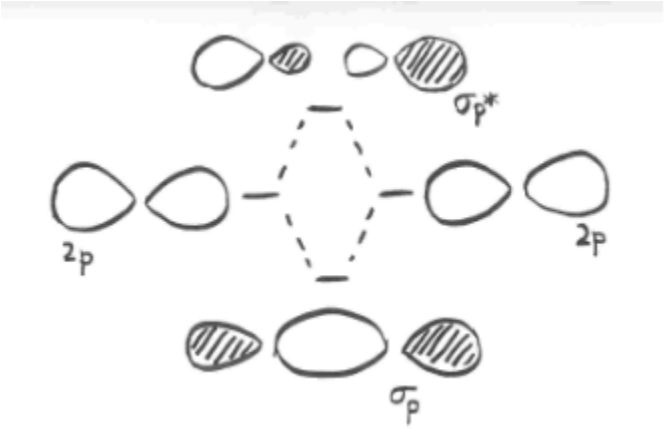
- Label the electron donating orbital
- Label the electron accepting orbital
- Populate the MO mixing diagram with electrons

o Draw a cartoon showing each reactant and product MO that contributes to the bonding interaction.

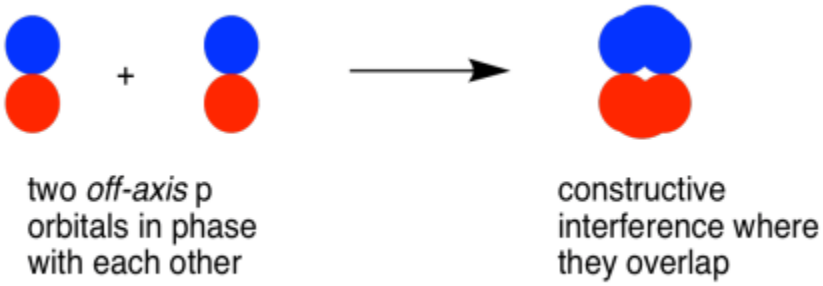
Answer available at the end of this section.

Pi-bonding with p-orbitals

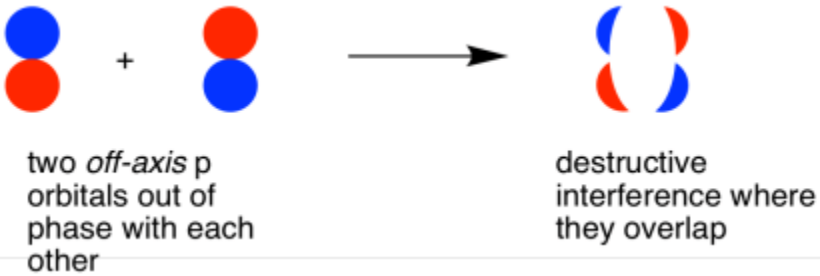
Earlier, we saw that p orbitals that lie along the same axis can interact to form bonds.



Parallel, but not collinear, p orbitals can also interact with each other. They would approach each other side by side, above and below the bond axis between the two atoms. They can be close enough to each other to overlap, although they do not overlap as strongly as orbitals lying along the bond axis. They can make an in-phase combination, as shown below.

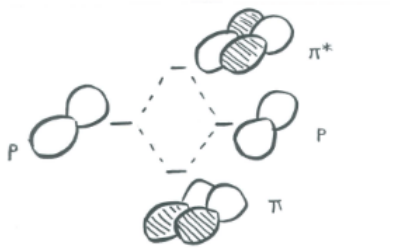


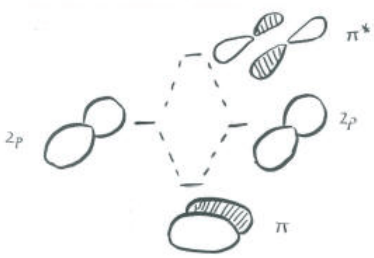
They could also make an out-of-phase combination, as shown below.



- parallel p orbitals can overlap to produce bonding and antibonding combinations.
- the resulting orbitals contain nodes along the bond axis.
- the electron density is found above and below the bond axis.
- this is called a p (pi) bond.

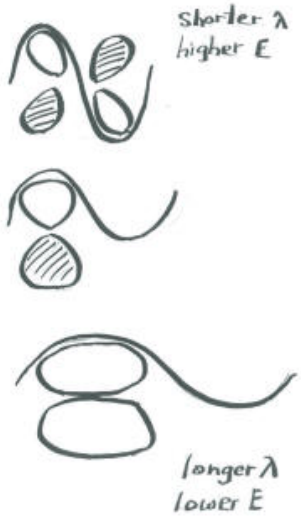
The illustration above is for one set of p orbitals that are orthogonal to the bond axis. The second picture shows the result of the constructive (or destructive) interference. A similar picture could be shown for the other set of p orbitals.



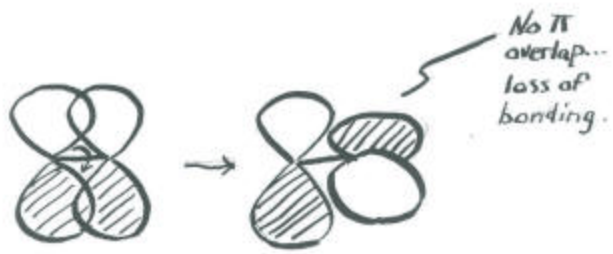


In a main group diatomic species like dinitrogen, one p orbital lying along the bond axis can engage in s bonding. The two p orbitals orthogonal to the bond axis can engage in p bonding. There will be both bonding and antibonding combinations.

Just as the sigma-bonding orbitals display progressively shorter wavelengths along the bonding axis as they go to higher energy, so do the pi bonding orbitals. In other words, there are more nodes in the higher-energy orbitals than in the lower-energy ones.



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.



Exercise 2.1.5.1.2.4

The combinations of _____ atomic orbitals leads to σ orbitals.

Draw pictures.

Answer available at the end of this section.

Exercise 2.1.5.1.2.5

The combinations of _____ atomic orbitals leads to π orbitals.

Draw pictures.

Answer available at the end of this section.

Exercise 2.1.5.1.2.6

Which molecular orbital is typically the highest in energy?
a. p
b. σ
c. π*
d. π
e. σ*

Answer available at the end of this section.

Exercise 2.1.5.1.2.7

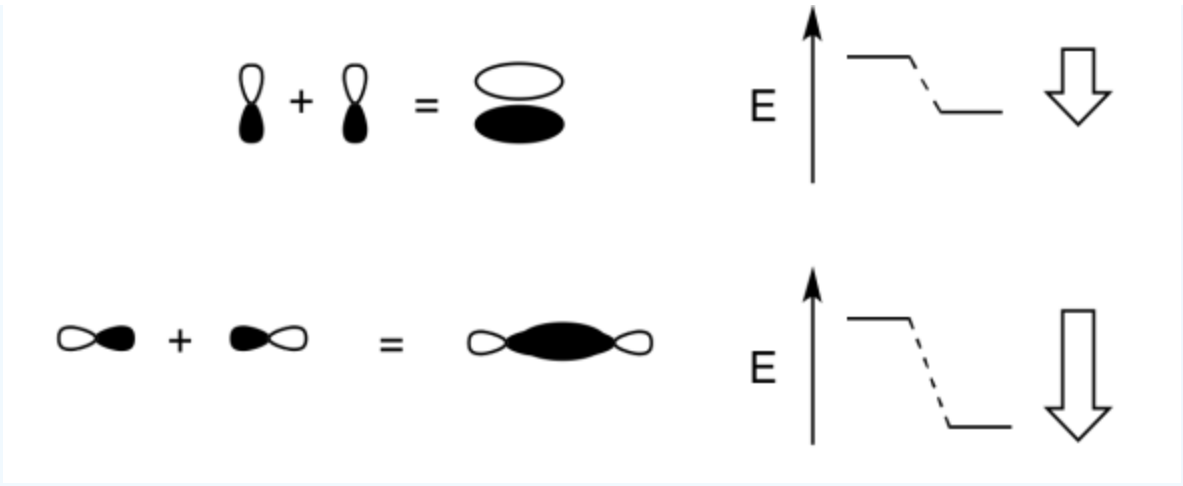
Why would a *core* 1s orbital not interact with a *valence* 2s orbital?

Hint: Why is a Li_2O bond stronger than a K_2O bond?

Answer available at the end of this section.

Exercise 2.1.5.1.2.8

Add a few words to explain the ideas conveyed in these drawings.



Answer available at the end of this section.

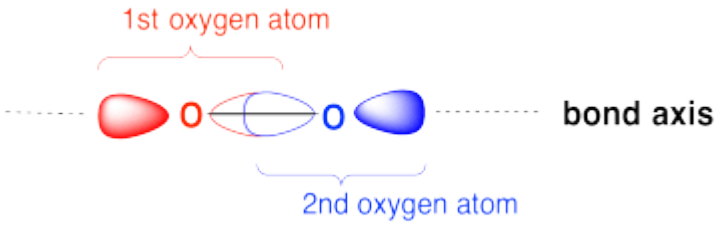
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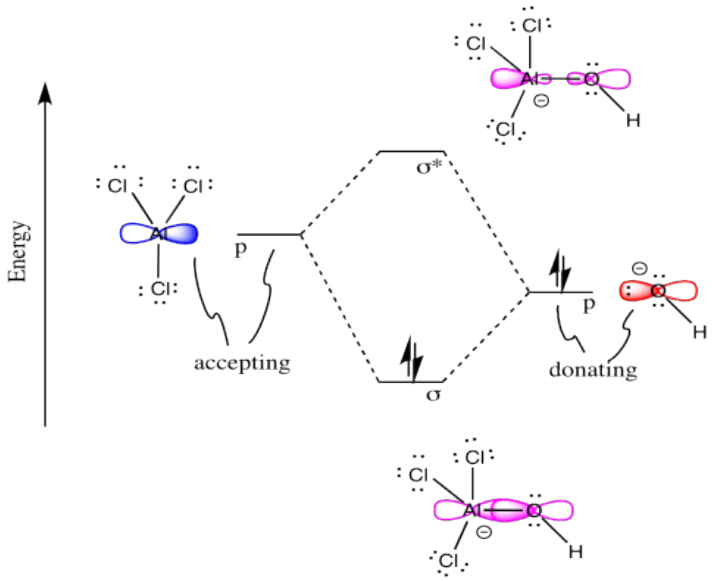
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Answers

Exercise 2.1.5.1.2.2

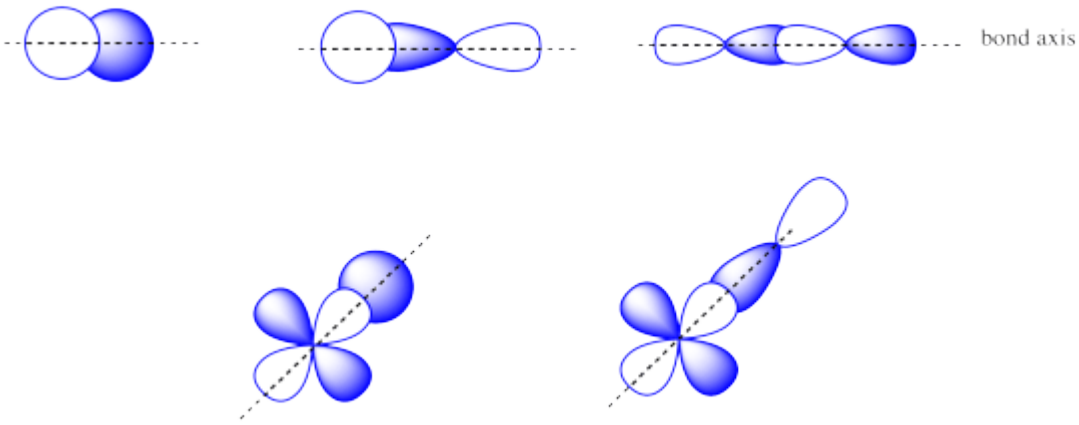


Exercise 2.1.5.1.2.3



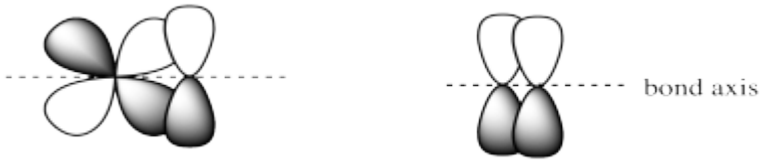
Exercise 2.1.5.1.2.4

The combinations of **s + s** OR **s + *p*** OR ***p* + *p*** OR **s + *d*** OR ***p* + *d*** atomic orbitals can lead to σ orbitals.



Exercise 2.1.5.1.2.5

The combinations of side by side p + p or p + d atomic orbitals leads to π orbitals.



Exercise 2.1.5.1.2.6

e) σ*

Exercise 2.1.5.1.2.7

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 2.1.5.1.2.8

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.

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2.1.5.1.3: 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.

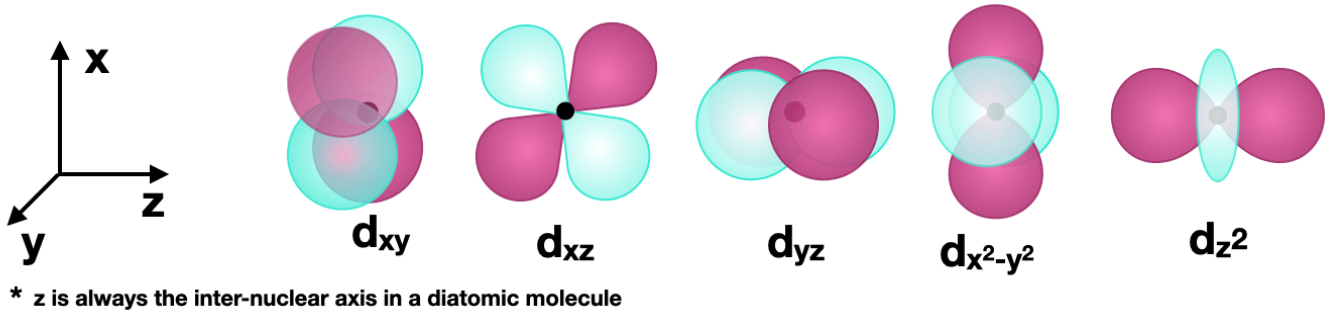


Figure 2.1.5.1.3.1: The five $3d$ orbitals are shown. The orientation of the axes is consistent and the z axis is horizontal for convenience in drawing bonding along the z axis (see examples below). (CC-BY-SA; Kathryn Haas)

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 2.1.5.1.3.2). 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 2.1.5.1.3.2.

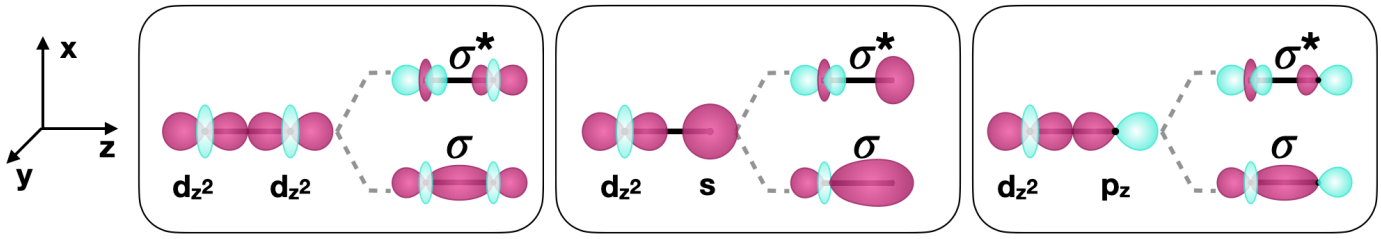


Figure 2.1.5.1.3.2: Selected examples of σ bonds involving d orbitals along the z internuclear axis (shown as a bold horizontal line) between two atoms. (CC-BY-SA; Kathryn Haas)

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 2.1.5.1.3.3). d orbitals can also form π bonds using p orbitals with compatible symmetry, as shown in Figure 2.1.5.1.3.3.

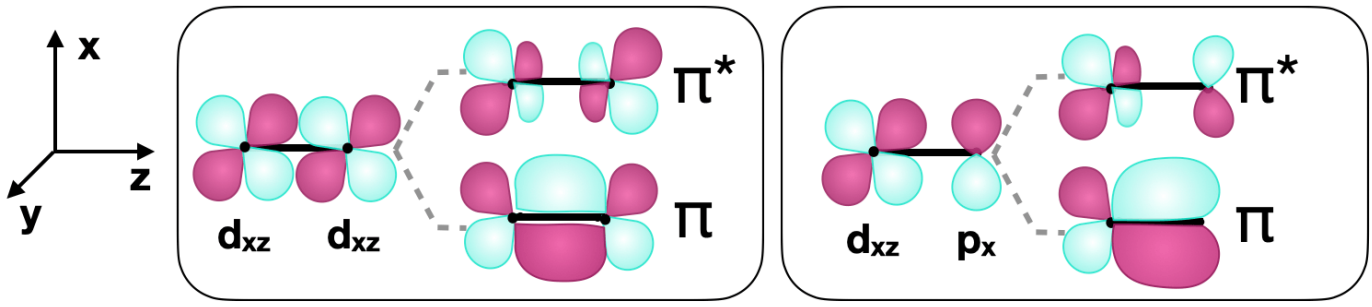


Figure 2.1.5.1.3.3: Selected examples of π bonds involving d orbitals along the z internuclear axis (shown as a bold horizontal line) between two atoms. (CC-BY-SA; Kathryn Haas)

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 2.1.5.1.3.4).

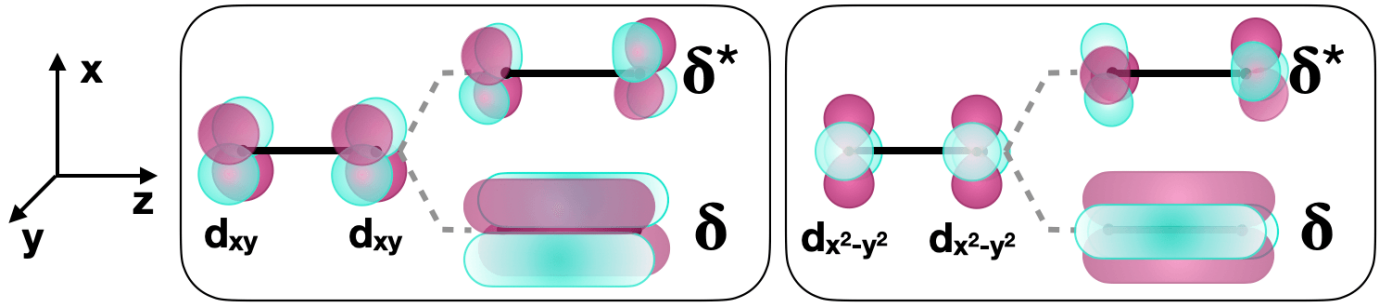


Figure 2.1.5.1.3.4: Selected examples of δ bonds involving d orbitals along the z internuclear axis (shown in bold horizontal line) between two atoms. (CC-BY-SA; Kathryn Haas)

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.

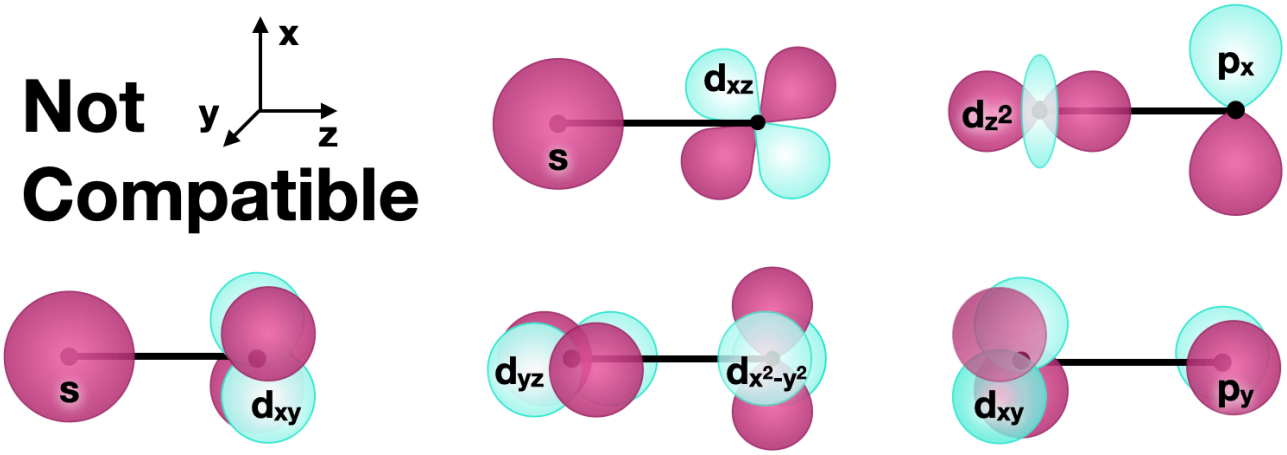


Figure 2.1.5.1.3.5: Several incompatible pairs of orbitals. (CC-BY-SA; Kathryn Haas)

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2.1.5.1.4: 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.

Two major factors to consider

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 2.1.5.1.4.1).

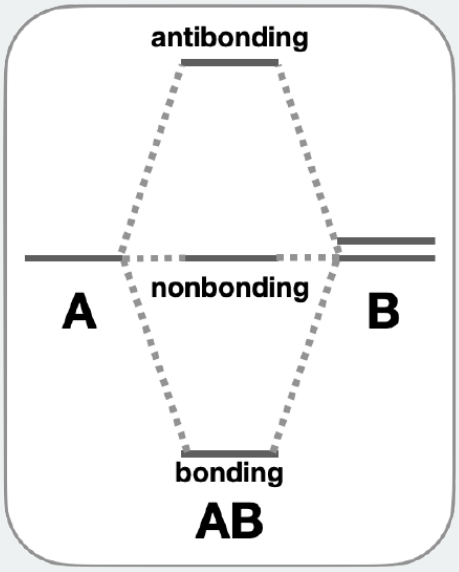


Figure 2.1.5.1.4.1. This figure illustrates the most common case for three atomic orbitals that combine to form three molecular orbitals; formation of one low-energy bonding, one high-energy antibonding, and one intermediate energy non-bonding molecular orbital. (CC-BY-NC-SA, Kathryn Haas)

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 2.1.5.1.4.2). When bonding or antibonding orbitals are close to the energies of the contributing atomic orbitals, those molecular orbitals may have some non-bonding character.

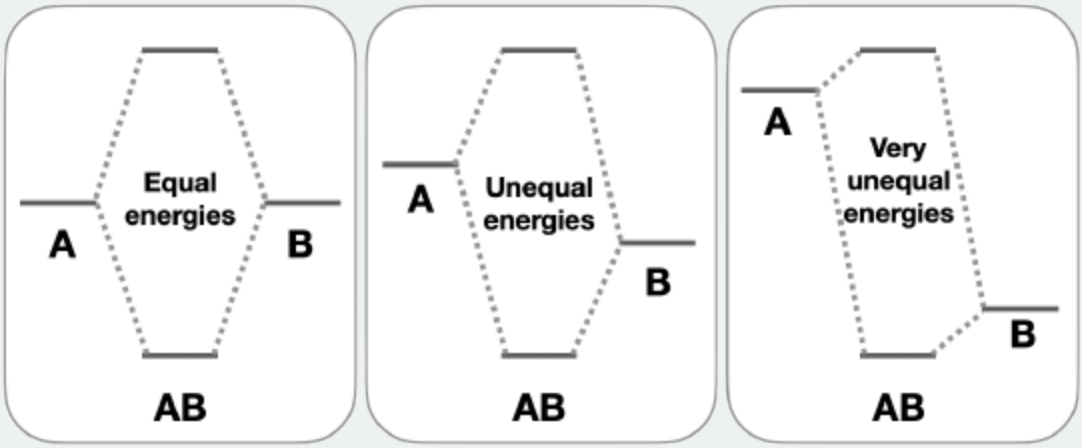


Figure 2.1.5.1.4.2. This figure illustrates how relative energies of atomic orbitals result in molecular orbitals that are more or less favorable. The greater the energy difference between atomic orbitals and the bonding molecular orbital, the more eneretically favorable it is for bonding to occur. (CC-BY-NC-SA, Kathryn Haas)

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2.1.5.2: HOMONUCLEAR DIATOMIC MOLECULES

In this section you will be introduced to the molecular orbital diagrams of several homonuclear diatomic molecules. Homonuclear diatomic molecules are molecules made of exactly two identical atoms, and they are relatively simple.

2.1.5.2.1: Molecular Orbitals

2.1.5.2.2: Orbital Mixing

2.1.5.2.3: Diatomic Molecules of the First and Second Periods

2.1.5.2.4: Photoelectron Spectroscopy

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2.1.5.2.1: Molecular Orbitals

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!

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

View this YouTube Video online

The magnetic properties of O_2 are easily rationalized by its **molecular orbital diagram**. A molecular orbital diagram is a diagram that shows the relative energies and identities of each molecular orbital in a molecule. Figure $2.1.5.2.1.1$ 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 (see next section).

There are some things you should note as you inspect Figure $2.1.5.2.1.1$ (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, notice that **each orbital in the diagram is rigorously labeled** using labels (σ and π) that include the subscripts u and g. These labels and subscripts indicate the symmetry of the orbitals. The σ symbol indicates that the orbital is symmetric with respect to the internuclear axis, while the π label indicates that there is one node along that axis. The g and u stand for *gerade* and *ungerade*, the German words for *even* and *uneven*, respectively. The subscript g is given to orbitals that are *even*, or *symmetric*, with respect to an inversion center. The subscript u is given to orbitals that are *uneven*, or *antisymetric*, with respect to an inversion center. The pictures of calculated molecular orbitals are shown in Figure $2.1.5.2.1.1$ to illustrate the symmetry of each orbital.

Another important thing to notice is that the diagram in Figure $2.1.5.2.1.1$ 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, 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:

$$\text{Bond order } = \frac{1}{2}\left[\begin{pmatrix}\text{number of electrons}\\ \text{in bonding orbitals}\end{pmatrix} - \begin{pmatrix}\text{number of electrons}\\ \text{in antibonding orbitals}\end{pmatrix}\right]$$

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.

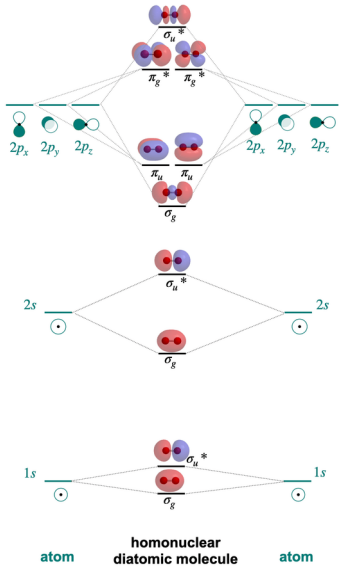


Figure 2.1.5.2.1.1: A generic molecular orbital diagram for a homonuclear diatomic molecule of second-row elements assuming no orbital mixing (interactions are formed by orbitals of the same energy from each atom). (CC-BY-NC-SA, Kathryn Haas)

Now, to see how this molecular orbital diagram can explain the magnetic behaviour of O_2, complete the example below.

Example 2.1.5.2.1.1

Let's change Figure 2.1.5.2.1.1 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 2.1.5.2.1.1 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 2.1.5.2.1.2.

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!

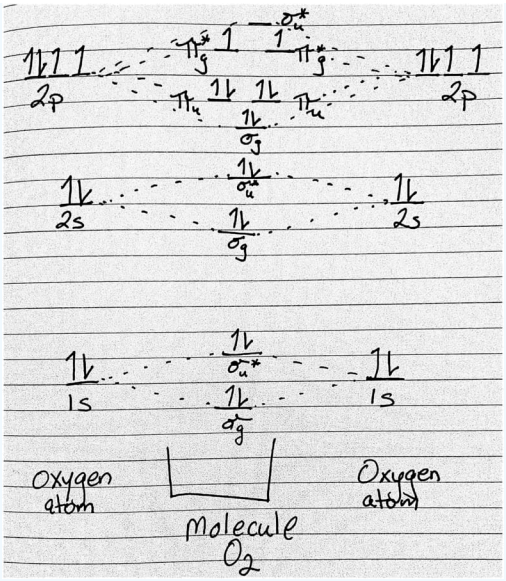


Figure 2.1.5.2.1.2: Hand-drawn molecular orbital diagram for dioxygen. (CC-BY-SA; Kathryn Haas)

Exercise 2.1.5.2.1.1

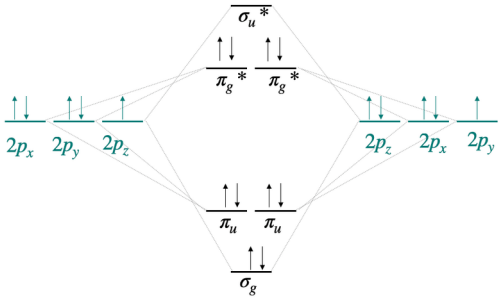
Draw the molecular orbital diagram for F_2; be sure to label your orbitals with the appropriate symmetry and count your orbitals to make sure that the total number of atomic orbitals and molecular orbitals is the same. As a shortcut, include only the valence orbitals and electrons. What is the bond order? Is the molecule diamagnetic or paramagnetic?

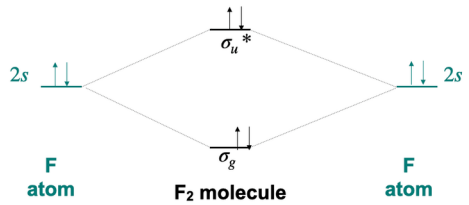
Answer available at the end of this section.

Answers

Exercise 2.1.5.2.1.1

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.





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2.1.5.2.2: Orbital Mixing

In the previous section, we introduced a simplified molecular orbital (MO) diagram, assuming that interactions were limited to degenerate orbitals of compatible symmetry. A version of that *simplified* diagram for second-row homonuclear diatomics is shown on the left side of Figure 2.1.5.2.2.1 (only valence orbitals shown).

In reality, orbitals of compatible symmetry can combine, or mix, even when they have different energies. When sets of orbitals mix, it has the effect of decreasing the energy of the lower-energy set and increasing the energy of the higher-energy set. There are two ways to explain mixing, described in the points below. The diagram on the right of side of Figure 2.1.5.2.2.1 shows how energy levels are affected by orbital mixing.

- **Starting from the simplified MO diagram and mixing molecular orbitals of like symmetry**: If we start with the "no mixing" simplified diagram shown on the left, we can pick out the orbitals with like symmetry and consider what will happen if these molecular orbitals mix. For example, starting from the MO diagram on the left side of Figure 2.1.5.2.2.1, we see that there are two σ_g orbitals that have identical symmetry (hence they have identical symmetry labels). Upon mixing, the lower-energy $\sigma_g(2s)$ will decrease in energy while the higher-energy $\sigma_g(2p)$ will increase in energy. Likewise, there are two σ_u^* orbitals that will mix, decreasing the energy of $\sigma_u^*(2s)$ while increasing the energy of $\sigma_u^*(2p)$.
- **Starting from and mixing atomic orbitals of compatible symmetry**: Starting from the atomic orbitals, we can select the orbitals that have compatible symmetry to make productive interactions, and combine them as a set to make molecular orbitals. From the two sets of atomic orbitals on the right panel in Figure 2.1.5.2.2.1, there are two sets of four orbitals with compatable symmetry; one is the set of two $2s$ and two $2p_z$ orbitals. These four orbitals can combine to form molecular orbitals with σ symmetry. They combine to form one lowest-energy bonding σ_g, a highest-energy σ_u^*, and two orbitals with intermediate energy (σ_g, and σ_u^*). This treatment can be expressed as the linear combination of four atomic orbitals:

  $$\Psi = c_1\psi(2s_a) \pm c_2\psi(2s_b) \pm c_3\psi(2p_a) \pm c_4\psi(2p_b)$$

  where the coefficients $c_1 = c_2$ and $c_3 = c_4$ for homonuclear diatomic molecules.

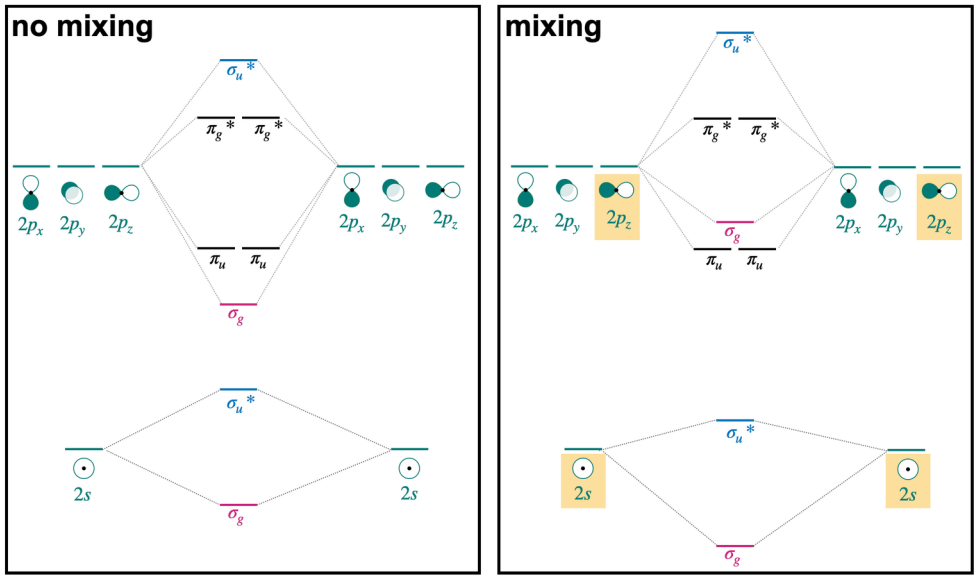


Figure 2.1.5.2.2.1: Mixing of orbitals with like symmetry affects the energies of molecular orbitals. The simplified case where no mixing occurs is shown on the left. The effects of mixing are shown on the right. The σ_g orbitals of like symmetry are highlighted in fuschia and the σ_u^* orbitals of like symmetry are highlighted in blue. A group of atomic orbitals of similar symmetry are highlighted in yellow boxes; these atomic orbitals combine to give all σ molecular orbitals. (CC-BY-SA, Kathryn Haas)

In the case of homonuclear diatomic molecules of the second row, orbital mixing has important consequences for the energetic order of the $\sigma_g(2p)$ and $\pi_u(2p)$ orbitals. This will be discussed in the next section.

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2.1.5.2.3: 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 nobel gases, He exists in the atomic form and does not form bonds at ordinary temperatures and pressures.

Exercise 2.1.5.2.3.1

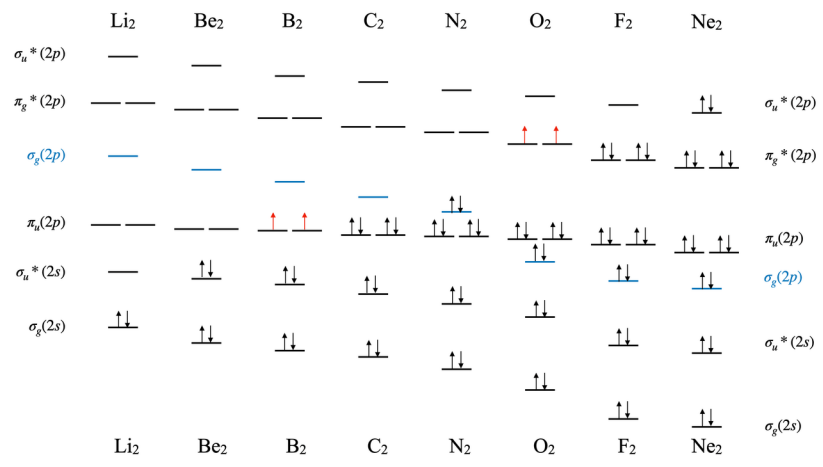
Draw the complete molecular orbital diagrams for H_2 and for He_2. Include sketches of the atomic and molecular orbitals.

Answer available at the end of this section.

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.

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 2.1.5.2.3.1). 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 (recall our previous discussion on penetration and shielding, and its effect on periodic trends). 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 2.1.5.2.3.1).



	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 2.1.5.2.3.1: 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 2.1.5.2.3.2). 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 2.1.5.2.3.2)

Exercise 2.1.5.2.3.2

Draw the complete molecular orbital diagram for O_2. Show calculation of its bond order and tell whether it is diamagnetic or paramagnetic.

Answer available at the end of this section.

Exercise 2.1.5.2.3.3: 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 available at the end of this section.

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 2.1.5.2.3.1, and shown in graphical format on the plot in Figure 2.1.5.2.3.2. 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 (N_2). The shortest bond distance is at N_2 due to its high bond order of 3. From N_2 to F_2 the bond distance increases despite the fact that atomic radius decreases.

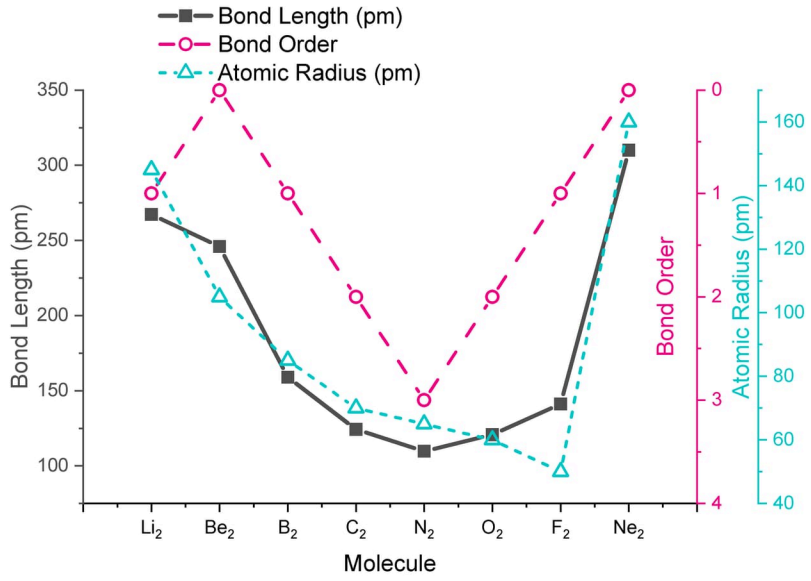


Figure 2.1.5.2.3.2: Overlayed plots of bond length (black squares), bond order (pink circles), and atomic radius (teal triangles) versus atomic number for second period homonuclear diatomic molecules. (CC-BY-NC-SA; Kathryn Haas)

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.

Answers

Exercise 2.1.5.2.3.1

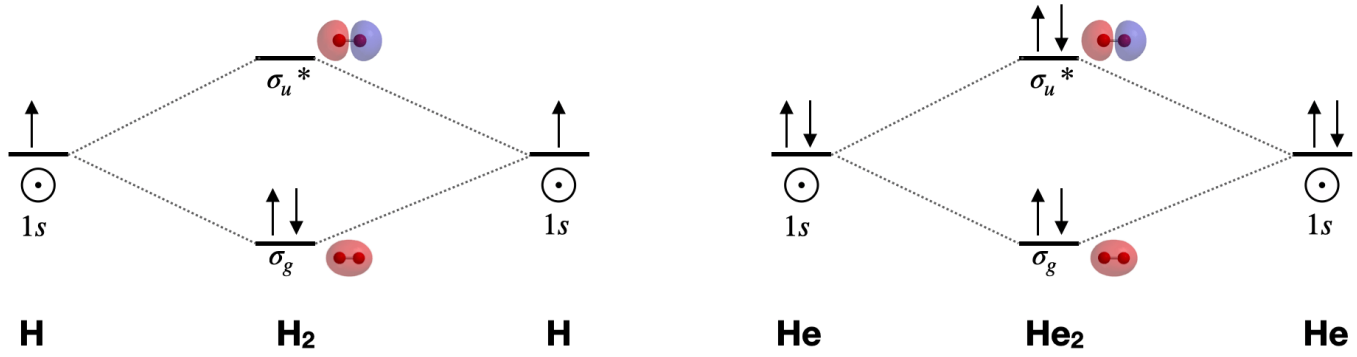


Figure for Exercise 2.1.5.2.3.1: Molecular orbital diagrams for dihydrogen and dihelium. Molecular orbital surfaces calculated using Spartan software. (CC-BY-NC-SA; Kathryn Haas)

A complete molecular orbital diagram includes all atomic orbitals and molecular orbitals, their symmetry labels, and electron filling.

Exercise 2.1.5.2.3.2

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.

$$\text{Bond order } = \frac{1}{2}\left[\left(\begin{array}{c}\text{8 electrons in}\\ \text{valence bonding orbitals}\end{array}\right) - \left(\begin{array}{c}\text{4 electrons in}\\ \text{valence antibonding orbitals}\end{array}\right)\right]$$

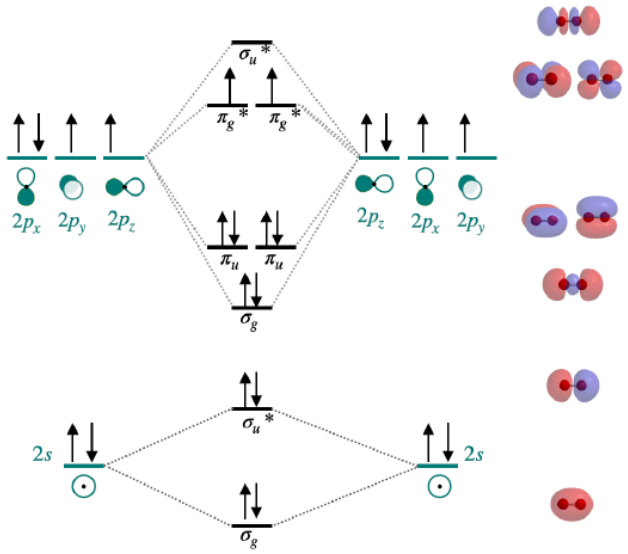


Figure for Exercise 2.1.5.2.3.2. Molecular orbital diagram of O_2. (CC-BY-NC-SA, Kathryn Haas)

Exercise 2.1.5.2.3.3**: The Peroxide Ion**

This diagram looks similar to that of 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.

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2.1.5.2.4: Photoelectron Spectroscopy

A photoelectron spectrum can show the relative energies of occupied molecular orbitals by ionization. The *ionization energy* is a direct measure of the energy required to just remove the electron concerned from its initial level to the vacuum level (free electron). Photoelectron spectroscopy measures the relative energies of the ground and excited positive ion states that are obtained by removal of single electrons from the neutral molecule.

$$A + \text{photon} \rightarrow A^+ + e^-$$

The information obtained from photoelectron spectroscopy is typically discussed in terms of the electronic structure and bonding in the ground states of neutral molecules, with ionization of electrons occurring from bonding molecular orbitals, lone pairs, antibonding molecular orbitals, or atomic cores. These descriptions reflect the relationship of ionization energies to the molecular orbital model of electronic structure.

Ionization energies are directly related to the energies of molecular orbitals (by Koopmans' theorem).

Example: Photoelectron spectrum of dihydrogen

The molecular orbital description of dihydrogen involves two $1s$ atomic orbitals generating two molecular orbitals: a bonding σ_g and an antibonding σ_u^*. The two electrons occupy the σ_g bonding orbital, leaving the molecule with a bond order of one (Figure $2.1.5.2.4.1$). The PES spectrum of dihydrogen (Figure $2.1.5.2.4.1$) has a single band that corresponds to the ionization of one electron from the σ_g. The multiple peaks are due to electrons ejecting from a range of stimulated vibrational energy levels. When extensive vibrational structure is resolved in a PES molecular orbital, then the removal of an electron from that molecular orbital induces a significant change in the bonding (in this case an increase in the bond length due to decrease in bond order).

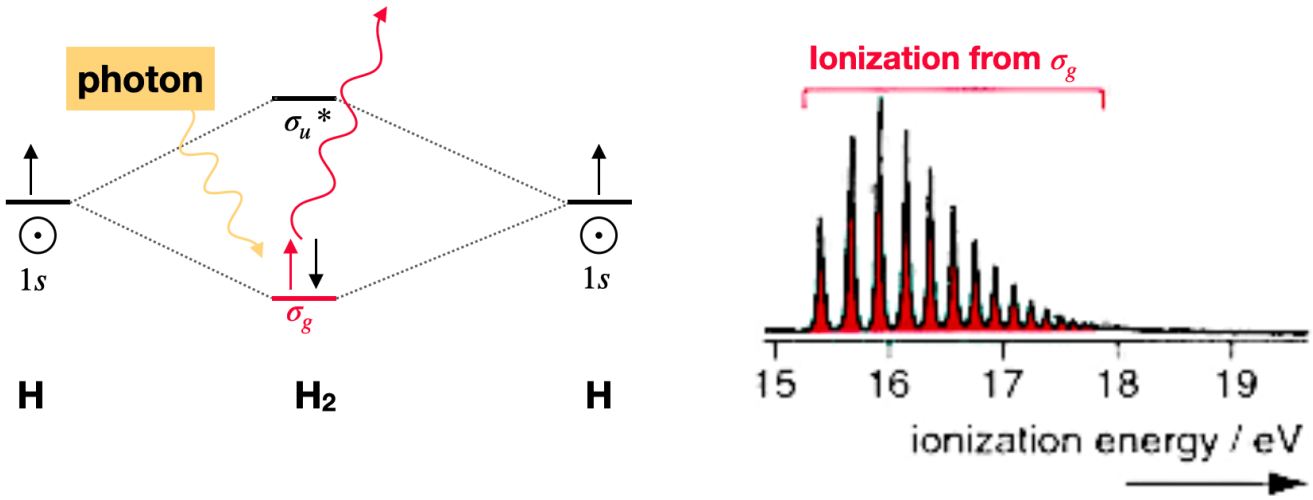


Figure $2.1.5.2.4.1$: The molecular orbital diagram and photoelectron spectrum of dihydrogen. (CC-BY-NC-SA; Libretexts)

Example: Photoelectron spectrum of dinitrogen

Diatomic nitrogen is more complex than hydrogen since multiple molecular orbitals are occupied. Five molecular orbitals are occupied; two of them are degenerate. Three bands in the photoelectron spectrum correspond to ionization of an electron in $\sigma_g(2p)$, $\pi_u(2p)$ and $\sigma_u^*(2s)$ molecular orbitals. Ionization of the fourth type of orbital, $\sigma_g(2s)$, does not appear in Figure $2.1.5.2.4.2$ because it is either off scale or because the incident light $h\nu$ used did not have sufficient energy to ionize electrons in that deeply stabilized molecular orbital. Note that extensive vibrational structure for the $\pi_u(2p)$ band indicates that the removal of an electron from this molecular orbital causes a significant change in the bonding.

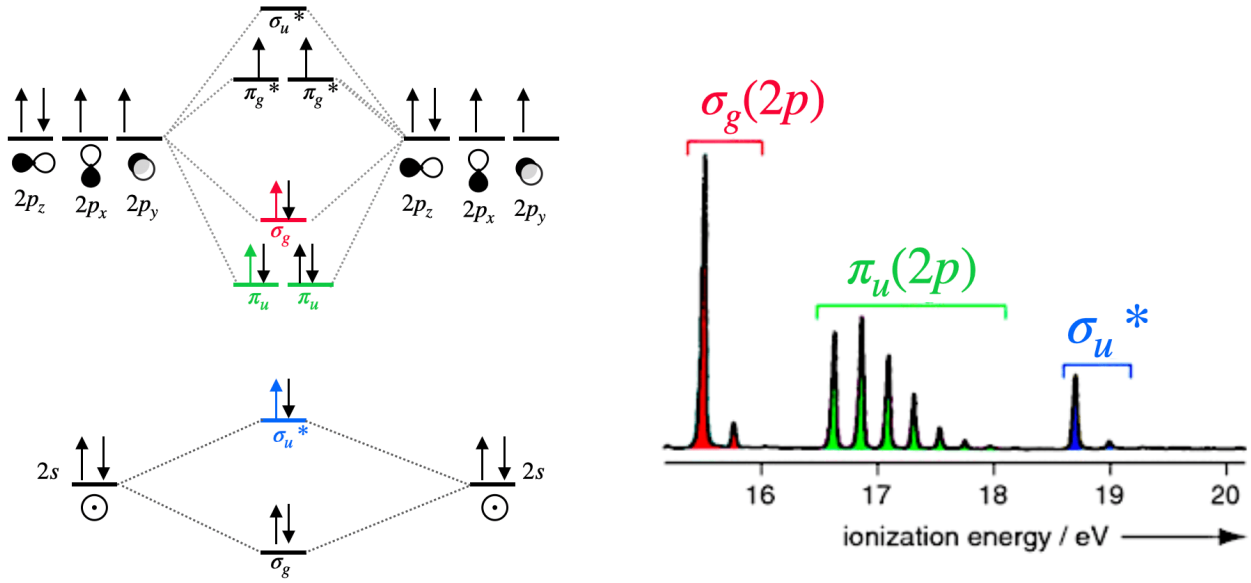


Figure 2.1.5.2.4.2: The molecular orbital diagram and photoelectron spectrum of dinitrogen. (CC-BY-NC-SA; Libretexts)

From the photoelectron spectrum of dinitrogen, we can see that the electrons in the $\sigma_g(2p)$ orbital can be ionized using less energy than required to ionize electrons in the $\pi_u(2p)$ orbital. This is evidence for $\sigma_g(2p)$ existing at a higher energy than the $\pi_u(2p)$ orbitals.

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- 10.4: Photoelectron Spectroscopy by Roger Nix is licensed CC BY 4.0.

2.1.5.3: 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 polar 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. Recall that atomic orbitals must have compatible symmetry and similar energy to combine into molecular 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.

In this section, you should learn how to generate molecular orbital diagrams of heteronuclear diatomic molecules. To approach such a problem, we must start with a knowledge of the relative energies of electrons in different atomic orbitals. In other words, we need knowledge of the orbital potential energies (or orbital ionization energies).

2.1.5.3.1: Orbital ionization energies

2.1.5.3.2: Polar bonds

2.1.5.3.3: Ionic Compounds and Molecular Orbitals

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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2.1.5.3.1: Orbital ionization energies

To generate molecular orbital diagrams of heteronuclear diatomic molecules, we must start with a knowledge of the relative energies of electrons in different atomic orbitals. In other words, we need knowledge of the orbital potential energies (or 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 2.1.5.3.1.1.
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 2.1.5.3.1.1: 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) Values are expressed in eV.



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2.1.5.3.2: Polar bonds

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 orbital diagrams may also look similar. A major difference is that the more electronegative atom will have orbitals at a lower energy level. 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 $2.1.5.3.2.1$) 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...). The orbital labeling system described previously is inappropriate for heteronuclear diatomic molecules that cannot be assigned g and u subscripts.

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 $2.1.5.3.2.1$. 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 $2.1.5.3.2.1$.

In the case of carbon monoxide (Figure $2.1.5.3.2.1$), 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.

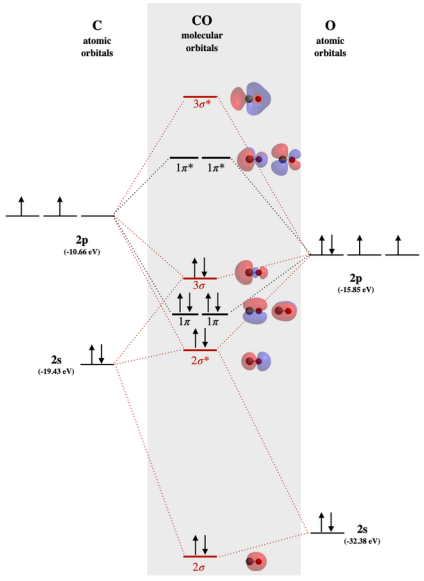
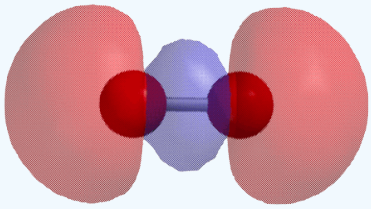


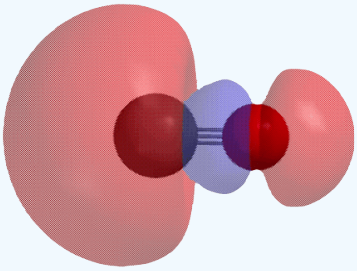
Figure $2.1.5.3.2.1$: Molecular orbital diagram of carbon monoxide. The labeling of molecular orbitals in this diagram follows a convention by which orbitals are given serial names according to the type of orbital (σ, π, etc.). The lowest energy orbitals of any type are assigned a value of 1 and higher 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)

Exercise 2.1.5.3.2.1

Examine the shape of the 3σ orbital of carbon monoxide in Figure 2.1.5.3.2.1. 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 available at the end of this section.

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 2.1.5.3.2.2.

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 5.3.1, 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.

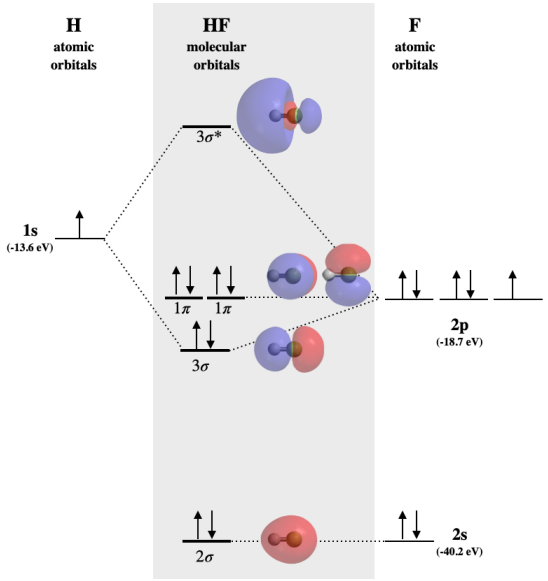


Figure 2.1.5.3.2.2: Molecular Orbital diagram of hydrogen fluoride. Molecular orbitals calculated using Spartan software. (Kathryn Haas, CC-BY-NC-SA)

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!

Exercise 2.1.5.3.2.2

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 available at the end of this section.

Answers

Exercise 2.1.5.3.2.1

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 2.1.5.3.2.2

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 2.1.5.3.2.1: the HOMO is the 3σ orbital (also discussed in Exercise 2.1.5.3.2.1). 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.

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2.1.5.3.3: 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 $3s$ orbital (-5.2 eV) is significantly higher in energy than the chlorine valence orbitals. The chlorine $3s$ 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 $3s$; still, the energy difference is large enough to make bonding weak. The Na $3s$ orbital combines with Cl $3p_z$ to form the molecular orbitals labeled 4σ and $4\sigma^*$ in Figure $2.1.5.3.3.1$. 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 $4\sigma^*$ 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.

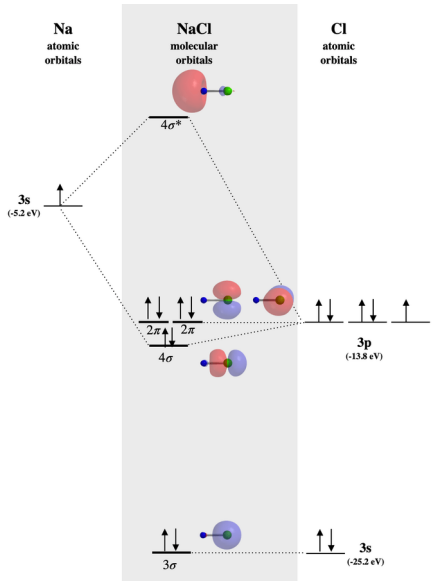


Figure $2.1.5.3.3.1$: The molecular orbital diagram for sodium chloride. Molecular orbital surfaces calculated using Spartan software indicate almost no covalent nature of bonding. (CC-BY-NC-SA, Kathryn Haas)

Exercise $2.1.5.3.3.1$

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 available at the end of this section.

Answers

Exercise 2.1.5.3.3.1

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 $3\sigma^*$

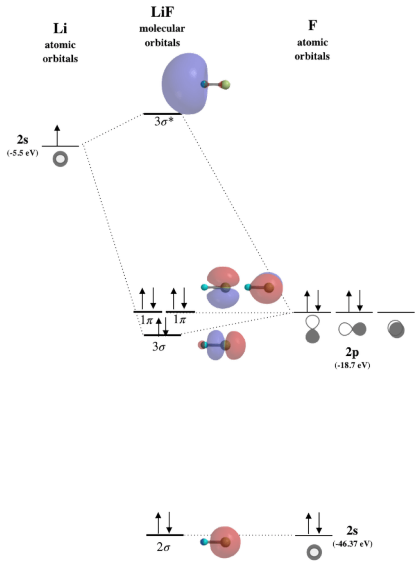


Figure for Exercise 2.1.5.3.3.1: Molecular orbital diagram for the ionic compund, LiF. (CC-BY-NC-SA, Kathryn Haas)

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2.1.5.P: Problems

Concept Review Questions

1. What are the assumptions (axioms) of molecular orbital (MO) theory?

2. Explain qualitatively why the vectorial addition of atomic orbitals creates molecular orbitals (which underlying physical phenomenon is described by the vectorial addition?).

3. Explain qualitatively why molecular orbital theory is suitable to describe covalent bonding.

4. What are the three criteria that determine the degree of covalent interaction in MO theory?

5. Which three rules determine the degree of orbital overlap in MO theory?

6. Explain why the combination of a large, diffuse orbital and a small orbital produces only weak covalent interaction.

7. Explain why sigma interactions between atomic orbitals typically produce larger orbital overlaps than pi interactions.

8. Explain why the combination of orbitals of the same energy leads to the largest degree of covalent interaction.

9. What can be said about energy and location of a bonding and an anti-bonding molecular orbital that are made from atomic orbitals of large energy difference?

10. MO theory – even though designed for covalent bonding – can also make statements about ionic bonding. Explain why.

11. Explain the principles of SALC.

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Homework Problems

Section 1

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 available at the end of this section.

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 available at the end of this section.

Exercise 3

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 available at the end of this section.

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 available at the end of this section.

Exercise 5

The CH_4 molecule belongs to the point group T_d. You can find the character table of the point group in the internet.

a) Calculate the reducible representation for the ligand group orbitals (LGOs).

b) Calculate the irreducible representations of the ligand group orbitals (LGOs).

c) Draw a qualitative molecular orbital diagram for CH_4.

Answer available at the end of this section.

Exercise 6

Which are the symmetry types of the central atom orbitals in the PCl_5 molecule?

Answer available at the end of this section.

Exercise 7

For the hypothetical $BrKr^+$ molecule: Toward which atom is the HOMO polarized? Explain briefly why.

Answer available at the end of this section.

Exercise 8

Reconstruct the MO diagram for water and NH_3 (repeat what we did in class without looking at your notes (only use the respective character tables).

Answer available at the end of this section.

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Exercise 2.1.5.P.1

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 available at the end of this section.

Exercise 2.1.5.P.2

A Molecular Orbital Diagram for a diatomic molecule (two atoms) varies in the number of electrons. How do you populate the electrons?

Answer available at the end of this section.

Exercise 2.1.5.P.3

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 available at the end of this section.

Exercise 2.1.5.P.4

a. Construct a qualitative molecular orbital diagram for oxygen, O_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. Compounds that have all of their electrons paired are referred to as diamagnetic. Those with unpaired electrons are referred to as paramagnetic. Paramagnetic materials are attracted by a magnetic field, but diamagnetic things are not. How would you expect molecular oxygen to behave?

Answer available at the end of this section.

Exercise 2.1.5.P.5

a. Construct a qualitative molecular orbital diagram for peroxide anion, O_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 dioxygen could be reduced to peroxide (through the addition of two electrons)?

Answer available at the end of this section.

Exercise 2.1.5.P.6

Construct a qualitative molecular orbital diagram for diboron, B_2. Do you think boron-boron bonds could form easily, based on this picture?

Answer available at the end of this section.

Exercise 2.1.5.P.7

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 available at the end of this section.

Exercise 2.1.5.P.8

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 available at the end of this section.

Exercise 2.1.5.P.9

Make drawings and notes to summarize the effect of populating antibonding orbitals.

Answer available at the end of this section.

Exercise 2.1.5.P.10

Researchers at Johns Hopkins recently reported the formation of Na_4Al_2 in a pulsed arc discharge (they put a lot of electric current through a sample of sodium and aluminum; Xinxing Zhang, Ivan A. Popov, Katie A. Lundell, Haopeng Wang, Chaonan Mu, Wei Wang, Hansgeorg Schnöckel, Alexander I. Boldyrev, Kit H. Bowen, *Angewandte Chemie International Edition*, **2018**, *57*(43), 14060-14064. Copyright 2018, John Wiley & Sons. Used with permission.).

a. The compound is ionic. Explain which atoms form the cations, based on periodic trends.
b. Therefore, what atoms form the anion?
c. The anion is one molecule. What is the charge on this molecule?
d. Show how to calculate the total valence electrons in this molecular anion.
e. Draw a Lewis structure for this molecular anion.
f. Construct a diatomic molecular orbital energy level diagram for this molecule. Label the energy levels (sigma, pi, etc.) and add in the correct number of electrons.
g. Show how to calculate the bond order in the molecule.

Answer available at the end of this section.

Exercise 2.1.5.P.1

Draw the molecular orbital diagram for (NO^-).

Answer available at the end of this section.

Exercise 2.1.5.P.1

Draw and compare the molecular orbital diagrams to the Lewis structure diagrams for O_2, O_2^-, and O_2^{2-}.

Answer available at the end of this section.

Exercise 2.1.5.P.1

Draw the molecular orbital diagram for hydroxide ion (OH^-).

Answer available at the end of this section.

Exercise 2.1.5.P.1

Draw the molecular orbital diagram for hydroxide fluoride (HF).

Answer available at the end of this section.

Exercise 2.1.5.P.1

Draw the molecular orbital diagram for borane (BN).

Answer available at the end of this section.

BH3

Exercise 2.1.5.P.1

Draw the molecular orbital diagram for (FeH_6).

Answer available at the end of this section.

Exercise 2.1.5.P.1

Draw the molecular orbital diagram for boron trifluoride (BF_3).

- What is the non-bonding orbital?
- What are the HOMO and LUMO orbitals?
- Why does e' have 2 lines of energy levels compared to a1', which has only a 1-line energy level?
- What is the bond order of BH_3 in this MO diagram?

Answer available at the end of this section.

Answers

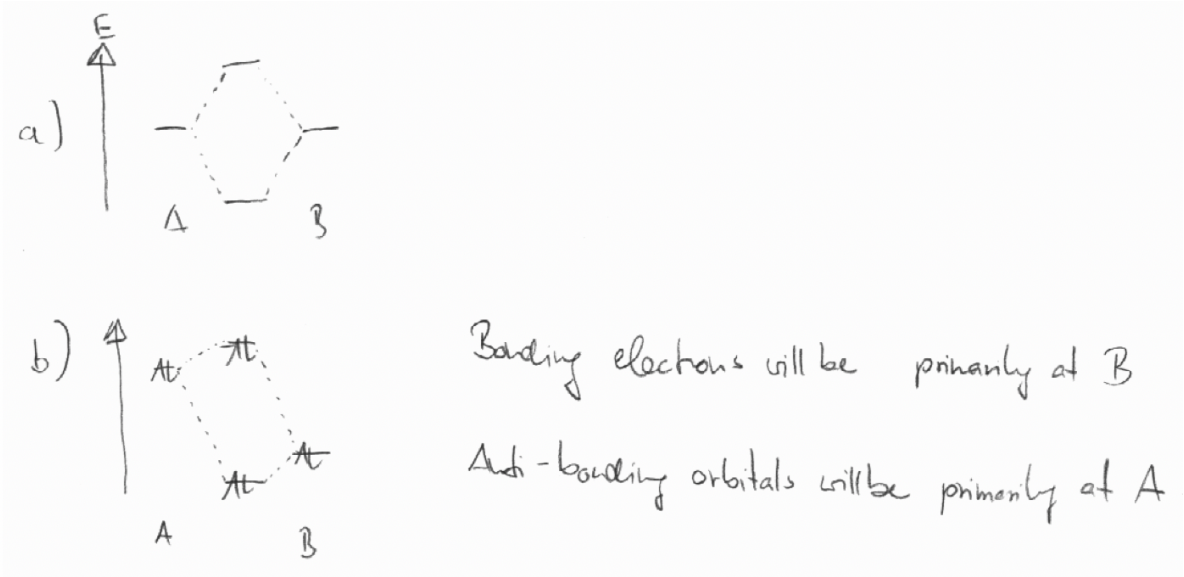
Exercise 1

a) Overlap of a small and a large orbital.

Exercise 2

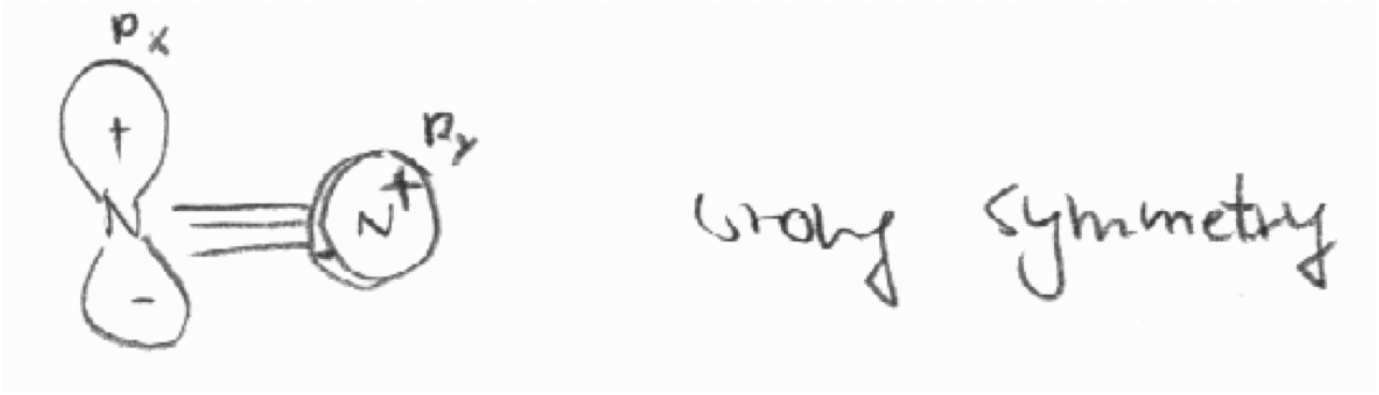
a) orbital overlap in sigma-fashion

Exercise 3

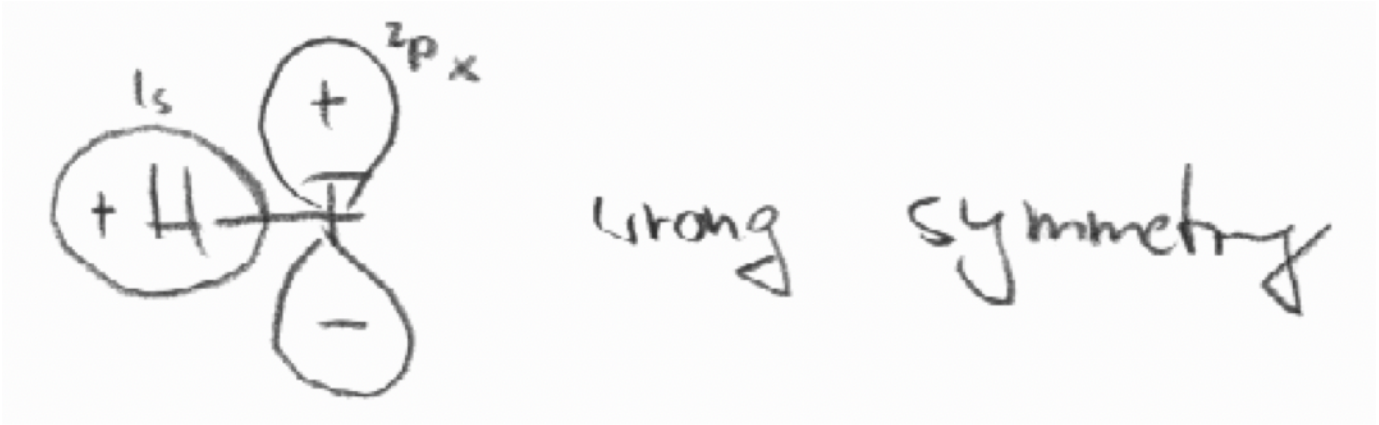


Exercise 4

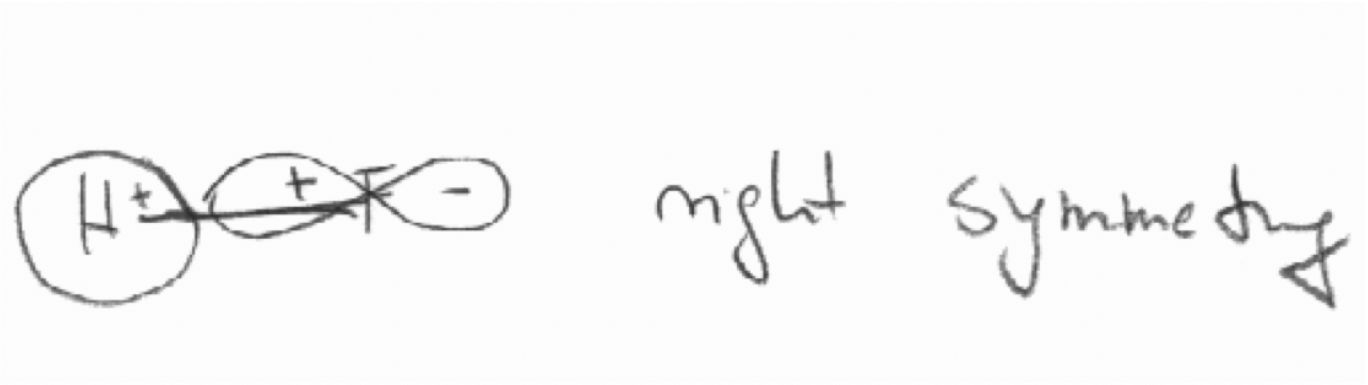
a)



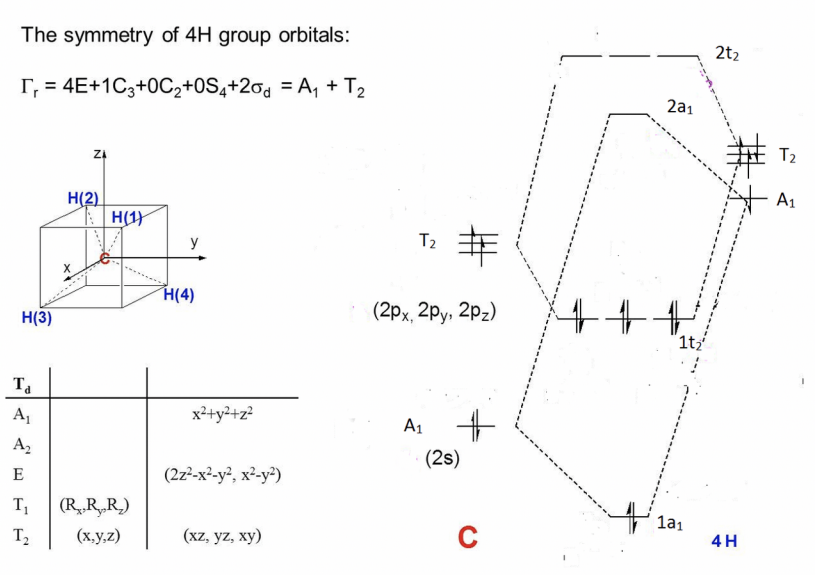
b)



c)



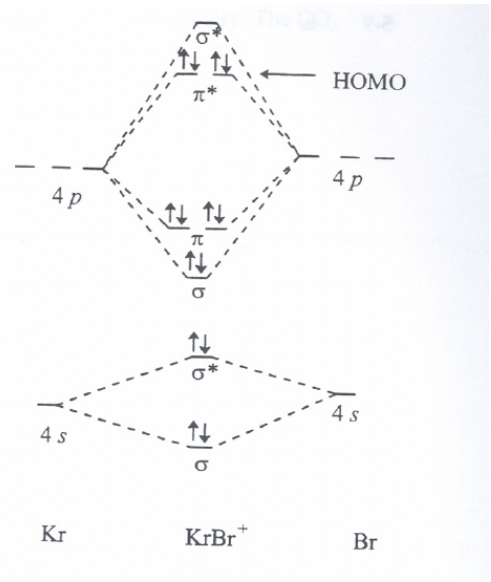
Exercise 5



Exercise 6

1. Determine point group of PCl_5. --> D_{3h}.
2. Decide what are the valence orbitals of the central atom: 3s, 3p
3. Look up the character table of D_{3h}, e.g., in the internet. You will find their symmetries to be: A_1' (3s), A_2'' ($3p_z$), E'($3p_x$, $3p_y$)

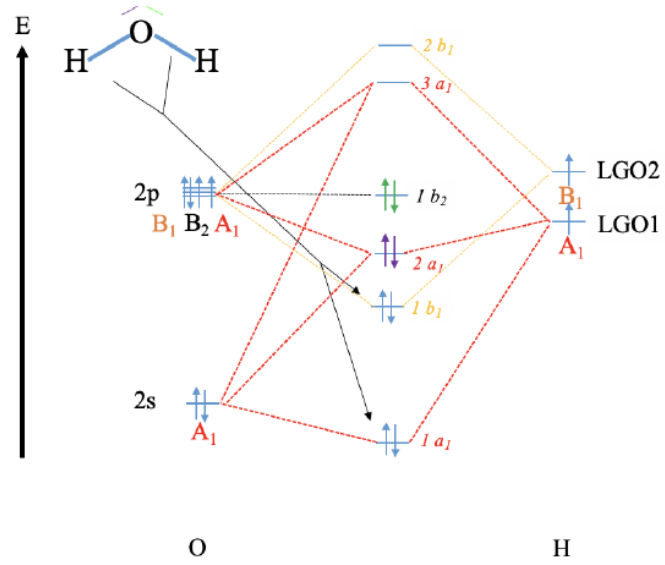
Exercise 7



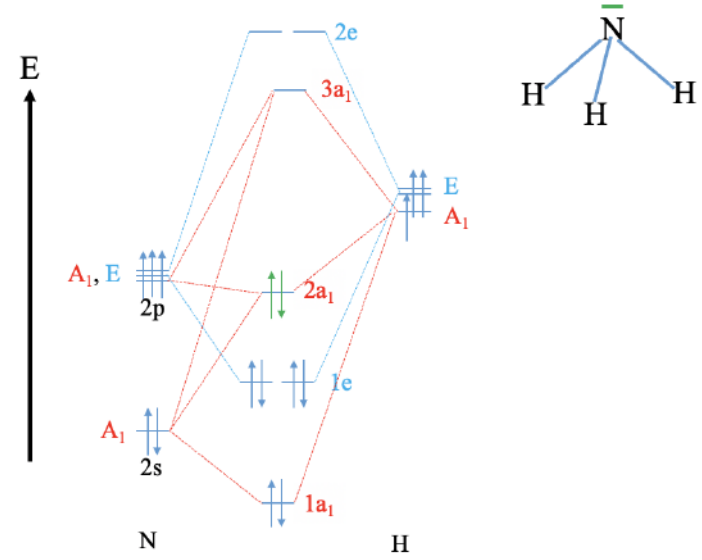
Orbital energies of Kr must be somewhat lower than the ones of Br because the electrons experience higher effective nuclear charge (Z_{eff} increases within a period). This means that the antibonding HOMO is polarized towards Br (HOMO energetically closer to 4p(Br) than 4p(Kr)).

Exercise 8

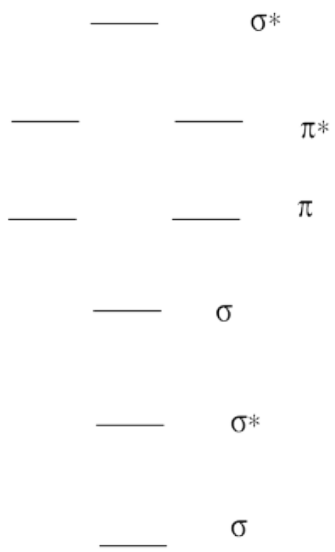
Water



NH_3



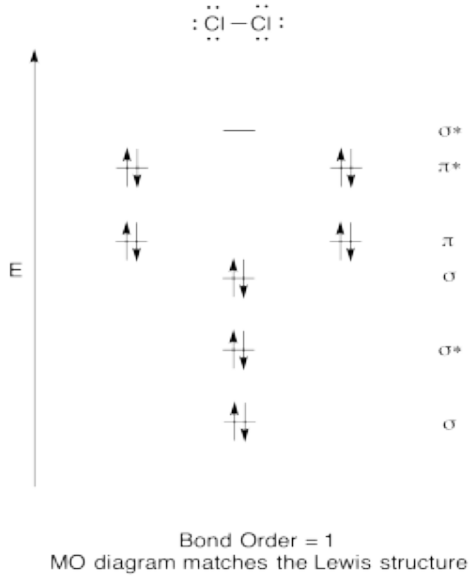
Exercise 2.1.5.*P*.1



Exercise 2.1.5.*P*.2

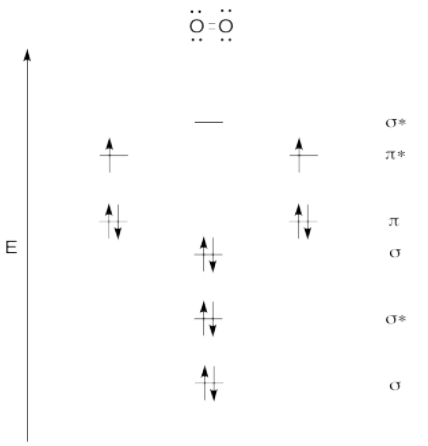
- Count the valence electrons on the molecule. That's the number of valence electrons on each atom, adjusted for any charge on the molecule. (eg C_2^{2-} has 10 valence electrons: 4 from each carbon -- that's 8 -- and two more for the 2- charge).
- Fill electrons into the lowest energy orbitals first.
- Pair electrons after all orbitals at the same energy level have one electron.

Exercise 2.1.5.*P*.3



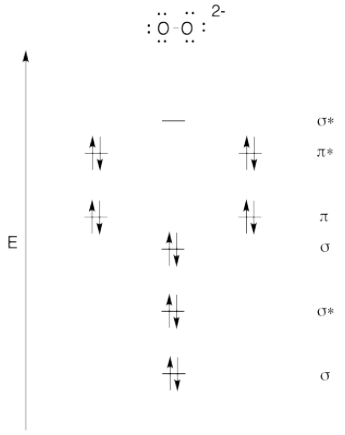
Bond Order = 1
MO diagram matches the Lewis structure

Exercise 2.1.5.*P*.4



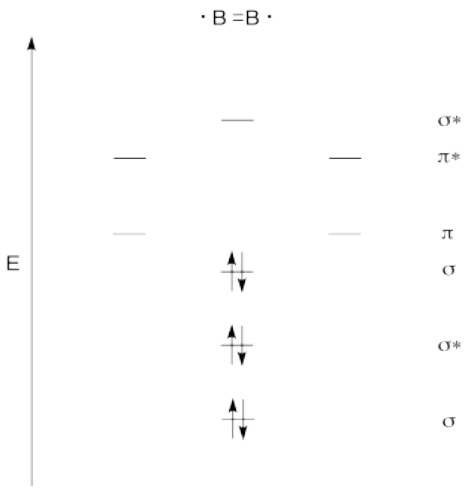
Bond Order = 2
MO diagram indicates two unpaired electrons and therefore does not match the Lewis structure. Based on the MO diagram oxygen would be paramagnetic and would be attracted to a magnetic field

Exercise 2.1.5.P.5



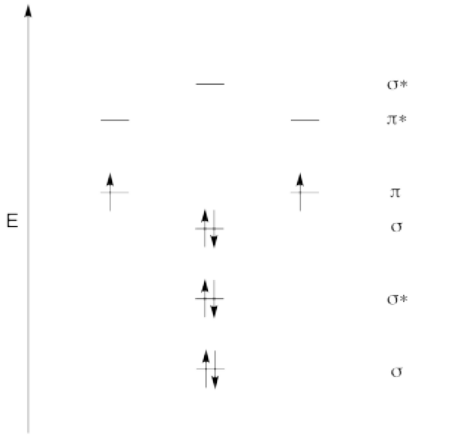
Bond Order = 1
MO diagram matches the Lewis structure. Both predict a Bond Order of 1 and 6 lone pairs of electrons. The addition of two electrons to O_2 to O_2^{2-} would be possible.

Exercise 2.1.5.P.6



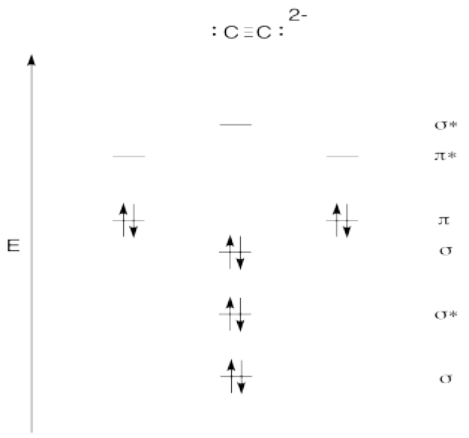
Bond Order = 1
Boron-Boron bonding should be possible

Exercise 2.1.5.*P*.7



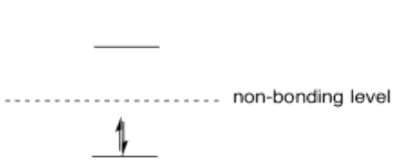
Bond Order = 2
MO diagram does not match the Lewis structure.
However, the MO diagram does concur about the
2 unpaired electrons.

Exercise 2.1.5.*P*.8

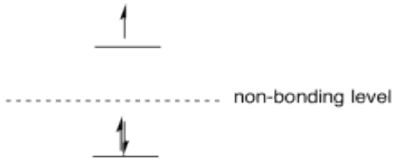


Bond Order = 3
MO diagram matches the Lewis structure. Both predict a Bond Order of 3 and 2 lone pairs of electrons. The addition of two electrons to C_2 to C_2^{2-} would be possible.

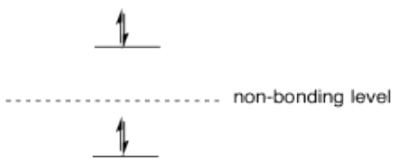
Exercise 2.1.5.*P*.9



I'm stable!!!
And I have ONE FULL BOND!!!!



I'm kinda stable I guess...
Still got a half a bond...
Don't worry about me...



Not stable together.
No bonds here.

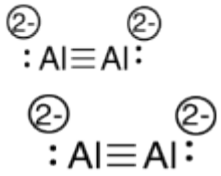
Exercise 2.1.5.*P*.10

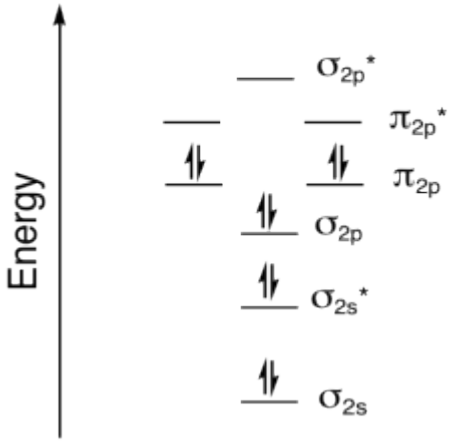
a) Na, because Na has a lower ionization potential (and a lower electronegativity) than Al.

b) Al

c) 4-, because there are four Na^+

d) total e^- = 2 x 3 e^- (per Al) + 4 e^- (for the negative charge) = 10 e-





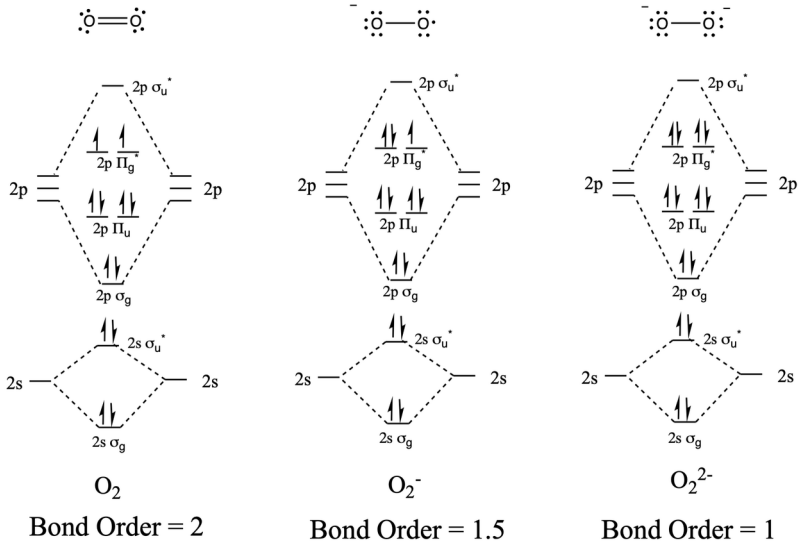
g) bond order $= \frac{(\#bonding\ e^- - \#antibonding\ 3^-)}{2} = \frac{8-2}{2} = 3$

Exercise 2.1.5.*P*.1

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Exercise 2.1.5.P.1

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.



Exercise 2.1.5.P.1

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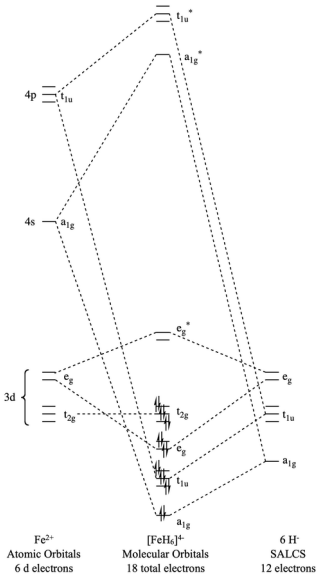
Exercise 2.1.5.P.1

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Exercise 2.1.5.P.1

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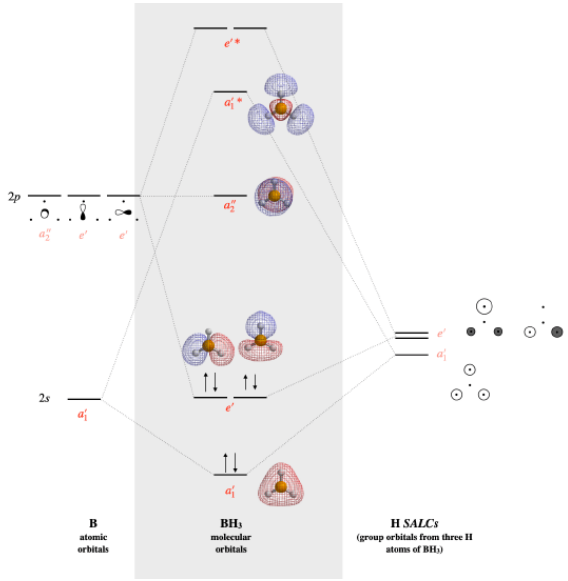
Exercise 2.1.5.P.1



Exercise 2.1.5.P.1

The calculated MO diagram is shown below.

- a_2'' is the lone non-bonding orbital.
- The HOMO is the a_2'' nonbonding orbital, the LUMO is a bonding e' set of two degenerate orbitals/
- e' is doubly degenerate
- The bond order is 3



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3: CHEM 2101 TOPIC 3 - MOLECULAR SYMMETRY

3.1: Introduction to Molecular Symmetry

3.1.1: Introduction

3.1.2: Symmetry Operations and Elements

3.1.3: Successive Operations

3.1.4: Point Groups

3.1.5: Symmetry and Group Theory

3.1.5.1: Symmetry Elements and Operations

3.1.5.2: Point Groups

3.1.5.2.1: Groups of Low and High Symmetry

3.1.5.2.2: Other Groups

3.1.6: Character Tables - An Introduction

3.1.7: Significance of Recognizing Symmetry Elements

3.1.8: Vibrational Spectroscopy

3.1.8A: Vibrational Spectroscopy

3.1.8C: Vibrational Spectroscopy of Linear and Bent triatomic Molecules

3.1.9: Chiral Molecules

3.1.P: Problems (under construction)

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3.1: INTRODUCTION TO MOLECULAR SYMMETRY

- Topic hierarchy

3.1.1: Introduction

3.1.2: Symmetry Operations and Elements

3.1.3: Successive Operations

3.1.4: Point Groups

3.1.5: Symmetry and Group Theory

3.1.5.1: Symmetry Elements and Operations

3.1.5.2: Point Groups

3.1.5.2.1: Groups of Low and High Symmetry

3.1.5.2.2: Other Groups

3.1.6: Character Tables - An Introduction

3.1.7: Significance of Recognizing Symmetry Elements

3.1.8: Vibrational Spectroscopy

3.1.8A: Vibrational Spectroscopy

3.1.8C: Vibrational Spectroscopy of Linear and Bent triatomic Molecules

3.1.9: Chiral Molecules

3.1.P: Problems (under construction)

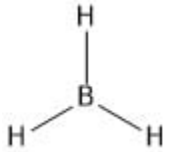
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3.1.1: Introduction

Symmetry is important in the study of chemistry. It can be studied on both the molecular level and the crystalline level, of which the former will be discussed in this book.

A molecule is symmetrical if it stays in an indistinguishable configuration after some movement. For example, the molecule BH_3 in **3.1** can be rotated about an axis perpendicular to the screen and passes through the boron atom. If the rotation angle is 120°, the new configuration is indistinguishable from the original form.



3.1

The study of symmetry has many applications, some of which will be introduced in this chapter. Also in this chapter, some of the terminology and definitions used in group theory, the mathematical representation of symmetry, will be introduced.

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3.1.2: Symmetry Operations and Elements

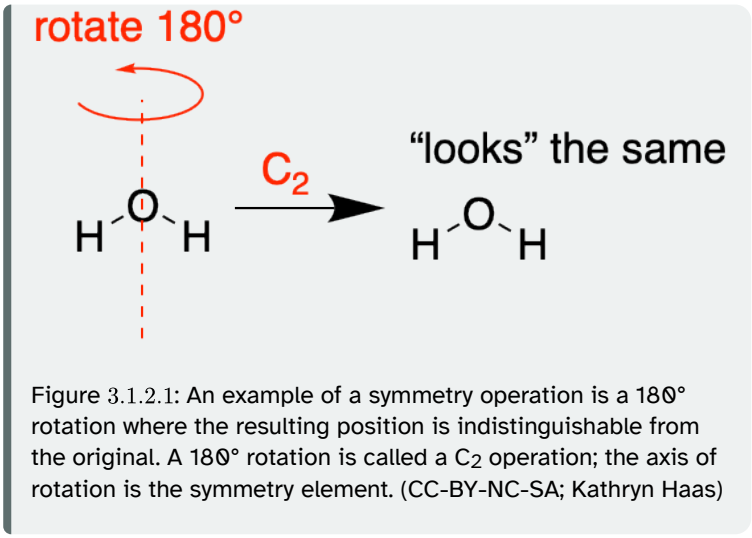


Figure 3.1.2.1: An example of a symmetry operation is a 180° rotation where the resulting position is indistinguishable from the original. A 180° rotation is called a C_2 operation; the axis of rotation is the symmetry element. (CC-BY-NC-SA; Kathryn Haas)

Introduction

The symmetry of a molecule consists of **symmetry operations** and **symmetry elements**. A symmetry operation is an operation that is performed to a molecule which leaves it indistinguishable and superimposable on the original position. Symmetry operations are performed with respect to symmetry elements (points, lines, or planes).

An example of a symmetry operation is a 180° rotation of a water molecule in which the resulting position of the molecule is indistinguishable from the original position (see Figure 3.1.2.1). In this example, the symmetry operation is the rotation and the symmetry element is the axis of rotation.

There are five types of symmetry operations including **identity**, **reflection**, **inversion**, **proper rotation**, and **improper rotation**. The improper rotation is the sum of a rotation followed by a reflection. The symmetry elements that correspond to the five types of symmetry operations are listed in Table 3.1.2.1.

Table 3.1.2.1: Table of elements and operations

Element	Operation	Symbol
Identity	identity	E
Proper axis	rotation by $(360/n)^o$	C_n
Symmetry plane	reflection in the plane	σ
Inversion center	inversion of a point at (x,y,z) to (-x,-y,-z)	*i*
Improper axis	rotation by $(360/n)^o$, followed by reflection in the plane perpendicular to the rotation axis	S_n

Symmetry Operations and Elements

Identity (E)

All molecules have the identity element. The identity operation is doing nothing to the molecule (it doesn't rotate, reflect, or invert...it just is).

Proper Rotation and Proper Axis (C_n)

A "proper" rotation is just a simple rotation operation about an axis. The symbol for any proper rotation or proper axis is $C_{(360/n)}$, where n is the degree of rotation. Thus, a 180° rotation is a C_2 rotation around a C_2 axis, and a 120° rotation is a C_3 rotation about a C_3 axis.

> **PRINCIPLE AXIS**: The principle axis of a molecule is the highest order proper rotation axis. For example, if a molecule had C_2 and C_4 axes, the C_4 is the principle axis.

Reflection and Symmetry Planes (σ)

Symmetry planes are mirror planes within the molecule. A reflection operation occurs with respect to a plane of symmetry. There are three classes of symmetry elements:

1. σ_h (horizontal): horizontal planes are perpendicular to principal axis
2. σ_v (vertical): vertical planes are parallel to the principal axis
3. σ_d (dihedral): dihedral planes are parallel to the principle axis and bisecting two C_2' axes

Inversion and Inversion Center (i)

The inversion operation requires a point of symmetry (a center of symmetry within a molecule). In other words, a point at the center of the molecule that can transform (x,y,z) into (-x,-y,-z) coordinate. Structures of tetrahedron, triangles, and pentagons lack an inversion center.

Improper rotation (S_n)

Improper rotation is a combination of a rotation with respect to an axis of rotation (C_n), followed by a reflection through a plane perpendicular to that C_n axis. In short, and S_n operation is equivalent to C_n followed by σ_h.

References

1. Introduction to Molecular Symmetry by J. S Ogden
2. Inorganic Chemistry by Catherine Housecroft And Alan G. Sharpe.

Problems

1. Water molecule H_2O was used as an example and was mentioned that water was rotated 180 degree around an axis bisecting the oxygen, then the molecule was superimposable on the original water molecule, how about CO_2? Is it going to be like the water molecule since CO_2 also has 2 atoms of oxygen.

Of course not, because every molecule has different molecular shape. To recognize the symmetry of any molecule the structure and the molecular shape of that molecule should be defined. The water molecule is bent but CO_2 is not, and if CO_2 is rotated 360 degree around the axis bisecting the C atom then it can be superimposed on the original molecule. We then see the symmetry for the CO_2.

2. Why should all of the five symmetry elements be done on a molecule in order to find the point group the molecule belongs to, why is performing only one or two of the symmetry elements not enough for recognizing the point group?

One or two of the symmetry elements will not be able to tell us everything about the molecule's symmetry since those one or two properties do not tell us everything about the molecule. Also, while different molecules may have one or two symmetrical properties in common, the five properties will not be the same for all molecules.

3. What does the symbol C_n stand for and what does n represent? Why is it important to identify n?

C is the axis of rotation and n is the order of the axis.

4. How are the character tables helpful?

The character table tells us about all the operational elements performed on the molecule and indicates if we have forgotten to perform any of the symmetry elements. The tables serve as a checklist because all the operational elements should be done on the molecule in order to find the point group of the molecule.

5. Why is important to find symmetry in molecules?

Symmetry tells us about bounding for that molecular bonding.

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3.1.3: Successive Operations

Sometimes, new symmetry operations form by carrying out two or more simpler operations successively to result in an indistinguishable configuration. For example, the improper rotation axis that was introduced in the last section results from rotation about an axis of rotation (C_n) followed by reflection about a plane perpendicular to that axis (σ_h).

$$S_n = C_n \times \sigma_h$$

Note also that C_n in this case need not be a symmetry element for the molecule. For example, staggered ethane has an S_6 symmetry element although it does not have a C_6. Another example of a symmetry element that results from a combination of two different elements is the inversion center (i), which results from a C_2 rotation followed by a reflection about a plane perpendicular to that axis (σ_h).

$$i = C_2 \times \sigma_h$$

Note that an inversion center is a special case of an improper rotation axis because it results when, in the first equation, $n = 2$. That is,

$$i = S_2$$

In fact, any symmetry operation can be carried out multiple time in a row. For example, when BH_3 is rotated twice by 120°, the two-step operation can be symboled by C_3^2. When the C_3 operation is performed a third time, the molecule returns to its original configuration; i.e,

$$C_3^3 = E$$

In general,

$$C_n^n = E$$

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3.1.4: Point Groups

Point groups are used to describe molecular symmetries and are a condensed representation of the symmetry elements a molecule may posses. This includes both bond and orbital symmetry. Knowing molecular symmetry allows for a greater understanding of molecular structure and can help to predict many molecular properties.

Introduction

Point groups are a quick and easy way to gain knowledge of a molecule. They not only contain a molecule's symmetry elements, but also give rise to a character table, which is a complete set of irreducible representations for a point group. A molecule's point group can be determined by either elucidating each symmetry element contained in a molecule or by properly using the Schreiber chart (see below).

Point groups usually consist of (but are not limited to) the following elements:

- E - The identity operator. This operation leaves a molecule completely unchanged and exists for mathematical purposes.
- C_n - The C_n proper axis of rotation is a 360/n° rotation that when performed leaves a molecule the same. A proper rotation with the highest value of n is known as the major axis of rotation.
- σ - The mirror plane. The mirror plane can be described as a plane which produces a reflection of part of a molecule that is unnoticeable and can be labeled as either σ_h , σ_v , σ_d.
- i - The inversion center. A molecule has a center of inversion if, when inverted, the molecule is unchanged.

See the section on symmetry elements for a more thorough explanation of each.

Each point group is associated with a specific combination of symmetry elements

Each point group has it's own combination of symmetry elements. Listed below are some of the many point groups and their respective symmetry elements, according to category, followed by a representative example.

Non axial groups

C_1: E C_1: E, i

C_n groups

C_2: E, C_2 (notice the major axis of rotation is the point group) C_3: E, C_3, C_3^2



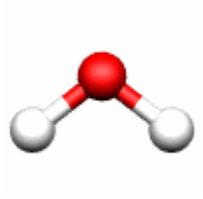
H_2O_2 C_2

D_n groups

D_2: E $C_2(z)$, $C_2(y)$, $C_2(x)$ D_3: E, $2C_3$, $3C_2$

C_{nv} groups

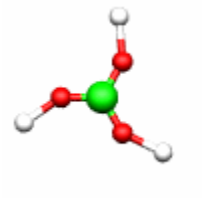
C_{2v}: E, C_2, $\sigma_v(xz)$, $\sigma_v'(yz)$ C_{3v}: E, $2C_3$, $3\sigma_v$



H_2O C_{2v}

C_{nh} groups

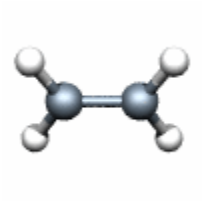
C_{2h}: E, C_2, i, σ_h C_{3h}: E, C_3, C_3^2, σ_h, S_3, S_3^3



$B(OH)_3$

D^{nh} groups

D_{2h}: E



C_2H_4 D_{2h}

How to determine a molecules point group

A molecule's point group can be determined by calculating all the symmetry elements of a molecule and matching them to a respective point group. This process, however, is greatly simplified when the Schreiber chart is used:

References

1. Housecroft, Catherine E.; Sharpe, Alan G., *Inorganic Chemistry,* 3rd Ed. Pearson Education Limited 2008, Chapter 4
2. Koster, George F.; Wheeler, Robert G.; Dimmock, John O., The Properties of Thirty-Two Point Groups, The MIT Press 1963
3. Bertolucci, Michael D.; Harris, Daniel C., Symmetry and Spectroscopy: An Introduction to Vibrational and Electronic Spectroscopy, Dover Publications 1989

Outside Links

- Point groups in 3-D

Problems

1. Determine the point group of BH_3 by calculating all it's symmetry elements then use the chart and determine which method is faster.
2. Determine the point groups of BH_3 and NH_3. Why is there a difference?
3. What is the point group of PPh_3?
4. Determine the point groups of CO_2 and H_2O and then compare them.
5. Propose a molecule with no symmetry. What is it's point group?

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3.1.5: SYMMETRY AND GROUP THEORY

3.1.5.1: Symmetry Elements and Operations

3.1.5.2: Point Groups

3.1.5.2.1: Groups of Low and High Symmetry

3.1.5.2.2: Other Groups

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3.1.5.1: Symmetry Elements and Operations

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Introduction

The symmetry of a molecule consists of **symmetry operations** and **symmetry elements**. A symmetry operation is an operation that is performed to a molecule which leaves it indistinguishable and superimposable on the original position. Symmetry operations are performed with respect to symmetry elements (points, lines, or planes).

An example of a symmetry operation is a 180° rotation of a water molecule in which the resulting position of the molecule is indistinguishable from the original position (see Figure 3.1.5.1.1). In this example, the symmetry operation is the rotation and the symmetry element is the axis of rotation.

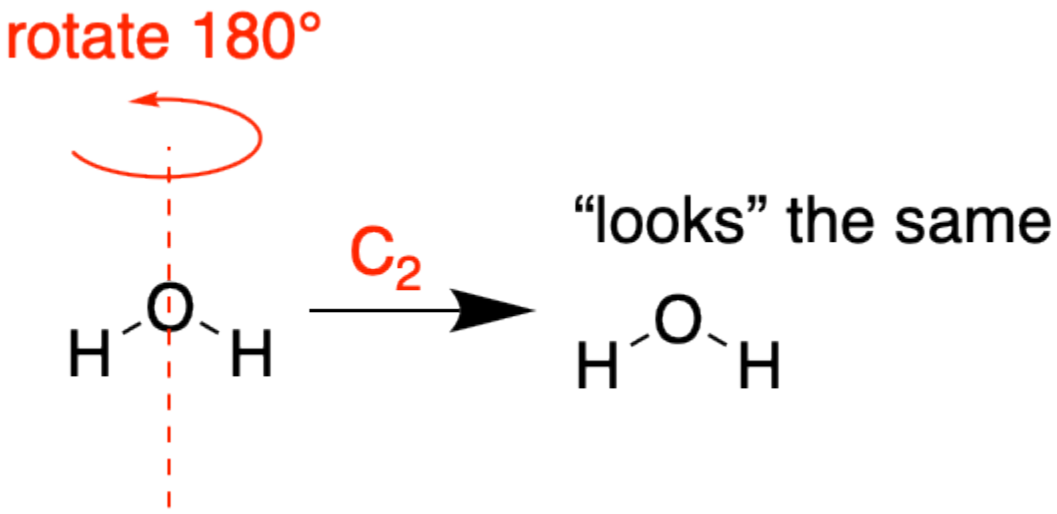


Figure 3.1.5.1.1: An example of a symmetry operation is a 180° rotation where the resulting position is indistinguishable from the original. A 180° rotation is called a C_2 operation; the axis of rotation is the symmetry element. (Kathryn Haas; CC-NC-BY-SA)

There are five types of symmetry operations including **identity**, **reflection**, **inversion**, **proper rotation**, and **improper rotation**. The improper rotation is the sum of a rotation followed by a reflection. The symmetry elements that correspond to the five types of symmetry operations are listed in Table 3.1.5.1.1.

Table 3.1.5.1.1: Table of elements and operations

Element	Operation	Symbol
Identity	identity	E
Proper axis	rotation by $(360/n)^o$	C_n
Symmetry plane	reflection in the plane	σ
Inversion center	inversion of a point at (x,y,z) to (-x,-y,-z)	*i*
Improper axis	rotation by $(360/n)^o$, followed by reflection in the plane perpendicular to the rotation axis	S_n

Symmetry Operations and Elements

Identity (E)

All molecules have the identity element. The identity operation is doing nothing to the molecule (it doesn't rotate, reflect, or invert...it just is).

Proper Rotation and Proper Axis (C_n)

A "proper" rotation is just a simple rotation operation about an axis. The symbol for any proper rotation or proper axis is $C_{(360/n)}$, where n is the degree of rotation. Thus, a 180° rotation is a C_2 rotation around a C_2 axis, and a 120° rotation is a C_3 rotation about a C_3 axis.

> **PRINCIPAL AXIS**: The principal axis of a molecule is the highest order proper rotation axis. For example, if a molecule had C_2 and C_4 axes, the C_4 is the principal axis.

Reflection and Symmetry Planes (σ)

Symmetry planes are mirror planes within the molecule. A reflection operation occurs with respect to a plane of symmetry. There are three classes of symmetry elements:

1. σ_h (horizontal): horizontal planes are perpendicular to principal axis
2. σ_v (vertical): vertical planes are parallel to the principal axis
3. σ_d (dihedral): dihedral planes are parallel to the principal axis and bisecting two C_2' axes

Inversion and Inversion Center (i)

The inversion operation requires a point of symmetry (a center of symmetry within a molecule). In other words, a point at the center of the molecule that can transform (x,y,z) into (-x,-y,-z) coordinate. Structures of tetrahedrons, triangles, and pentagons lack an inversion center.

Improper rotation (S_n)

Improper rotation is a combination of a rotation with respect to an axis of rotation (C_n), followed by a reflection through a plane perpendicular to that C_n axis. In short, an S_n operation is equivalent to C_n followed by σ_h.

References

1. Introduction to Molecular Symmetry by J. S Ogden
2. Inorganic Chemistry by Catherine Housecroft And Alan G. Sharpe.

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3.1.5.2: Point Groups

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Introduction

A **Point Group** describes all the symmetry operations that can be performed on a molecule that result in a conformation indistinguishable from the original. Point groups are used in Group Theory, the mathematical analysis of groups, to determine properties such as a molecule's molecular orbitals.

Assigning Point Groups

While a point group contains all of the symmetry operations that can be performed on a given molecule, it is not necessary to identify all of these operations to determine the molecule's overall point group. Instead, a molecule's point group can be determined by following a set of steps which analyze the presence (or absence) of particular symmetry elements.

Steps for assigning a molecule's point group:

1. Determine if the molecule is of high or low symmetry.
2. If not, find the highest order rotation axis, C_n.
3. Determine whether the molecule has any C_2 axes perpendicular to the principal C_n axis. If so, then there are n such C_2 axes, and the molecule is in the D set of point groups. If not, it is in either the C or S set of point groups.
4. Determine whether the molecule has a horizontal mirror plane (σ_h) perpendicular to the principal C_n axis. If so, the molecule is either in the C_{nh} or D_{nh} set of point groups.
5. Determine whether the molecule has a vertical mirror plane (σ_v) containing the principal C_n axis. If so, the molecule is either in the C_{nv} or D_{nd} set of point groups. If not, and if the molecule has n perpendicular C_2 axes, then it is part of the D_n set of point groups.
6. Determine whether there is an improper rotation axis, S_{2n}, collinear with the principal C_n axis. If so, the molecule is in the S_{2n} point group. If not, the molecule is in the C_n point group.

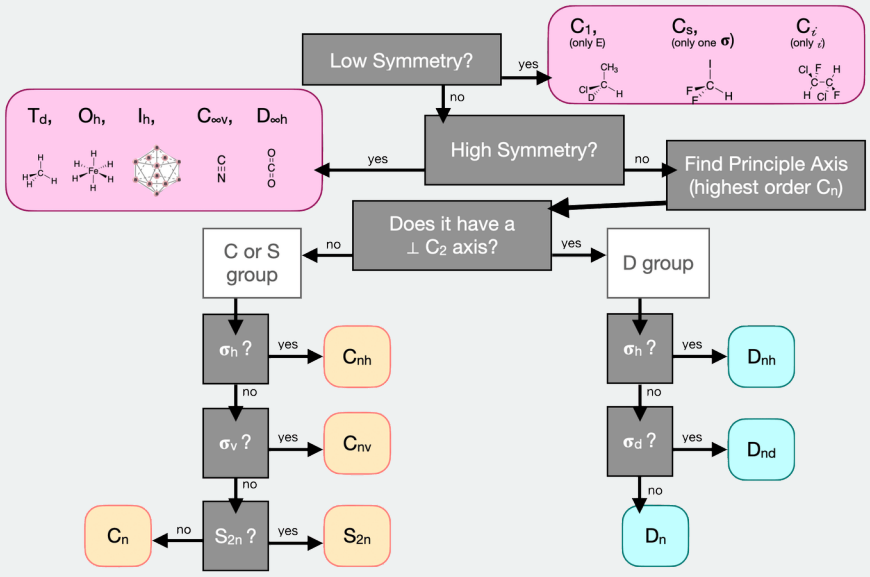


Figure 3.1.5.2.1: Decision tree for determining a molecule's point group (CC-BY-NC-SA; Kathryn Haas)

Example 3.1.5.2.1

Find the point group of benzene (C_6H_6).

Answer available at the end of this section.

See Also

Symmetry Gallery

Answers

Example 3.1.5.2.1

Solution

1. Benzene is neither high nor low symmetry
2. Highest order rotation axis: C_6
3. There are 6 C_2 axes perpendicular to the principal axis
4. There is a horizontal mirror plane (σ_h)

Benzene is in the D_{6h} point group.

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3.1.5.2.1: Groups of Low and High Symmetry

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Low Symmetry Point Groups

Low symmetry point groups include the C_1, C_s, and C_i groups

Group	Description	Example
C_1	only the identity operation (E)	CHFClBr
C_s	only the identity operation (E) and one mirror plane	C_2H_2ClBr
C_i	only the identity operation (E) and a center of inversion (i)	$C_2H_2Cl_2Br$

High Symmetry Point Groups

High symmetry point groups include the T_d, O_h, I_h, $C_{\infty v}$, and $D_{\infty h}$ groups. The table below describes their characteristic symmetry operations. The full set of symmetry operations included in the point group is described in the corresponding character table.

Group	Description	Example
$C_{\infty v}$	linear molecule with an infinite number of rotation axes and vertical mirror planes (σ_v)	HBr
$D_{\infty h}$	linear molecule with an infinite number of rotation axes, vertical mirror planes (σ_v), perpendicular C_2 axes, a horizontal mirror plane (σ_h), and an inversion center (i)	CO_2
T_d	typically have tetrahedral geometry, with 4 C_4 axes, 3 C_2 axes, 3 S_4 axes, and 6 dihedral mirror planes (σ_d)	CH_4
O_h	typically have octahedral geometry, with 3 C_4 axes, 4 C_3 axes, and an inversion center (i) as characteristic symmetry operations	SF_6
I_h	typically have an icosahedral structure, with 6 C_5 axes as characteristic symmetry operations	$B_{12}H_{12}^{2-}$

See Also

Symmetry Gallery

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3.1.5.2.2: Other Groups

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D Groups

The D set of point groups is classified as D_{nh}, D_{nd}, or D_n, where n refers to the principal axis of rotation. Overall, the D groups are characterized by the presence of n C_2 axes perpendicular to the principal C_n axis. Further classification of a molecule in the D groups depends on the presence of horizontal or vertical/dihedral mirror planes.

Group	Description	Example
D_{nh}	n perpendicular C_2 axes, and a horizontal mirror plane (σ_h)	benzene, C_6H_6 is D_{6h}
D_{nd}	n perpendicular C_2 axes, and a vertical mirror plane (σ_v)	propadiene, C_3H_4 is D_{2d}
D_n	n perpendicular C_2 axes, no mirror planes	$[Co(en)_3]^{3+}$ is D_3

C Groups

The C set of point groups is classified as C_{nh}, C_{nv}, or C_n, where n refers to the principal axis of rotation. The C set of groups is characterized by the absence of n C_2 axes perpendicular to the principal C_n axis. Further classification of a molecule in the C groups depends on the presence of horizontal or vertical/dihedral mirror planes.

Group	Description	Example
C_{nh}	horizontal mirror plane (σ_h) perpendicular to the principal C_n axis	boric acid, H_3BO_3, is C_{3h}
C_{nv}	vertical mirror plane (σ_v) containing the principal C_n axis	ammonia, NH_3, is C_{3v}
C_n	no mirror planes	$P(C_6H_5)_3$ is C_3

S Groups

The S set of point groups is classified as S_{2n}, where n refers to the principal axis of rotation. The S set of groups is characterized by the absence of n C_2 axes perpendicular to the principal C_n axis, as well as the absence of horizontal and vertical/dihedral mirror planes. However, there is an improper rotation (or a rotation-reflection) axis collinear with the principal C_n axis.

Group	Description	Example
S_{2n}	improper rotation (or a rotation-reflection) axis collinear with the principal C_n axis	12-crown-4 is S_4

See Also

Symmetry Gallery

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3.1.6: Character Tables - An Introduction

Although the method of assigning a point group to a molecule depends on some knowledge of the symmetry elements the molecule has, it does not require the consideration of all elements. For example, the molecule CO_2 can be assigned the point group $D_{\infty h}$ using the scheme in section 3.4 by merely knowing that the molecule is linear and that it has the a center io inversion i. The point group assignment in this case did not require knowing that the molecule also has σ_h, for example. This type of knowledge is gained by examining character tables.

Definition

A character table is a table that contains the symmetry information of the molecule. This information can be used to analyze the molecule's behavior in many application, among which is spectroscopy. Each point group has its own character table. The following table is the character table of the point group C_{2v}:

Table 1: *The character table of the point group C_{2v}.*

C_{2v}	E	C_2 (z)	σ_v(xz)	σ_v(yz)	h = 4	
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

Understanding Character Tables

Symbols under the first column of the character tables

A (Mulliken Symbol)	(singly degenerate or one dimensional) symmetric with respect to rotation of the principle axis
B (Mulliken Symbol)	(singly degenerate or one dimensional) anti-symmetric with respect to rotation of the principle axis
E (Mulliken Symbol)	(doubly degenerate or two dimensional)
T (Mulliken Symbol)	(thirdly degenerate or three dimensional)
Subscript 1	symmetric with respect to the $C_n$principle axis, if no perpendicular axis, then it is with respect to σ_v
Subscript 2	anti-symmetric with respect to the $C_n$principle axis, if no perpendicular axis, then it is with respect to σ_v
Subscript g	symmetric with respect to the inverse
subscript u	anti-symmetric with respect to the inverse
prime	symmetric with respect to σ_h (reflection in horizontal plane)
double prime	anti-symmetric with respect to σ_h (opposite reflection in horizontal plane)

Symbols in the first row of the character tables

E	describes the degeneracy of the row (A and B= 1) (E=2) (T=3)

C_n	2pi/n= number of turns in one circle on the main axis without changing the look of a molecule (rotation of the molecule)
C_n'	2π/n= number of turns in one circle perpendicular to the main axis, without changing the structure of the molecule
C_n''	2π/n= number of turns in one circle perpendicular to the C_n' and the main axis, without changing the structure
σ'	reflection of the molecule perpendicular to the other sigma
σ_v (vertical)	reflection of the molecule vertically compared to the horizontal highest fold axis.
σ_h or σ_d (horizontal)	reflection of the molecule horizontally compared to the horizontal highest fold axis.
i	Inversion of the molecule from the center
S_n	rotation of 2π/n and then reflected in a plane perpendicular to rotation axis.
#C_n	the # stands for the number of irreducible representation for the C_n
#σ	the # stands for the number irreducible representations for the sigmas.
the number in superscript	in the same rotation there is another rotation, for instance O_h has $3C_2=C_4^2$
other useful definitions	
(R_x,R_y)	the (,) means they are the same and can be counted once.
x^2+y^2, z^2	without (,) means they are different and can be counted twice.

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3.1.7: Significance of Recognizing Symmetry Elements

In the forgoing sections of this chapter, the necessary tools to assign a point group to a molecule and to be able to read a character table were introduced. A good question at this point is: What is the importance of these tools in inorganic chemistry?

In fact, there are many applications in the study of inorganic chemistry where these symmetry tools become handy. In general, these applications belong to one of the following categories:

- Understanding the spectroscopic properties of moelcules (introduced in section 3.7);
- Determining the chirality of molecular species (introduced in section 3.8);
- Constructing molecular and hybrid orbitals (Chapter 5).

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3.1.8: VIBRATIONAL SPECTROSCOPY

- Topic hierarchy

3.1.8A: Vibrational Spectroscopy

3.1.8C: Vibrational Spectroscopy of Linear and Bent triatomic Molecules

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3.1.8A: Vibrational Spectroscopy

All molecules are constantly vibrating, and can absorb energy from an incoming photon to increase their vibrations. The two types of vibrational spectroscopy are infrared spectroscopy and Raman spectroscopy. Vibrational spectroscopy is the science of measuring exactly which wavelengths of light are absorbed by a molecule. This technique could be used identify an unknown molecule by comparing its absorption to that of other molecules. Or vibrational spectroscopy could be used to gain further understanding of the physical properties of a known molecule.

Introduction

Molecular vibration can be modeled by balls attached by springs. Displacing an atom from its most stable position requires energy proportional to the displacement. IR spectroscopy can be used to characterize a molecule is the energy of its vibrations falls in the infrared range. Alternatively, higher energy light can be absorbed, the re-emitted at a different wavelength and/or in a different direction; this leads to Raman spectroscopy. So a molecule can absorb radiation to change bond lengths or positions with respect to the other atoms in the molecule.[3]

From the number, frequency, and intensity of these absorptions or emissions we can gain insight into the composition of the sample being measured. The number of different absorptions is indicative of the number of different atoms and shape of the molecule. The frequency or wavelength absorbed is indicative of the energy of the bonds and vibrations. And the intensity of the absorptions is related to the concentration of the analyte.[1]

Vibrational Modes

The different possible vibrations are called vibrational modes. Vibrational modes are determined by all the different ways the atoms in the molecule can move with respect to eachother, called the vibrational degrees of freedom. Vibrational degrees of freedom differ from the total degrees of freedom in that translation (movement through space) and rotation do not contribute to the vibrational degrees of freedom.[4]

To find the number of vibrational modes one must first know the point group of the molecule. From there, the point group's character table will list all of the possible symmetry operations for the molecule. Each symmetry operation will leave some atoms in the molecule in place and/or move other atoms in the molecule. Count up the number of atoms that do not move for each symmetry operation, and multiply that number by the symmetry operation's contribution. This gives the total representation of atomic motion. From there, the vibrational modes can be found by reducing the total representation, according to the equation:

$$n = 1/h * \Sigma XR * XI * N$$

where n is the number of modes with that symmetry, h is the total number of symmetry operations, X_I is the number of irreducible representations (the value calculated above), X_R is the number of reducible representations (the entry in the character table), and N is the number of identical symmetry operations. Finally, subtracting the rotational modes and translational modes from the reduced representation gives the number of vibrational modes.[6]

Symmetrical stretching.gifAsymmetrical stretching.gifScissoring.gif

Three of the vibrational modes for the C_{2V} point group. Used with permission from http://en.Wikipedia.org/wiki/Infrared_spectroscopy

Infrared Spectroscopy

A vibrational mode will be observed in an infrared spectrum if it leads to a change in the molecular dipole moment. Compared to Raman spectroscopy, the infrared photon is completely absorbed and its energy is transfered to the vibration of the molecule, not re-emitted.[4]

Different bonds have different energies associated with them, and require different amounts of energy to stretch or bend. In general, the stronger the bond, the more energy required to deform it. So very weak bonds will only be deformed by low energy radiation, and strong bonds will only be deformed by high energy radiation. This leads to characteristic frequencies where only certain vibrations are absorbed. For example, C-H bonds are typically the only bonds observed in the range from 2960-2850 cm^{-1}. So if an absorption is present at that frequency, it can be assumed that it is due to a C-H bond.[1]

Raman Spectroscopy

alt

A vibrational mode will be observed in Raman spectroscopy if it leads to a change in the polarizability of the electron cloud of a molecule.[4]

If a photon has energy that is significantly higher than the energy of the vibrational states, it may either be deflected without any change in energy, or it may interact with the molecule and either take energy from it or give energy to it.[2]

When the photon is absorbed and re-emitted in a different direction, it is called Rayleigh scattering, and this is strongly dependent on the wavelength of the incoming light. When there is a change in the energy of the photon, it is called Stokes scattering or anti-Stokes scattering, depending on whether energy is absorbed or lost by the molecule. This change in the behavior of the incoming photons can be measured, and will provide information about the concentration and chemical properties of the analyte.[3]

Diagram used with permission from http://en.Wikipedia.org/wiki/Raman_spectroscopy

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Outside Links

- http://www2.ess.ucla.edu/~schauble/m...vibrations.htm
- http://www.webqc.org/symmetry.php
- www.ch.embnet.org/MD_tutorial/
- http://en.Wikipedia.org/wiki/Molecular_vibration
- http://en.Wikipedia.org/wiki/Raman_spectroscopy

Problems

1. Why is it that the symmetric stretch of carbon dioxide (CO_2) is IR inactive, while the symmetric stretch of carbonyl sulfide (COS) is IR active?

A: Because the symmetric stretch of CO_2 does not lead to a change in the dipole moment of the molecule, but the symmetric stretch of COS does.

2. How many vibrational modes are IR and Raman active for C_{20}?

A: 17 IR active modes, 29 Raman Active modes.

3. Are there any differences between the vibrational spectrums of H_2O, H_2S, and H_2Se?

A: Although they have the same number of atoms, the same point group, and the same number of vibrational modes, the

frequencies at which the vibrational modes occur will be different.

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3.1.8C: Vibrational Spectroscopy of Linear and Bent triatomic Molecules

Vibrational spectroscopy, AKA Infrared (IR) Spectroscopy, is a highly useful and beneficial tool for determining structures and functional groups contained in compounds. Although used for many different structure types of polyatomic molecules, this particular Module is dedicated to triatomic molecules with bent and linear spacial molecular geometry.

Introduction

Triatomic molecules are molecules that contain three atoms. The atoms in triatomic molecules can all be the same, as in I_3^-, all be different, as in HCN, or can be a mix like CO_2. Examples include H_2O, which is a bent and has a bond angle of 109^o, and a linear triatomic molecule such as CO_2. All bent tri-atomic molecules belong to the point group C_{2v}, while all the liner tri-atomic molecules with an inversion center belong to the $D_{infinity\text{-}h}$ point group; Those without an inversion center belong to the point group $C_{infinity\text{-}v}$. This gives these two structures very different infrared spectrum even though they have the same number of atoms.

Linear molecules

Using VESPR theory there are several ways to achieve a linear structure. Tri-atomic molecules where the central atom is using ALL of its electrons in the bonds with the surrounding molecules, or in other words the central atom does not have any lone pairs surrounding it, will give rise to a linear molecule. Examples include CO_2 and BeH_3. This electronic configuration gives the central atom a sp hybridization. Triatomic molecules where the central atom does not use all of its electron pairs in the bonds between the other two atoms will, under certain circumstances, also give rise to a linear species. When the central atom is surrounded by three, or four lone pairs in addition to the two elements already attached will also give rise to a linear molecule. Examples include KrF_2.

Bent Molecules

There are also several ways to give rise to bent molecules using VESPR theory. A tri-atomic molecule with one, or two lone pair on the central atom will also give rise to bent species. One lone pair examples include SO_2, and two lone pair examples include H_2O

References

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3.1.9: Chiral Molecules

Introduction

Around the year 1847, the French scientist Louis Pasteur provided an explanation for the optical activity of tartaric acid salts. when he carried out a particular reaction, Pasteur observed that two types of crystals precipitated. Patiently and carefully using tweezers, Pasteur was able to separate the two types of crystals. Pasteur noticed that the types rotated the plane polarized by the same amount but in different directions. These two compounds are called enantiomers.

What are Enantiomers?

Two compounds are enantiomers if they are non-superimposable mirror images of each other. As was mentioned, enantiomers are characterized by their ability to rotate plane-polarized light. They also have the same physical properties (e.g., melting point, etc.) relative to each other. As a result, they are also referred to as being optically active. When it comes to symmetry, there are some general rules of thumb that help determine whether a molecule is chiral or achiral. This can be very useful because sometimes molecules can have relatively complicated structures and geometries that knowing whether or not they are chiral becomes a daunting task. The goal, as a result, is to determine the point group of the molecule and the symmetry elements associated with it, then inferring the chirality of the molecule.

Using Symmetry to Determine Chirality

For a molecule to be chiral, it must lack:

1. Center of inversion i and a plane of symmetry σ.
2. An improper rotation axis (rotation-reflection axis) S_n.

However, since, by definition, an improper rotation axis is a rotation about an certain axis followed by reflection about a plane perpendicular to that axis, and an inversion center is simply S_2, the absence of an improper axis requires, in most cases, that absence of both a plane of symmetry and an inversion center. As a result, it suffices, in most cases, to check for improper rotation axes to determine whether a molecule is chiral or not.

As a result of the previous discussion, there are a few classes of point groups that lack an improper axis. Those classes are C_1, C_n, and D_n. Cis-dichlorobis(ethylenediamine)cobalt (III) has two enantiomers that are chiral (figure 1), but the trans compound is achiral.

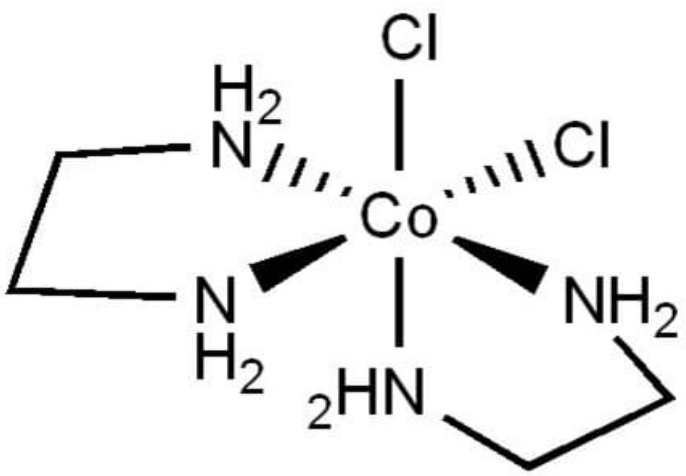


Figure 1: One of the chiral enantiomers of Cis-dichlorobis(ethylenediamine)cobalt (III).

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3.1.P: Problems (under construction)

Problems

1. Chlorophyll *a* is a green pigment that is found in plants. Its molecular formula is $C_{55}H_{77}O_5N_4Mg$. How many degrees of freedom does this molecule possess? How many vibrational degrees of freedom does it have?
2. CCl_4 was commonly used as an organic solvent until its severe carcinogenic properties were discovered. How many vibrational modes does CCl_4 have? Are they IR and/or Raman active?
3. The same vibrational modes in H_2O are IR and Raman active. WF_6^- has IR active modes that are not Raman active and vice versa. Explain why this is the case.
4. How many IR peaks do you expect from SO_3? Estimate where these peaks are positioned in an IR spectrum.
5. Calculate the symmetries of the normal coordinates of planar BF_3.

Answers to Problems

1. Chlorophyll *a* has 426 degrees of freedom and 420 vibrational modes.
2. The point group is T_d, $T_{vib} = a_1 + e + 2t_2$; a_1 and e are Raman active, t_2 is both IR and Raman active.
3. For molecules that possess a center of inversion i, modes cannot be simultaneously IR and Raman active.
4. Point group is D_{3h}; one would expect three IR active peaks. Asymmetric stretch highest (1391 cm^{-1}), two bending modes (both around 500 cm^{-1}). The symmetric stretch is IR inactive.
5. $T_{3N} = A_1' + A_2' + 3E' + 2\ A_2'' + E''$ and $T_{vib} = A_1' + 2E' + A_2''$

Contributors and Attributions

- Kristin Kowolik, University of California, Davis

Problems

1. The water molecule H_2O was used as an example; it was mentioned that when water was rotated 180 degrees around an axis bisecting the oxygen, the molecule was superimposable on the original water molecule. How about CO_2? Will it be like the water molecule since CO_2 also has 2 atoms of oxygen?

Of course not, because every molecule has a different molecular shape. To recognize the symmetry of any molecule, the structure and the molecular shape of that molecule should be defined. The water molecule is bent but CO_2 is not, and if CO_2 is rotated 360 degrees around the axis bisecting the C atom, then it can be superimposed on the original molecule. We then see the symmetry for the CO_2.

2. Why should all of the five symmetry elements be done on a molecule in order to find the point group the molecule belongs to? Why is performing only one or two of the symmetry elements not enough for recognizing the point group?

One or two of the symmetry elements will not be able to tell us everything about the molecule's symmetry, since those one or two properties do not tell us everything about the molecule. Also, while different molecules may have one or two symmetrical properties in common, the five properties will not be the same for all molecules.

3. What does the symbol C_n stand for and what does n represent? Why is it important to identify n?

C is the axis of rotation and n is the order of the axis.

4. How are the character tables helpful?

The character table tells us about all the operational elements performed on the molecule and indicates whether we have forgotten to perform any of the symmetry elements. The tables serve as a checklist because all the operational elements should be done on the molecule in order to find the point group of the molecule.

5. Why is important to find symmetry in molecules?

Symmetry tells us about bonding for that molecule.

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4.1.1: Introduction

Crystalline solids

- The atoms, molecules or ions pack together in an ordered arrangement
- Such solids typically have flat surfaces, with unique angles between faces and unique
- 3-dimensional shape
- Examples of crystalline solids include diamonds, and quartz crystals

Amorphous solids

- No ordered structure to the particles of the solid
- No well defined faces, angles or shapes
- Often are mixtures of molecules which do not stack together well, or large flexible molecules
- Examples would include glass and rubber

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4.1.2: PACKING OF SPHERES

- Topic hierarchy

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4.1.2D: Non-closed Packing- Simple Cubic and Body Centered Cubic

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4.1.2A: Cubic and Hexagonal Closed Packing

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4.1.2B: The Unit Cell of HPC and CCP

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1.1: The Unit Cell

The Unit Cell refers to a part of a simple crystal lattice, a repetitive unit of solid, brick-like structures with opposite faces, and equivalent edge points. In 1850, Auguste Bravais proved that crystals could be split into fourteen unit cells. Although there are several types of unit cells found in cubic lattices, we will be discussing the basic ones: Simple Cubic, Body-centered Cubic, and Face-centered Cubic. If any atom recrystalizes, it will eventually become the original lattice. Crystallization refers the purification processes of molecular or structures;.

Introduction

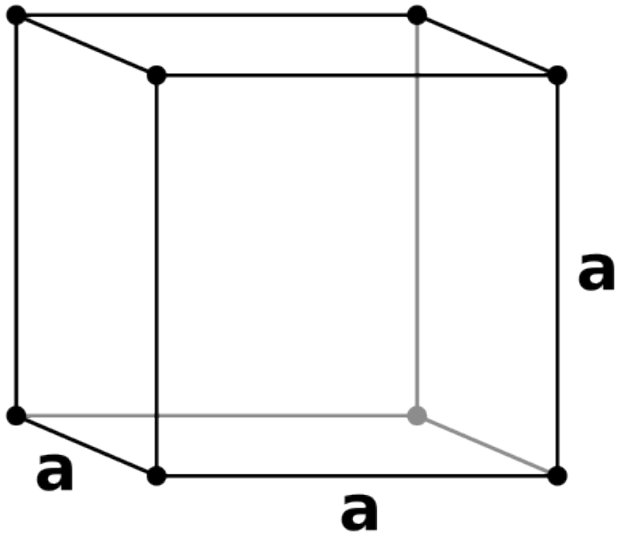
The Unit Cell contains seven crystal systems and fourteen crystal lattices. These unit cells are given types and titles of symmetries, but we will be focusing on cubic unit cells. One of the most commonly known unit cells is rock salt NaCl (Sodium Chloride), an octahedral geometric unit cell. The whole lattice can be reproduced when the unit cell is duplicated in a three dimensional structure. These unit cells are imperative for quite a few metals and ionic solids crystallize into these cubic structures. Calculating with unit cells is a simple task because edge-lengths of the cell are equal along with all 90^0 angles.

Simple Cubic Unit Cells

Simple Cubic unit cells indicate when lattice points are only at the corners. They are the simplest (hence the title) repetitive unit cell. The lattice points at the corners make it easier for metals, ions, or molecules to be found within the crystalline structure. This phenomena is rare due to the low packing of density, but the closed packed directions give the cube shape.

Since the edges of each unit cell are equidistant, each unit cell is identical. In order to be labeled as a "Simple Cubic" unit cell, each eight cornered same particle must at each of the eight corners. This unit cell only contains one atom. Its packing efficiency is about 52%.

To packing efficiency, we multiply eight corners by one-eighth (for only one-eighth of the atom is part of each unit cell), giving us one atom.



8 Corners of a given atom x 1/8 of the given atom's unit cell = 1 atom

To calculate edge length in terms of *r* the equation is as follows:

$$2r$$

An example of a Simple Cubic unit cell is Polonium.

Body-centered Cubic Unit Cells

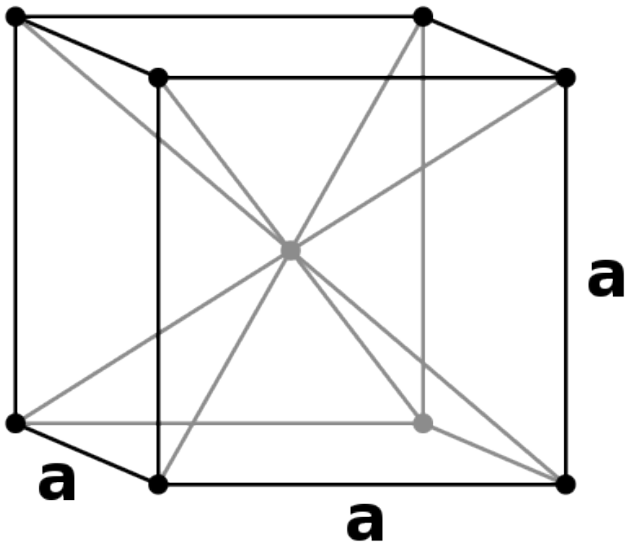
Body-centered Cubic (BCC) unit cells indicate where the lattice points appear not only at the corners but in the center of the unit cell as well. The atoms touch one another along the cube's diagonal crossing, but the atoms don't touch the edge of the cube. All atoms are identical. This type of unit cell is more common than that of the Simple Cubic unit cell due to tightly packed atoms. Its packing efficiency is about 68% compared to the Simple Cubic unit cell's 52%.

This unit cells contains two atoms.

To determine this, we multiply the previous eight corners by one-eighth and *add* one for the additional lattice point in the center.

(8 Corners of a given atom x 1/8 of the given atom's unit cell) + 1 additional lattice point = 2 atoms)

To calculate edge length in terms of *r* the equation is as follows:



$$\frac{4r}{\sqrt{3}} \tag{1.1.1}$$

Some examples of BCCs are Iron, Chromium, and Potassium.

It is a common mistake for CsCl to be considered bcc, but it is not. Instead, it is non-closed packed.

Face-centered Cubic Unit Cells

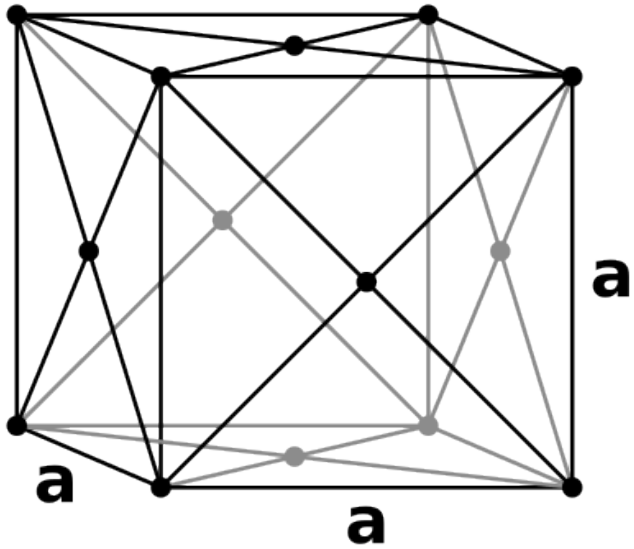
Face-centered Cubic (FCC) unit cells indicate where the lattice points are at both corners and on each face of the cell.

This is a more common type of unit cell since the atoms are more tightly packed than that of a Simple Cubic unit cell. Like the BCC, the atoms don't touch the edge of the cube, but rather the atoms touch diagonal to each face. Its packing efficiency is the highest with a percentage of 74%. Atoms touch one another along the face diagonals. All atoms are identical.

This unit cell contains four atoms.

To determine this, we take the equation from the aforementioned Simple Cubic unit cell and *add* to the parenthesized six faces of the unit cell multiplied by one-half (due to the lattice points on each face of the cubic cell).

(8 corners of a given atom x 1/8 of the given atom's unit cell) + (6 faces x 1/2 contribution) = 4 atoms)



To calculate edge length in terms of *r* the equation is as follows:

$$2\sqrt{2}r \tag{1.1.2}$$

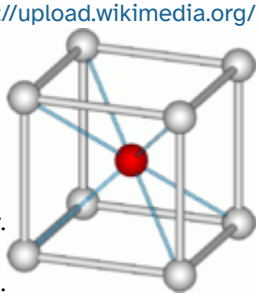
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- Simple Cubic Unit Cell image adapted from the Wikimedia Commons file "Image: http://en.Wikipedia.org/wiki/File:La...mple_cubic.svg"
- Body-centered Cubic Unit Cell image adapted from the Wikimedia Commons file "http://en.Wikipedia.org/wiki/File:La...ered_cubic.svg"
- Face-centered Cubic Unit Cell image adapted from the Wikimedia Commons file "Image: http://en.Wikipedia.org/wiki/File:La...ered_cubic.svg"
- Image from Problem 3 adapted from the Wikimedia Commons file "Image: http://upload.wikimedia.org/wikipedi...Cl_crystal.png"



Problems

1. What is the edge length of the atom Polonium if its radius is 167 pm?
2. What type of unit cell is Caesium Chloride as seen in the picture. Briefly explain your answer. Diagram---------->
3. Give two other examples (none of which is shown above) of a Face-Centered Cubic Structure metal. Briefly explain your reasonings.
4. Silver crystallizes with a FCC; the raidus of the atom is 160 pm. What is the density of the solid silver in grams per cubic centimeters?

Answers

1. Polonium is a Simple Cubic unit cell, so the equation for the edge length is *2r*. Therefore, 2(167pm) = 334pm
2. Caesium Chloride is a non-closed packed unit cell. It is common for one to mistake this as a body-centered cubic, but it is not. The reason for this is because the ions do not touch one another. Also, in order to be considered BCC, all the atoms must be the same. Since the middle atome is different than the corner atoms, this is not a BCC.
3. Two examples of a FCC cubic structure metals are Lead and Aluminum. Each contains four atoms, six of which run diagonally on each face.
4. We approach this problem by first finding the mass of the unit cell. Mass of Silver is 107.87 g/mol, thus we divide by Avagadro's number 6.022 x $10^{-22.}$

We end up with 1.79 x 10^{-22} g/atom. Next we find the mass of the unit cell by multiplying the number of atoms in the unit cell by the mass of each atom (1.79 x 10^{-22} g/atom)(4) = 7.167 x 10^{-22} grams.

Next we find the edge length by:

$$2\sqrt{2} * 160pm \tag{1.1.3}$$

Which equals 4.525 x 10^{-10} meters.

Now we find the volume which equals the edge length to the third power. We convert meters into centimeters by dividing the edge length by 1 cm/10^{-2}m to the third power. (4.525 x 10^{-10} m x 1cm/10^{-2}m = 9.265 x 10^{-23} cubic centimeters.)

Finally, we find the density by mass divided by volume. So, 7.167 x 10^{-22} grams/9.265 x 10^{-23} cubic centimeters = 7.74 g/cm^3

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4.1.2C: Interstitial Holes in HCP and CCP

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4.1.3: THE PACKING OF SPHERES MODEL APPLIED TO THE STRUCTURES OF ELEMENTS



- Topic hierarchy

4.1.3A: Group 18 Elements in the Solid State

4.1.3B: H_2 and F_2 Solids

4.1.3C: Solid Metallic Elements

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4.1.3A: Group 18 Elements in the Solid State

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4.1.3B: H_2 and F_2 Solids

Hydrogen and Fluorine, as well as Chlorine, Bromine and Iodine, exist as diatomic molecules. Both diatomic Hydrogen and diatomic Florine exist as gasses at room temperature and exhibit extremely low melting and boiling points. If the temperature of the system is lowered below the respective melting points of Hydrogen or Fluorine, molecular motion is reduced and a crystalline lattice is formed, creating a solid.

Solid State Hydrogen and Fluorine

Elemental Hydrogen and Elemental Fluorine, H_2 and F_2 respectively, exist as gases at room temperature. Though the melting point of H_2 is 20.4 K (-252.75 °C), a temperature of 14.0 K (-259.15 °C) is required for the solidification of H_2.[3,4] As the solid structure is formed, the diatomic Hydrogen molecules adopt a hexagonal close packing (hcp) structure.[4] Fluorine exhibits similar behaviour. The melting point of Fluorine is 53.54K (-219.61 °C), at which point the diatomic Fluorine adopts a cubic close packed crystalline arrangement (ccp), instead of a hexagonal close packed arrangement.[3,4]

Ability to use the sphere model of Crystalline structure for H_2 and F_2 solids

When solid, both dihydrogen and difluorine are small enough to allow for rotation within the solid structure (the radius of Fluorine is about equivalent to that of Hydrogen). This rotation occurs about a central axis midway between the two distal atoms of the molecule, creating two equal radii from the middle of the H-H or F-F bond to the outer boundary of each H or F atom. This rotation occurs 360° in the x, y and z directions of the central axis, as well as all manner of combinations of these three variables. The rotation of the molecule in all directions creates what can be though of as a spherical shell, the boundary of which is created by the distal atoms.[4]

Some common uses for solid hydrogen include gamma-ray ablation cages for elemental analysis, and a solid state cage in which to look at hydrogen bonding within molecules. [1,2]

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4. Sharpe, Housecroft "Inorganic Chemistry" 3 ed.

Outside Links

- This is not meant for references used for constructing the module, but as secondary and unvetted information available at other site
- Link to outside sources. Wikipedia entries should probably be referenced here.

Problems

1. Why can F_2 and H_2 be considered similar molecules and thus exhibit similar behaviour in rotation?

2. What is the different between a cubic close packing structure and hexagonal close packing?

3. Why do difluorine and dihydrogen exhibit different packing structures.

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4.1.3C: Solid Metallic Elements

A metal (from Greek μέταλλον métallon, "mine, quarry, metal") is a material (an element, compound, or alloy) that is typically hard, opaque, shiny, and has good electrical and thermal conductivity. Metals are generally *malleable* - that is, they can be hammered or pressed permanently out of shape without breaking or cracking - as well as *fusible* (able to be fused or melted) and *ductile* (able to be drawn out into a thin wire). About 91 of the 118 elements in the periodic table are metals (some elements appear in both metallic and non-metallic forms).

Atoms of metals readily lose their outer shell electrons, resulting in a free flowing cloud of electrons within their otherwise solid arrangement. This provides the ability of metallic substances to easily transmit heat and electricity. While this flow of electrons occurs, the solid characteristic of the metal is produced by electrostatic interactions between each atom and the electron cloud. This type of bond is called a metallic bond.

Cubic and hexagonal close packing.

Crystalline solids consist of repeating patterns of its components in three dimensions (a crystal lattice) and can be represented by drawing the structure of the smallest identical units that, when stacked together, form the crystal. This basic repeating unit is called a *unit cell*.

Many metals adopt close packed structures i.e. cubic close packed (face centred cubic) and hexagonal close packed structures. A simple model for both of these is to assume that the metal atoms are spherical and are packed together in the most efficient way (close packing or closest packing). For closest packing, every atom has 12 equidistant nearest neighbours, and therefore a coordination number of 12. If the close packed structures are considered as being built of layers of spheres then the difference between hexagonal close packing and cubic close packed is how each layer is positioned relative to others. It can be envisaged that for a regular buildup of layers:

- hexagonal close packing has alternate layers positioned directly above/below each other, A,B,A,B,...
- cubic close packed (face centered cubic) has every third layer directly above/below each other, A,B,C,A,B,C,...

Body centred cubic

This is not a close packed structure. Here each metal atom is at the centre of a cube with 8 nearest neighbors, however the 6 atoms at the centres of the adjacent cubes are only approximately 15% further away so the coordination number can therefore be considered to be 14 when these are included. Note that if the body centered cubic unit cell is compressed along one 4 fold axis the structure becomes cubic close packed (face centred cubic).

lattice types

cubic close packing (ccp) packing efficiency =74% CN=12	

hexagonal close packing (hcp) packing efficiency =74% CN=12	

body-centred cubic packing (bcc) packing efficiency =68% CN=8

Trends in melting point

Melting points are chosen as a simple measure of the stability or strength of the metallic lattice. Some simple trends can be noted. The transition metals have generally higher melting points than the others. In the alkali metals (Group 1) and alkaline earth metals (Group 2) the melting point decreases as atomic number increases, but in transition metal groups with incomplete d-orbital subshells, the heavier elements have higher melting points. For a given period, the melting points reach a maximum at around Group 6 and then fall with increasing atomic number.

Mercury, caesium and gallium have melting points below 30 °C whereas all the other metals have sufficiently high melting points to be solids at "room temperature". The structures of the metals can be summarised by the table below which shows that most metals crystallise in roughly equal amounts of bcc, hcp and ccp lattices.

Crystal structure of metallic elements in the periodic table

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
H																
453.69 Li bcc	1560 Be hcp					MP (K) At. Symbol Lattice type						B	C	N	O	F
370.87 Na bcc	923 Mg hcp											933.47 Al ccp	Si	P	S	Cl
336.53 K bcc	1115 Ca ccp	1814 Sc hcp	1941 Ti hcp	2183 V bcc	2180 Cr bcc	1519 Mn	1811 Fe bcc	1768 Co hcp	1728 Ni ccp	1357.8 Cu ccp	692.68 Zn hcp	302.91 Ga	Ge	As	Se	Br
312.46 Rb bcc	1050 Sr ccp	1799 Y hcp	2128 Zr hcp	2750 Nb bcc	2896 Mo bcc	2430 Tc hcp	2607 Ru hcp	2237 Rh ccp	1828 Pd ccp	1235 Ag ccp	594 Cd	430 In	505 Sn	904 Sb	Te	I
301.59 Cs bcc	1000 Ba bcc		2506 Hf hcp	3290 Ta bcc	3695 W bcc	3459 Re hcp	3306 Os hcp	2719 Ir ccp	2041.4 Pt ccp	1337.33 Au ccp	234.32 Hg	577 Tl hcp	600.61 Pb ccp	544.7 Bi	527 Po	At

Group 1: Alkali metals

The alkali metals have their outermost electron in an s-orbital and this electronic configuration results in their characteristic properties. The alkali metals provide the best example of group trends in properties in the periodic table, with elements exhibiting well-characterized homologous behaviour.

The alkali metals have very similar properties: they are all shiny, soft, highly reactive metals at standard temperature and pressure and readily lose their outermost electron to form cations with charge +1. They can all be cut easily with a knife due to their softness, exposing a shiny surface that tarnishes rapidly in air due to oxidation by atmospheric moisture and oxygen. Because of their high reactivity, they must be stored under oil to prevent reaction with air, and are found naturally only in salts and never as the free element. In the modern IUPAC nomenclature, the alkali metals comprise the group 1 elements, excluding hydrogen (H), which is only nominally considered a group 1 element.

Group 2: Alkali Earth Metals

extended structures of Li, Mg, Ca

Lithium -bcc	

Magnesium -hcp ☐Spacefill ☐UnitCell ☐All Layers ☐ A ☐B ☐ A ☐ B ☐ A layers	

Calcium -ccp
☐Spacefill ☐UnitCell ☐All Layers
☐ A ☐B ☐C
☐ A ☐ B ☐C layers

Note that Housecroft and Sharpe has Ca and Sr both listed as hexagonal and not cubic (face) close packed lattices. Calcium and Strontium exist in several allotropic forms and the lowest temperature forms (for Ca < 450 °C) are ccp. At high temperatures phase transitions occur to give hexagonal.

Return to the course outline or move on to Lecture 5: Structure of the elements Boron, Carbon and Phosphorus, Sulfur.

References

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'Inorganic Chemistry' - C. Housecroft and A.G. Sharpe, Prentice Hall, 4th Ed., 2012, ISBN13: 978-0273742753, pps 24-27, 43-50, 172-176, 552-558, 299-301, 207-212
'Basic Inorganic Chemistry' - F.A. Cotton, G. Wilkinson and P.L. Gaus, John Wiley and Sons, Inc. 3rd Ed., 1994.
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4.1.4: POLYMORPHISM IN METALS

Polymorphism is the ability of a solid material to exist in more than one form or crystal structure.



- Topic hierarchy

4.1.4A: Polymorphism - Phase Changes in the Solid State

4.1.4B: Phase Diagrams

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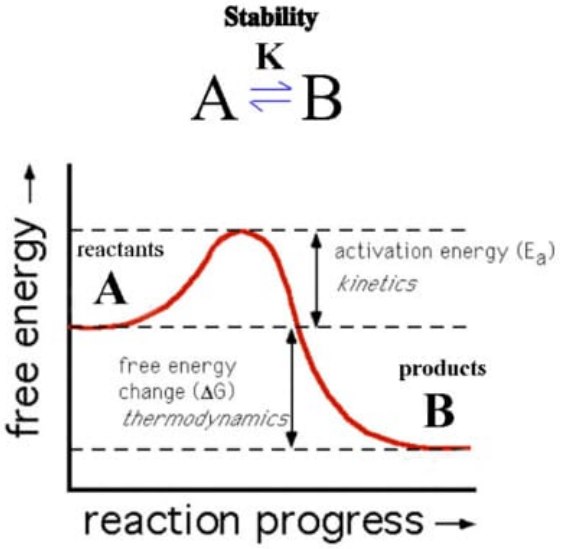
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4.1.4A: Polymorphism - Phase Changes in the Solid State

Polymorphism is when a solid material can exist in more than one form or crystal structure. Polymorphism is very similar to Allotropy, but they should not be confused, polymorphism describes molecules, while Allotropy is used to describe atoms. Polymorphism has many uses whether it was in pharmaceutical, explosives or even food. This process was discovered by Eilhard Mitscherlich in 1821.

Kinetic vs. Thermodynamic Stability

When discussing the concept of Stability it is necessary to distinguish between thermodynamic and kinetic stability.



Here B is at lower energy than A so that ΔG is negative. The reaction should therefore proceed spontaneously and B is the more thermodynamically stable species.

The reaction as shown though has a barrier to the progress of the reaction called the Activation Barrier (Ea) and so the reaction may proceed very slowly. The thermodynamics describes only the starting and ending position of the reaction and not the intermediate or transition state. If the kinetics is slow, A is described as being **inert** while if it proceeds quickly then A is described as being **labile**.

The conditions that distinguish them are:
if the reaction takes longer than 1 minute under the conditions of concentration 0.1 M, temperature 25°C, then it is INERT,
if under the same conditions the reaction time < 1 minute, then it is LABILE.

In the lecture on isomerism, we depend on the samples being kinetically stable i.e. inert.

In the lecture on Chelation and Stability we concentrate on thermodynamic stability and look at the changes in free energy, enthalpy and entropy during the reaction. When we consider thermodynamic stability we need to be familiar with 2 formulae:

$\Delta G^{\ominus} = - RT \ln(K)$ or alternatively $\Delta G^{\ominus} = - 2.303RT \log_{10}(K)$ ---(1)
$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$ ---(2)

The first relates the free energy to the stability constant and the second shows the breakdown into the component enthalpy and entropy terms.

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4.1.4B: Phase Diagrams

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4.1.5: Metallic Radii

Atomic radius is the radius of an atom which measures the distant from its nucleus to the electron. And metallic radii are the radii of the metallic atoms. It is the size of a metallic atom. However the actually measurement of the radius is very vague because electrons don't stay at one point, they orbits around.

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4.1.6: Melting Points and Standard Enthalpies of Atomization of Metals

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4.1.7: ALLOYS AND INTERMETALLIC COMPOUNDS

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).



- Topic hierarchy

4.1.7A: Substitutional Alloys

4.1.7B: Interstitial Alloys

4.1.7C: Intermetallic Compounds

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4.1.7A: Substitutional Alloys

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.

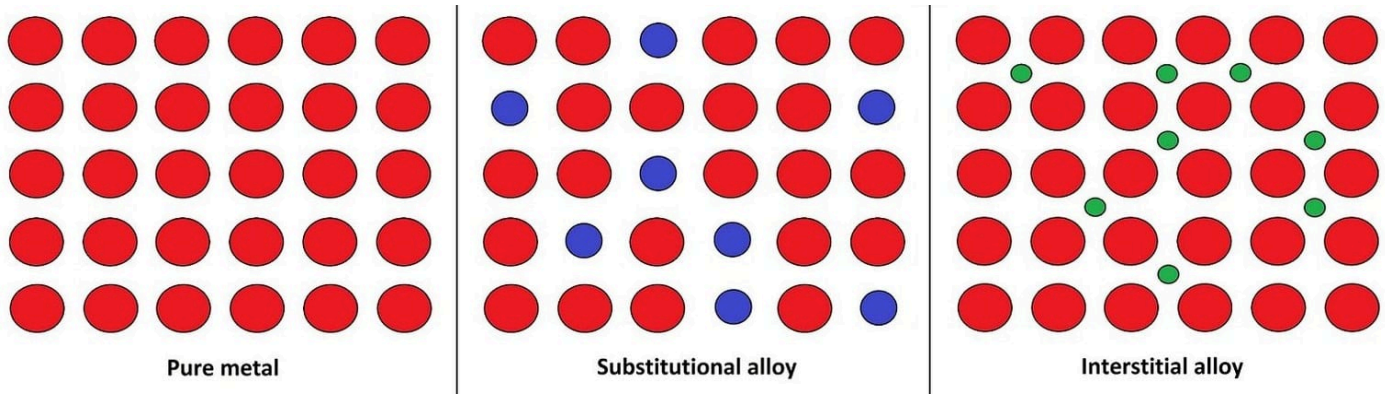


Figure 4.1.7A.1: Different atomic mechanisms of alloy formation, showing pure metal, substitutional, and interstitial structures. (CCO; Hbf878 via Wikipedia)

Why Substitutional Alloys Occur: Bonding

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 can change depending on the different specific metals involved and how 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.

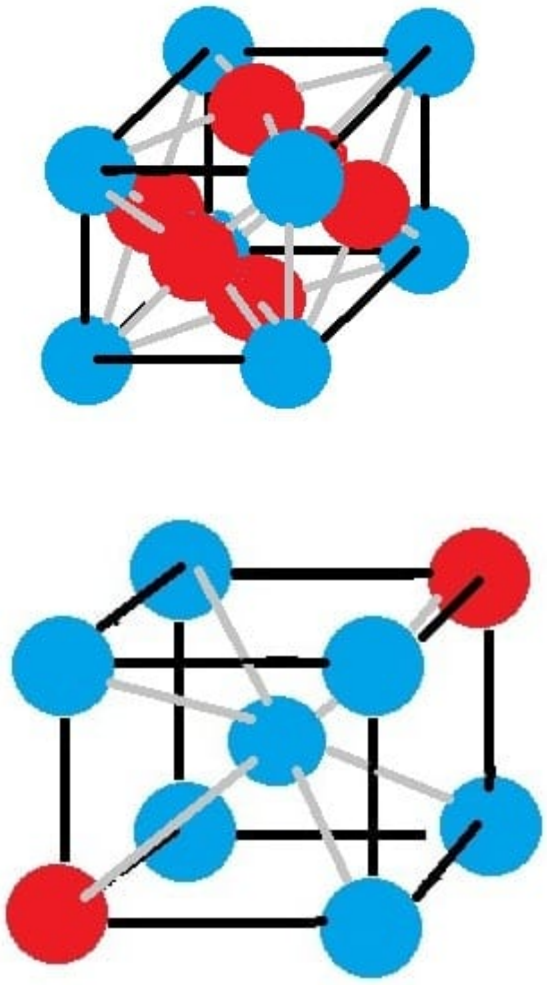


Figure 4.1.7A.2: Examples of Substitutional Metal Alloys. Depending on the specific type of substitutional alloy they can have multiple crystal structures. Two of the possible structures include Face Center Cubic (left), and Cubic Center Cubic (right). The structure of the metal alloy is not limited 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 characteristics of the alloy decrease. 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.(1) 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.

Summary

An alloy is a mixture of metals that has bulk metallic properties different from those of its constituent elements. Alloys can be formed by substituting one metal atom for another of similar size in the lattice (substitutional alloys), by inserting smaller atoms into holes in the metal lattice (interstitial alloys), or by a combination of both. Although the elemental composition of most alloys can vary over wide ranges, certain metals combine in only fixed proportions to form intermetallic compo

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2. Wang, F. E.. (2005). *Bonding theory for metals and alloys*. Amsterdam: Elsevier.
3. Dickinson, O. T. P. K. (1994). *The Aegean Bronze age*. Cambridge world archeology. Cambridge: Cambridge University Press.

Problems

1. Are substitutional metal alloys naturally occurring on earths surface?
2. What are two characteristics of a metal required for a substitutional alloy to form?
3. Can Oxygen or Nitrogen be a part of the crystal structure of a substitutional alloy?

Solutions

1. No, the oxidizing nature of the earths atmosphere, as well as the need for specific and concentrated metals keeps these from being found naturally occurring.
2. Similar radii and similar electronegativity.
3. Only metallic elements can form the necessary metallic bonds that allow alloys to form.

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4.1.7B: Interstitial Alloys

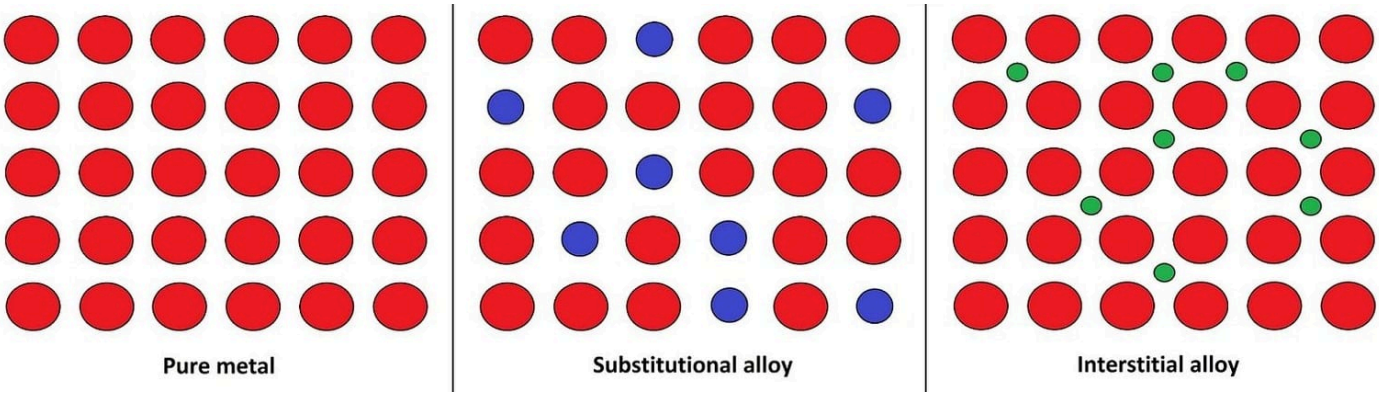


Figure 6.7B.1: *Different atomic mechanisms of alloy formation, showing pure metal, substitutional, and interstitial structures. from Wikipedia.*

With the interstitial mechanism, one atom is usually much smaller than the other, so cannot successfully replace an atom in the crystals of the base metal. The smaller atoms become trapped in the spaces between the atoms in the crystal matrix, called the *interstices*. 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.

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4.1.7C: Intermetallic Compounds

Intermetallic compounds are solid phases containing two or more metallic elements, with optionally one or more non-metallic elements, whose crystal structure differs from that of the other constituents. Under this definition the following are included

- The definition of a metal is taken to include:
  - the so-called post-transition metals, i.e. aluminium, gallium, indium, thallium, tin and lead
  - some, if not all, of the metalloids, e.g. silicon, germanium, arsenic, antimony and tellurium.

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4.1.8: BONDING IN METALS AND SEMICONDOCTORS

4.1.8A: Electrical Conductivity and Resistivity

4.1.8B: Band Theory of Metals and Insulators

4.1.8C: The Fermi Level

4.1.8D: Band Theory of Semiconductors

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4.1.8A: 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:

$$\rho = \frac{1}{\sigma} \tag{4.1.8A.1}$$

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

$$\frac{E}{J} = \rho \tag{4.1.8A.2}$$

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.

$$E = \frac{V}{l} \tag{4.1.8A.3}$$

The current density is calculated by the equation below

$$J = \frac{I}{A} \tag{4.1.8A.4}$$

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.

$$R = \frac{V}{I} \tag{4.1.8A.5}$$

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 = ρ ---> J=E/ρ = 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 = ρ

E=V/l

J=I/A ---> ρ=(V/l)/(I/A) = (150V/5m)/(62A/(24m x 5m) = 58Ωm

ρ = 1/σ ---> 1/ρ = σ = 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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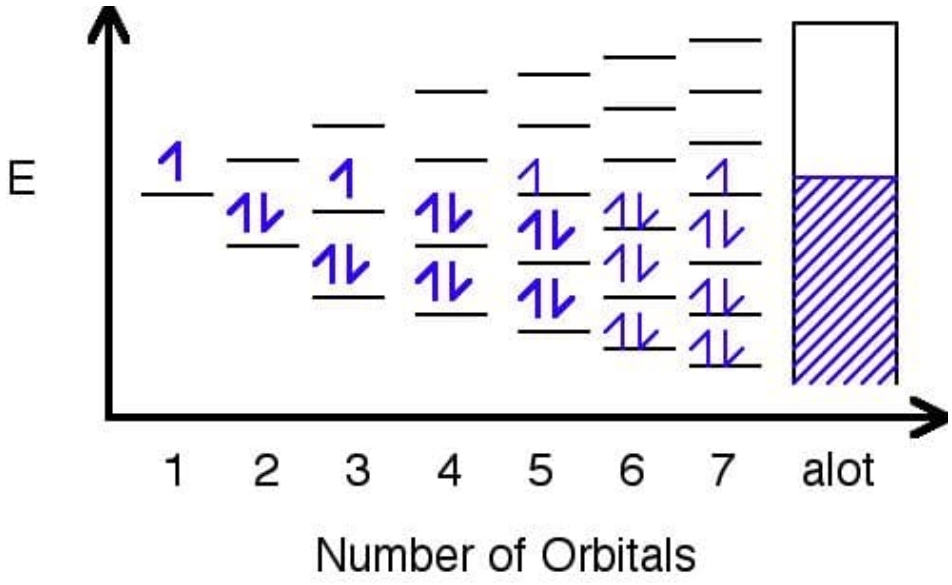
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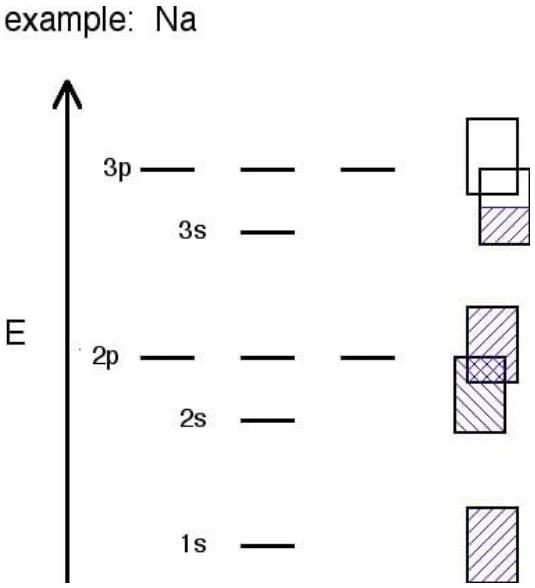
4.1.8B: Band Theory of Metals and Insulators

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:

$$P = \frac{1}{e^{\Delta E/RT} + 1} \tag{4.1.8B.1}$$

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

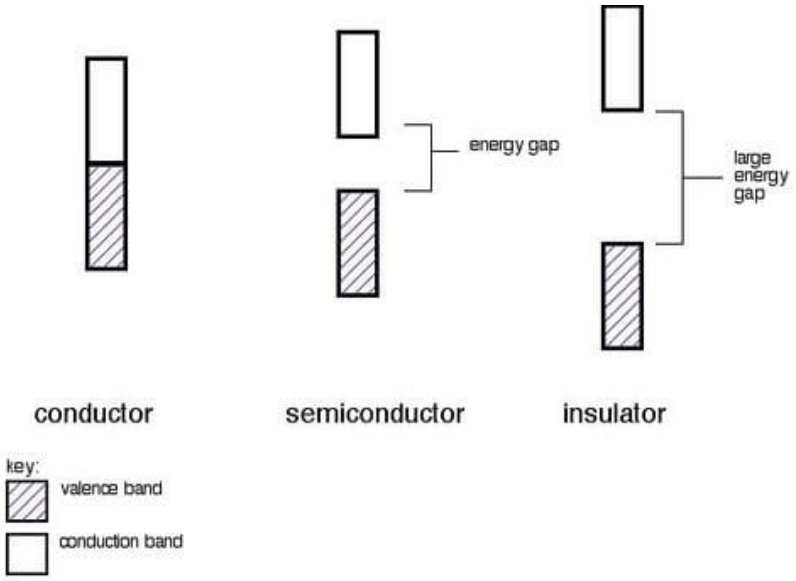


Diagram comparing conductor, semiconductor, and insulator energy bands. Conductor has overlapping bands; semiconductor has small gap; insulator has large gap. Key: valence and conduction bands.

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

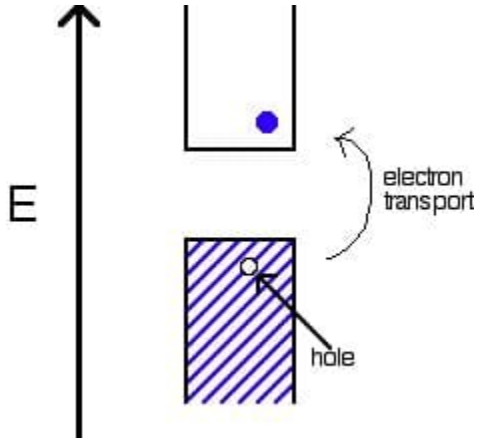
In insulators, the band gap between the valence band the the conduction band is so large that electrons cannot make the energy jump from the valence band to the conduction band.

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**.

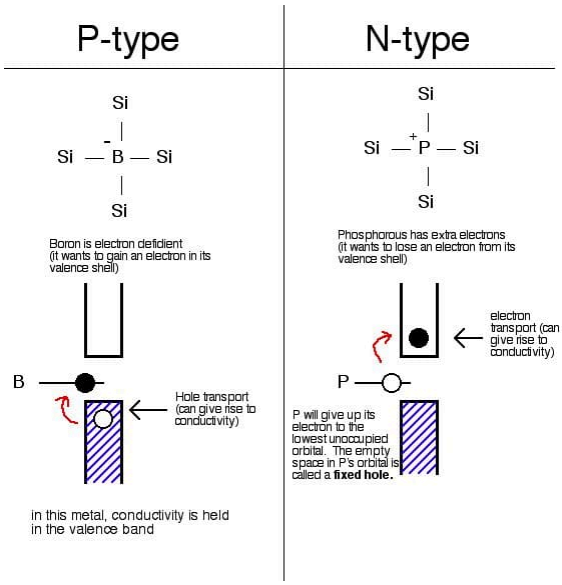
i. Intrinsic Semiconductors

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 4.1.8B.1

How do you distinguish between a valence band and a conduction band?

Answer available at the end of this section.

Exercise 4.1.8B.2

Is the energy gap between an insulator smaller or larger than the energy gap between a semiconductor?

Answer available at the end of this section.

Exercise 4.1.8B.3

What two methods bring conductivity to semiconductors?

Answer available at the end of this section.

Exercise 4.1.8B.4

You are more likely to find electrons in a conduction band if the energy gap is smaller/larger?

Answer available at the end of this section.

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.

Answers

Exercise $4.1.8B.1$

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 $4.1.8B.2$

Larger

Exercise $4.1.8B.3$

Electron transport and hole transport

Exercise $4.1.8B.4$

Smaller

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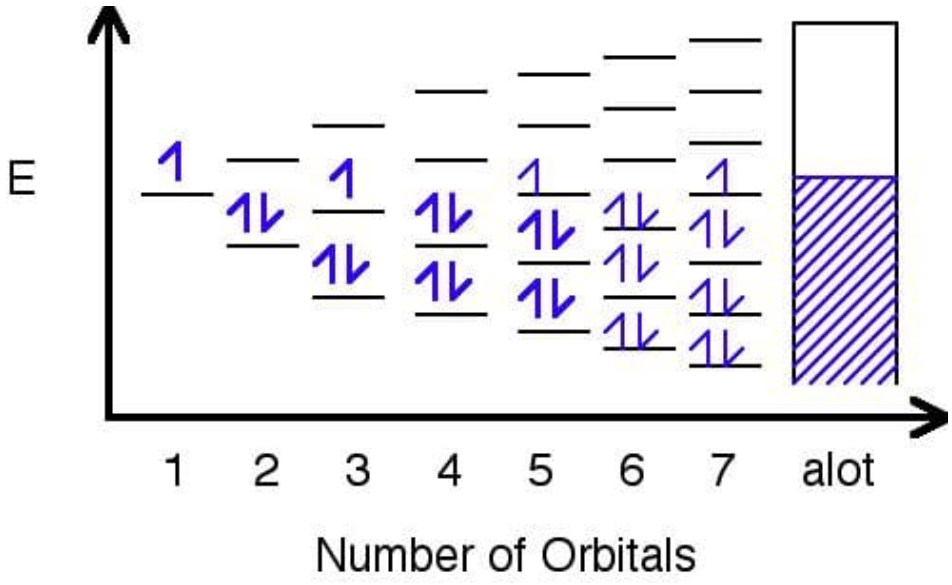
4.1.8C: The Fermi Level

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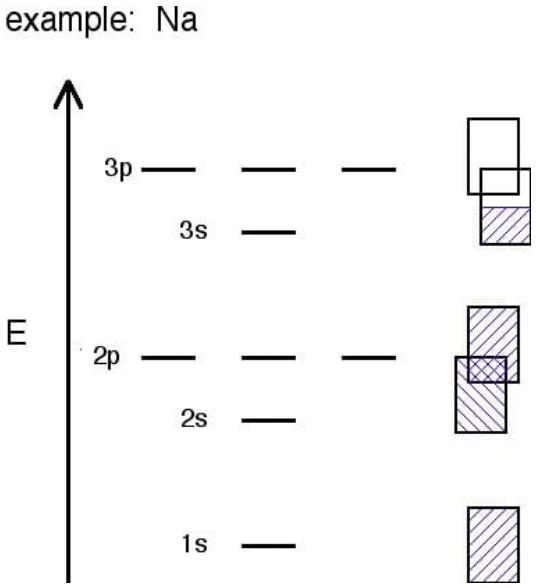
4.1.8D: Band Theory of Semiconductors

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:

$$P = \frac{1}{e^{\Delta E/RT} + 1} \tag{4.1.8D.1}$$

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

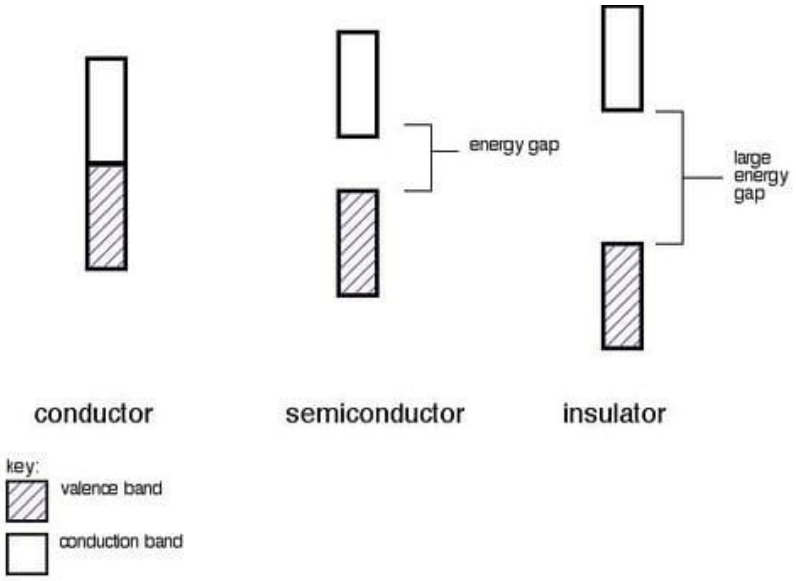


Diagram comparing conductor, semiconductor, and insulator energy bands. Conductor has overlapping bands; semiconductor has small gap; insulator has large gap. Key: valence and conduction bands.

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

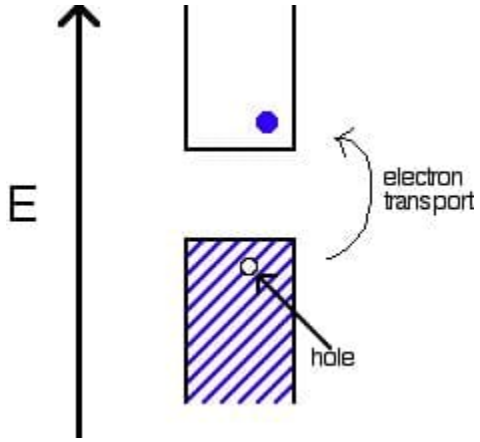
In insulators, the band gap between the valence band the the conduction band is so large that electrons cannot make the energy jump from the valence band to the conduction band.

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**.

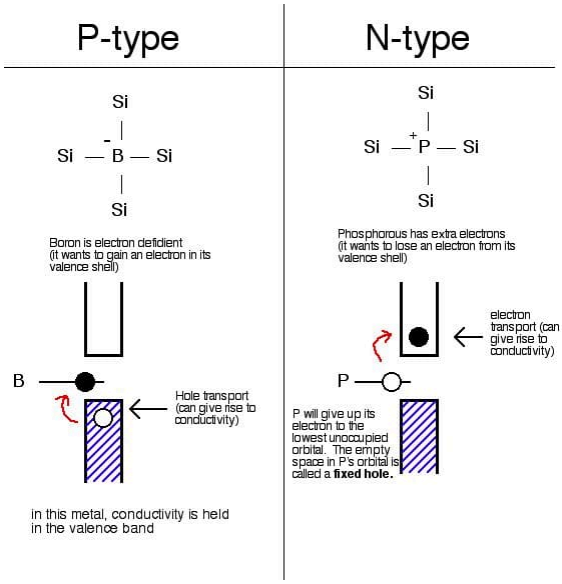
i. Intrinsic Semiconductors

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Exercise 4.1.8D.1

How do you distinguish between a valence band and a conduction band?

Answer available at the end of this section.

Exercise 4.1.8D.2

Is the energy gap between an insulator smaller or larger than the energy gap between a semiconductor?

Answer available at the end of this section.

Exercise 4.1.8D.3

What two methods bring conductivity to semiconductors?

Answer available at the end of this section.

Exercise 4.1.8D.4

You are more likely to find electrons in a conduction band if the energy gap is smaller/larger?

Answer available at the end of this section.

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.

Answers

Exercise $4.1.8D.1$

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 $4.1.8D.2$

Larger

Exercise $4.1.8D.3$

Electron transport and hole transport

Exercise $4.1.8D.4$

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4.1.9: SEMICONDUCTORS

- Topic hierarchy

4.1.9A: Intrinsic Semiconductors

4.1.9B: Extrinsic (n-type and p-type) Semiconductors

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4.1.9A: Intrinsic Semiconductors

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4.1.9B: Extrinsic (n-type and p-type) Semiconductors

Extrinsic Semiconductors

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4.1.10: SIZE OF IONS

- Topic hierarchy

4.1.10A: Ionic Radii

4.1.10B: Periodic Trends in Ionic Radii

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4.1.10A: Ionic Radii

In a crystal lattice, the ionic radius is a measure of the size of the atom's ion.[6] When formed, ionic atoms change in size with respect to their orginal atom. Cation radii will decrease and the anion radii will increase in size compared to their neutral atoms. Questions such as: "What methodology is used by chemists to measure ionic radii?" and "Are there any non-experimental ways to estimate the size of ionic radii?" will be answered in this module. Accordingly, there are many ways to determine ionic radii.

1. Introduction
2. Hard-Sphere model
3. Periodic Trends
4. References
5. Outside Links
6. Problems
7. Answers

Introduction

In the past, after an atom is ionized, X-ray diffraction is used to measure how much the radius of the atom increased or decreased. However, scientists wanted to use another technique, due to the fact, that X-ray diffraction is difficult to distinguish a boundary between two ions. As a result, the *hard sphere model* can be used.

Hard-Sphere model

The Hard-Sphere model are impenetrable spheres that do not overlap in space.[5] The Hard-Sphere model has been tested by well-known scientists; Lande', Pauling and Goldsmidt. The ion radii measured under crystal state of ionic compound which cations and anions are stacking in pattern as shown below.

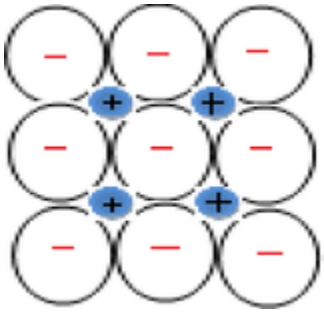


Figure 1: Schematic of the hard-sphere model

The Hard-Sphere model can be applied to metallic and ionic compounds such as NaCl, which is shown below.

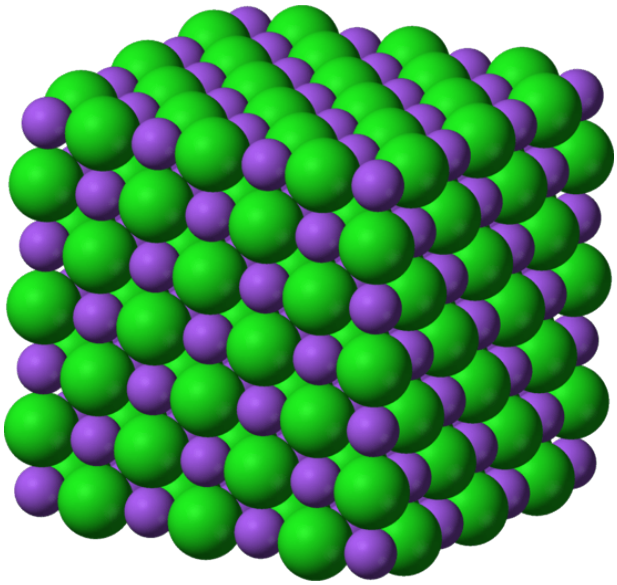


Figure 2: 3-D hard sphere model of Sodium Chloride, taken with permission from en.Wikipedia.org/wiki/File:So...e-3D-ionic.png

In general, scientists uses formula of Internuclear distance to test out the radii of ion then compared with the ion radii had done on X-ray diffraction:

$$\text{Internuclear distance (d)} = r_{cation} + r_{anion}\ ^{2}$$

*To calculate ion radii, Lande used ionic compound under solid state (ex: NaCl). This will minize the distribution of electrons.

1. Find the radii of anion (r^-) atom.
2. Find internuclear distance (d) between anion and cation.
3. Use Internuclear distance formula to find the r^+.

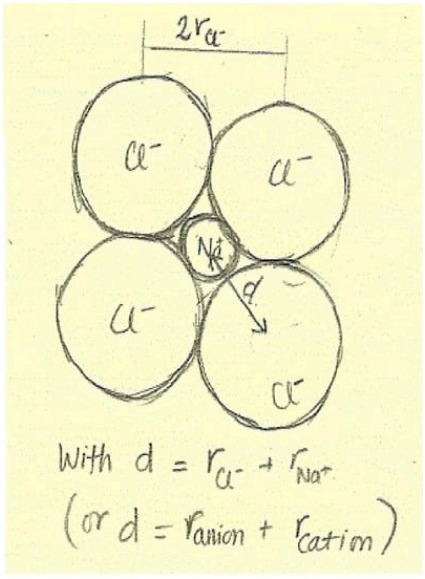


Figure 3: The Hard sphere model can roughly determine the ion radii.

Periodic Trends

As described earlier, cations are smaller in size compared to their neutral atoms while anions are larger in size.Cations are smaller than its neutral atoms because the positive nuclear charge, which holds the electrons in closer, exceeds the negative charge

when a metal atom loses an electron. On the contrary, anions are larger because the electrons are not held as tightly, repulsions of electrons increase, and the electrons spread out more due to nonmetal atoms gaining an electron. Refer to the outside link to learn more about the periodic trends for ionic radii (http://abulafia.mt.ic.ac.uk/shannon/ptable.php).

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1. Kotz, Treichel, Weaver,2006, *Chemistry and Chemical Reactivity*, Thomson Brooks/Cole, Mason, OH, p.358-364
2. Housecroft C., and Shappe A., 2008, *Inorganic Chemistry 3rd edition,* Pearson Education Limited, England, p.162-164
3. Barrera, M, and FZuloagat. "*Determination of the ionic radii by means of the Kohn-Sham potential: Identification of the chemical potential*." International journal of quantum chemistry 106.9 (2006):2044-2053.
4. "*Ionic radii for Group 1 and Group 2 halide, hydride, fluoride, oxide, sulfide, selenide and telluride crystals*." Dalton transactions 39.33 (2010):7786-.
5. http://en.Wikipedia.org/wiki/Hard_spheres
6. http://en.Wikipedia.org/wiki/Ionic_radius

Outside Links

- http://abulafia.mt.ic.ac.uk/shannon/ptable.php

Problems

1. What is the most general formula that used to determine the ion radii for hard sphere model?

2. Find radius for Cacium ion in Calcium Chloride ($CaCl_{2)}$. List out all the steps (numbers are not necessary)

3. Determine which is larger:

a) K^+ or Cs^+?

b) La^{3+} or Lu^{3+}?

c) Ca^{2+} or Zn^{2+}?

Answers

1. Internuclear distance (d) = $r_{cation} + r_{anion}$

2. Find the radii of anion (r^-*) atom; Find internuclear distance (d) between anion and cation; Use Internuclear distance formula to find the* r^+.

3. a.) Cs^+ b.) La^{3+} c.) Ca^{2+}

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4.1.10B: Periodic Trends in Ionic Radii

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4.1.11: IONIC LATTICES

- Topic hierarchy

4.1.11A: Structure - Rock Salt (NaCl)

4.1.11B: Structure - Caesium Chloride (CsCl)

4.1.11C: Structure - Fluorite (CaF_2)

4.1.11D: Structure - Antifluorite

4.1.11E: Structure - Zinc Blende (ZnS)

4.1.11F: Structure - β-Cristobalite (SiO_2)

4.1.11H: Structure - Rutile (TiO_2)

4.1.11I: Structure - Layers (CdI_2 and $CdCl_2$)

4.1.11J: Structure - Perovskite ($CaTiO_3$)

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4.1.11A: 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 $4.1.11A.1$ 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.

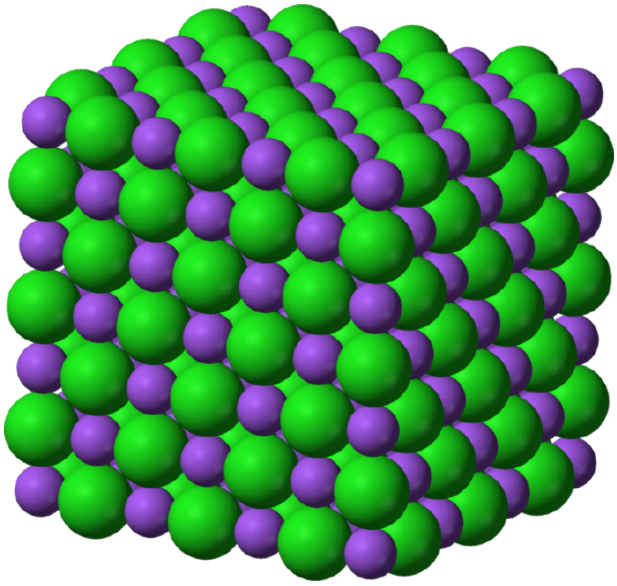


Figure $4.1.11A.1$: The crystal structure of sodium chloride, NaCl, a typical ionic compound. The smaller purple spheres represent sodium cations, $\mathrm{Na^+}$, and the larger green spheres represent chloride anions, $\mathrm{Cl^-}$. (Public Domain; Benjah-bmm27 via Wikipedia)

A Unit Cell

The unit cell of NaCl consists of $\mathrm{Na^+}$ ions and $\mathrm{Cl^-}$ 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.

- $\mathrm{Na^+}$:

$$1_{center} + 12_{edge} \times \frac{1}{4} = 4 \,\text{sodium ions total per cell}$$

- 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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3. Jun Soo, Kim, and Yethiraj Arun. "A Diffusive Anomaly of Water in Aqueous Sodium Chloride Solutions at Low Temperatures." *Journal of Physical Chemistry B* 112.6 (2008): 1729-1735. *Academic Search Complete*. EBSCO. Web.

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4.1.11B: 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:

$$\mathrm{Cs_2CO_3 + 2\,HCl \longrightarrow 2\,CsCl + H_2O + CO_2} \tag{4.1.11B.1}$$

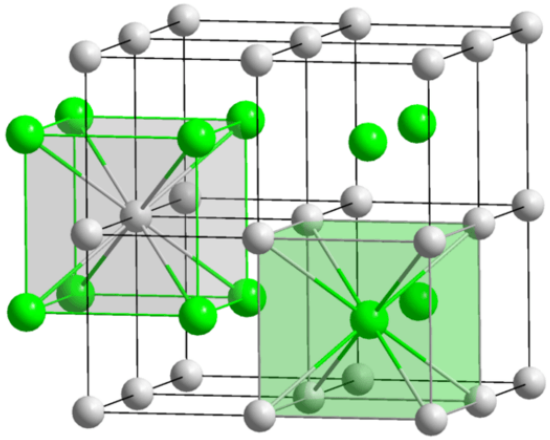


Figure $4.1.11B.1$: CsCl Coordination Cubes. (Public Domain; Solid State via Wikipedia)

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.

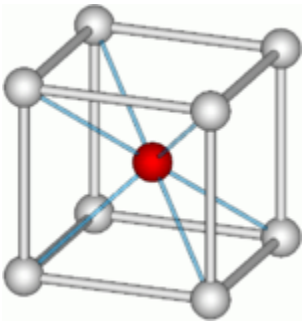


Figure $4.1.11B.2$: Unit Cell of CsCl (en.Wikipedia.org/wiki/Caesium_chloride

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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4.1.11C: Structure - Fluorite (CaF_2)

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 $4.1.11C.1$) 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.

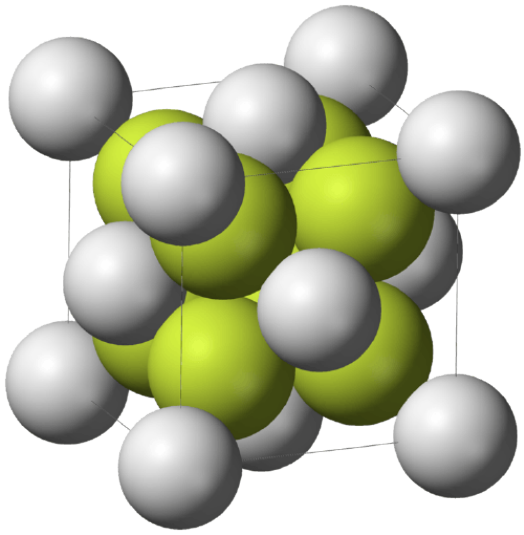


Figure $4.1.11C.1$: Fluorite unit cell. (Public Domain; Benjah-bmm27 via Wikipedia)

Calcium Fluoride is Quasilinear

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. $\mathrm{CaF_2}$ 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. Figures two and three show how the d-orbitals cause the molecule to bend.

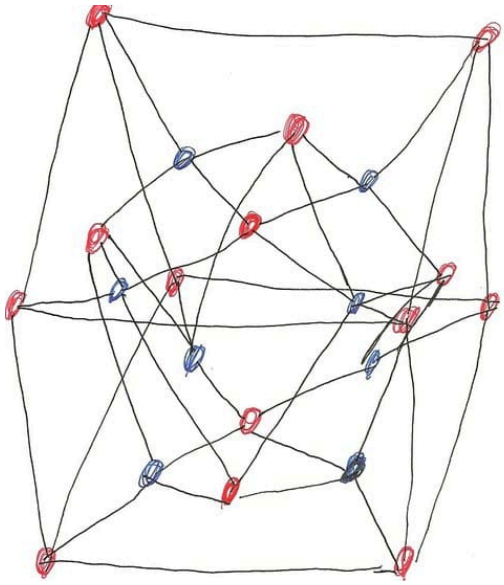


Fig # 1

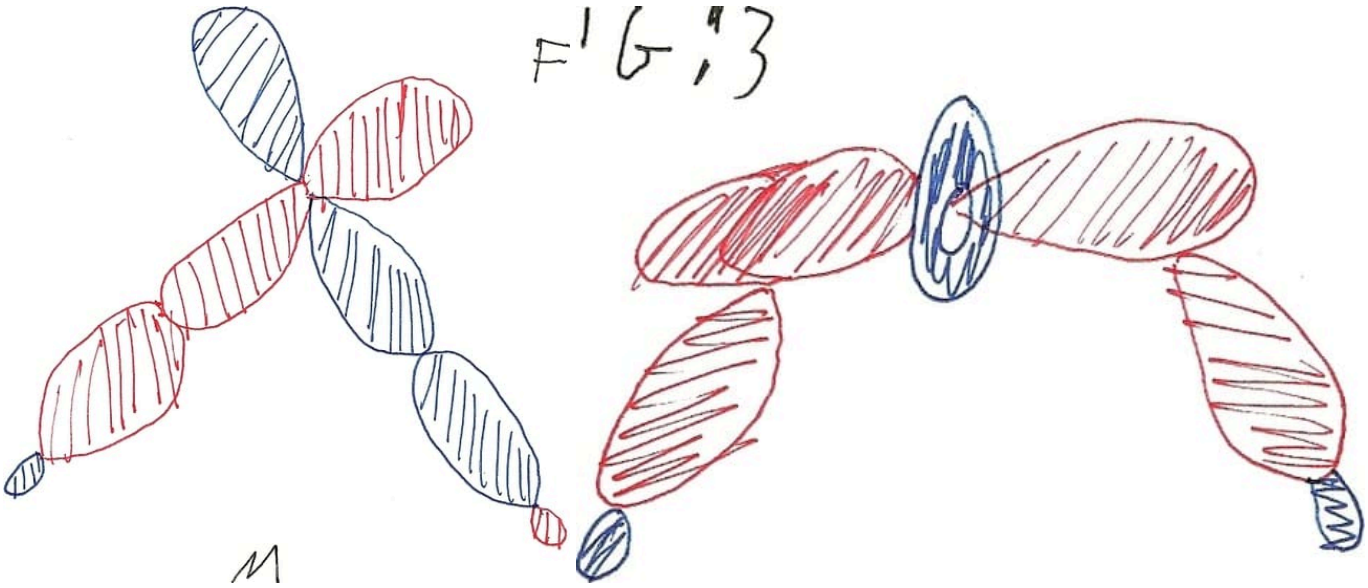


Fig # 2 Fig # 3

References

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2. Fergus, Jeffery W. The Application of Solid Fluoride Electrolytes in Chemical Sensors. Sensors and Actuators B: Chemical. Web Journal, 22. no 2. www.sciencedirect.com/science...f&searchtype=a (Oct 7, 2010)
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4.1.11D: Structure - 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 $4.1.11D.1$).

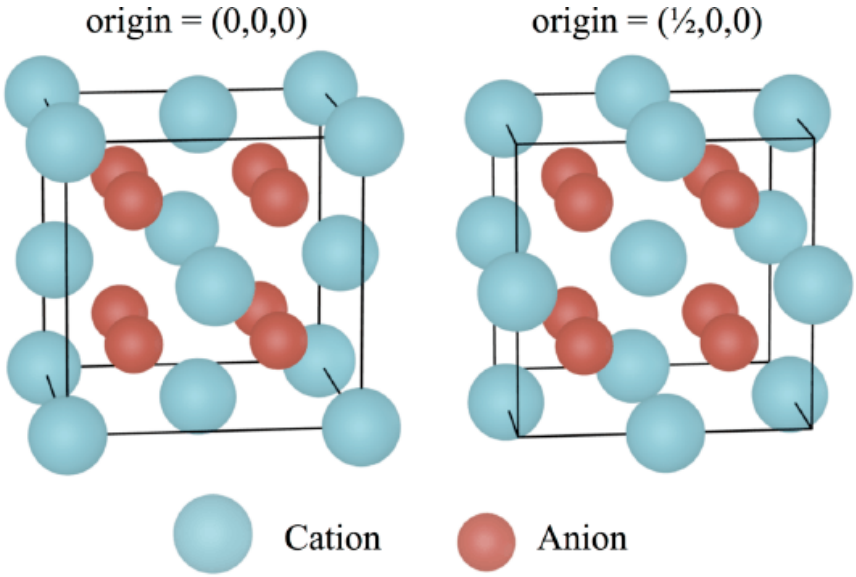


Figure $4.1.11D.1$: Unit cell of the fluorite structure, from two equivalent perspectives. In the antifluorite structure, the blue positions are taken by the anion, the red positions by the cation. (CC BY-SA 4.0; Paburr via source)

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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4.1.11E: 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.

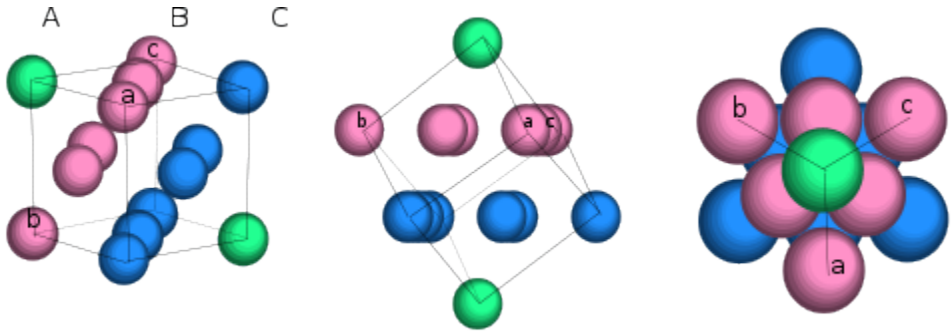


Fig. 1. A break down of cubic closest packing. (Author: Maghémite Date: May 5, 2008. Licensed under the Creative Commons Attribution-Share Alike 3.0 Unported, 2.5 Generic, 2.0 Generic and 1.0 Generic license.)

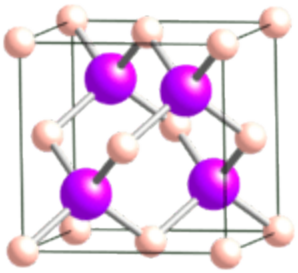


Fig. 2. A representation of ccp structure. (from Public Domain)

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.

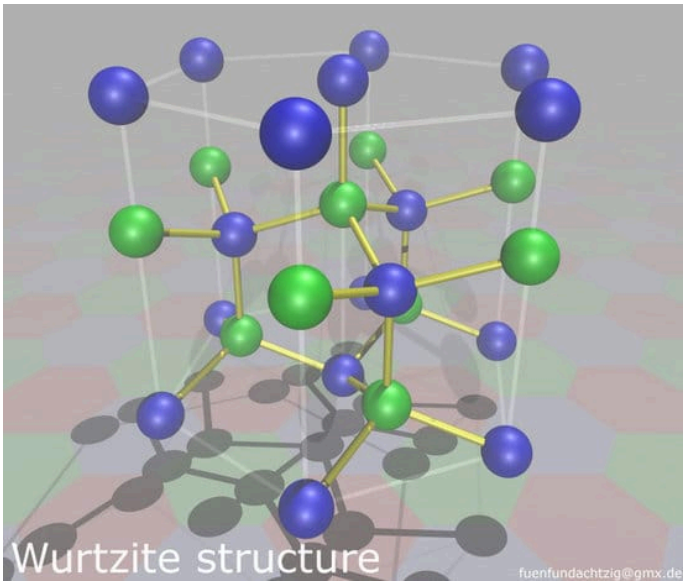


Fig 3. HCP structure of wurtzite. (Creator: Alexander Mann Date: 01/14/2006 Licensed under the Creative Commons Attribution-Share Alike 2.0 Germany license)

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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4.1.11F: 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.

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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2. Pacific Rim Conference on Ceramic and Glass Technology. 2006. Advances in Glass and Optical Materials II. American Ceramic Society. Westerville, Ohio.
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4.1.11H: Structure - Rutile (TiO_2)

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4.1.11I: Structure - Layers (CdI_2 and $CdCl_2$)

The following headers are meant as a guide to the sections that you need in your module. Here, before the table of contents, give a two-four sentence overview of the Module. Be straight to the point. No examples and no figures in this section. Keep the following text for automatic table of contents based on the headings below (seen in edit mode only).

1. Introduction
2. Heading #1
3. Heading #2
4. References
5. Outside Links
6. Problems
7. Contributors and Attributions

Introduction

Please use only heading 2 and lower, heading 1 is ugly and is avoided. In this section, give a short introduction to your topic to put it in context. The module should be easy to read; please reduce excess space, crop figures to remove white spaces, full justify all text, with the exception of equations, which should use the equation command for construction (see FAQ).

Heading #1

Rename to desired sub-topic. This is where you put the core text of your module. Add any number of headings necessary for your topic. Try to reduce unnecessary discussion and get to the point in a terse, yet informative, manner possible.

Heading #2

Rename to desired sub-topic. You can delete the header for this section and place your own related to the topic. Remember to hyperlink your module to other modules via the link button on the editor toolbar.

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1. This is meant for references used for constructing the module. They must be primary and accessible to readers at a library.
2. You need at least two different sources here. Websites are not allowed. DOI links to J. Chem. Ed. are ideal Do not reference class notes. Also, do not reference textbooks for maximal credit. Using the insert citation button to automatically handle references is highly suggested (bottom right button on editor toolbar).

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- Link to outside sources. Wikipedia entries should probably be referenced here.

Problems

Be careful not to copy from existing textbooks. Originality is rewarded. Make up some practice problems for the future readers. Five original with varying difficulty questions (and answers) are ideal.

Contributors and Attributions

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- Name #2 here with university affiliation

Tags below. If no tags exist, then add two new ones: "Vet1" and the level of the module content (e.g. "Fundamental"). See FAQ for more details.

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4.1.11J: Structure - Perovskite ($CaTiO_3$)

Figure 2: A distroted perovskite SmNiO3 with orthorhombic symmetry.

Figure 2: Superconducting Sr_2RuO_4 (wikis.lib.ncsu.edu/index.php/Perovskite)

Some other unique properties that sets perovskites apart and makes them ideal for technological applications include: it is the only crystal structure that is ferroelectric (spontaneous alignment of the electric dipoles caused by interactions between them) not because of an external magnetic field but due to its crystal structure, its ferro-, pyro-, and piezo-electric properties, and structural properties such as durability and chemical flexibility.

Contributors and Attributions

- Matthew Ibbotson: Undergraduate in Chemical Engineering, Senior

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4.1.12: Crystal Structure of Semiconductors

- Topic hierarchy

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4.1.13: LATTICE ENERGY - ESTIMATES FROM AN ELECTROSTATIC MODEL

- Topic hierarchy

4.1.13A: Coulombic Attraction Within an Isolated Ion-Pair

4.1.13B: Coulombic Interactions in an Ionic Lattice

4.1.13C: Born Forces

4.1.13D: The Born-Landé Equation

4.1.13E: Madelung Constants

4.1.13F: Refinements to the Born-Lande Equation

4.1.13G: Overview

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4.1.13A: Coulombic Attraction Within an Isolated Ion-Pair

Coulombic Forces

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4.1.13B: Coulombic Interactions in an Ionic Lattice

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4.1.13C: Born Forces

Born forces are one type of force that acts upon atoms in an ionic lattice. In simplest terms, because ions have some finite size, electron-electron and nucleus-nucleus interactions occur and give rise to repulsion forces and electrostatic potential, both called Born forces.

Introduction

Lattice energy is the energy released when gaseous cations and anions bond to form a solid ionic compound. With the Born-Lande equation one can calculate the lattice energy of a crystalline ionic compound. Born and Lande theorized around the turn of the century, that lattice energy of a crystalline ionic compound could be found by calculating terms of electrostatic potential and a repulsive potential.

$$\Delta U = \frac{-LA|Z_+||Z_-|e^2}{4\pi\epsilon_o r} \tag{1}$$

with

- L is the avagadro's constant (6.022 \times 10^{23}\) and
- 'A is the Madelung Constant

The first potential is the force of attraction. It is a negative value because it pulls the two atoms closer together, and the forming of a bond is energetically favorable. The negative value of Avogadro's number (6.022x10^{23}) times a Madelung Constant (varies) times the absolute value of the charge of the cation times the absolute value of the charge of the anion, times the charge of an electron (1.6022x10^{-19} C) all over four times pi times the emissivity of space times the ion radius.

$$\Delta U = \frac{-LB}{r^n} \tag{2}$$

with

- B is the repulsion coefficient and
- 'N is the Born exponent

The second equation is the repulsive force. It found by multiplying Avogadro's number (6.022x10^{23}) by a repulsion coefficient, and dividing that by the ionic radius raised to the power of a Born exponent (some number between 5 and 12).

Implications of Born Forces

Attractive forces are affected by the charge of the ions and their radii. Ions with large charges (like Mg^{7+} or O^{2-}) have greater attractive potential than those with smaller charges (like Na^{1+} or F^{1-}). Smaller ions (like Li^{+} or Cl^{-}) also have greater electrostatic potential than larger ions (like I^{-} or Cs^{+}). The Madelung constant is dependent on the crystal structure type. This value is found in tables online or in a text, but in general can be thought of as large with larger cation-cation distances and anion-anion distances. A structure with fluorite geometry has a relatively large A value, whereas rock salt crystals have a much lower A value.

Repulsive forces are mainly determined by the born exponent. The Born exponent is dictated by the electronic configuration of the noble gas in the row above it on the periodic table (a closed shell).

Max Born

Max Born was a German physicist and mathematician who was instrumental in the development of quantum mechanics. He also made contributions to solid-state physics and optics and supervised the work of a number of notable physicists in the 1920s and 30s.



Figure: Max Born (1882–1970)

Born won the 1954 Nobel Prize in Physics for his "fundamental research in Quantum Mechanics, especially in the statistical interpretation of the wave function".

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1. Housecroft, E. Catherine et.al.. Inorganic Chemistry, Third Edition. Person Education Limited. Harlow, England. 2008.
2. McQuarrie, A. Donald et. al.. Physical Chemistry, A Molecular Approach. University Sciience Books. USA. 1997.
3. Petrucci, H. Ralph et. al.. General Chemistry, Ninth Edition. Prentice Hall. Upper Saddle River, New Jersey. 2007.
4. Brown, I.D. et. al.. The Chemical Bond in Inorganic Chemistry, IUCr monographs in crystallography. Oxford University Press. 2002.

Problems

Plug in and cancel SI units to the Born-Lande equation to find the units of lattice energy, electrostatic potential, and repulsion forces. All energies are in units of kJ/mol

1. Looking at the equations for Born forces and a periodic table what do you expect to have a higher lattice energy (most negative enthalpy): NaCl, LiF, or KCl?
2. Looking at the equations for Born forces and a periodic table what do you expect to have a higher lattice energy (most negative enthalpy): NaOH, Al_2O_3, or $Mg(OH)_2$?
3. What lattice structure type Rutile or CsCl has the greater relative Madelung constant? (You need not look in a table if you know the shapes of these crystal geometries)
4. What are the oxidation states of Barium and Oxygen in the crystalline lattice BaO?
5. Calculate the lattice energy of Sodium Chloride using the Born-Lande equation (find all needed information from tables). Compare this calculated value to experimentally found value of -787kJ/mol.

Solutions

1. LiF
2. Al_2O_3
3. Rutile
4. Ba^{2+} and O^{2-}
5. The calculated value is -756kJ/mol.

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4.1.13D: The Born-Landé Equation

The Born-Landé equation is a concept originally formulated in 1918 by the scientists Born and Landé and is used to calculate the lattice energy (measure of the strength of bonds) of a compound. This expression takes into account both the Born interactions as well as the Coulomb attractions.

Introduction

Due to its high simplicity and ease, the Born-Landé equation is commonly used by chemists when solving for lattice energy. This equation proposed by Max Born and Alfred Landé states that lattice energy can be derived from ionic lattice based on electrostatic potential and the potential energy due to repulsion. 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:

$$\Delta U = -\frac{N_A M \left|Z^+\right| \left|Z^-\right| e^2}{4\pi\epsilon_o r} \tag{4.1.13D.1}$$

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:

$$\Delta U = \frac{N_A B}{r^n} \tag{4.1.13D.2}$$

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 to form:

$$\Delta U(0K) = \frac{N_A M \left|Z^+\right| \left|Z^-\right| e^2}{4\pi\epsilon_o r_o}\left(1 - \frac{1}{n}\right) \tag{4.1.13D.3}$$

with

- r_0 is the closest ion distance

Calculate Lattice Energy

Lattice energy, based on the equation from above, is dependent on multiple factors. We see that the charge of ions is proportional to the increase in lattice energy. In addition, as ions come into closer contact, lattice energy also increases.

Example $4.1.13D.1$

Which compound has the greatest lattice energy?

- AlF_3
- NACl
- LiF
- $CaCl_2$

Solution

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.

Example $4.1.13D.2$

What is the lattice energy of NaCl? (Hint: you must look up the values for the constants for this compound)

Solution

-756 kJ/mol (again, this value is found in a table of constants)

Example $4.1.13D.3$

Calculate the lattice energy of NaCl.

Solution

$$Lattice\ Energy\ of\ NaCl = -\frac{\frac{6.022\,x\,10^{23}}{mole}\left(1.6022^{-19}\right)\times 1.747}{4\pi \times 8.85\,x\,10^{-12}\frac{c^2}{m}\times 282\,x\,10^{-12}m}\left(1-\frac{1}{9}\right) \approx -756\ \frac{kJ}{mol}$$

References

1. Johnson, D. A. *Metals and Chemical Change*. Cambridge: Royal Society of Chemistry, 2002.
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4.1.13E: Madelung Constants

There are many factors to be considered such as covalent character and electron-electron interactions in ionic solids. But for simplicity, let us consider the ionic solids as a collection of positive and negative ions. In this simple view, appropriate number of cations and anions come together to form a solid. The positive ions experience both attraction and repulsion from ions of opposite charge and ions of the same charge. The Madelung constant is a property of the crystal structure and depends on the lattice parameters, anion-cation distances, and molecular volume of the crystal.

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 $4.1.13E.1$).

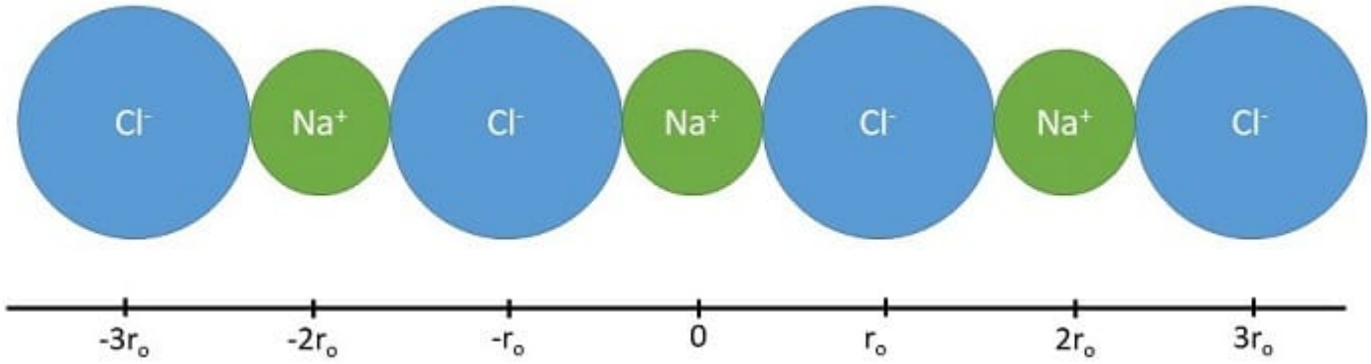


Figure $4.1.13E.1$: A hypothetical one-dimensional NaCl lattice.

Let us select the positive sodium ion in the middle (at $x = 0$) as a reference and let r_0 be the shortest distance between adjacent ions (the sum of ionic radii). The Coulomb energy of the other ions in this 1D lattice on this sodium atom can be decomposed by proximity (or "shells").

- **Nearest Neighbors (first shell):** This reference sodium ion has two negative chloride ions as its neighbors on either side at $\pm r_0$ so the Coulombic energy of these interactions is

$$\underbrace{\frac{-e^2}{4\pi\epsilon_o r_o}}_{\text{left chloride ion}} + \underbrace{\frac{-e^2}{4\pi\epsilon_o r_o}}_{\text{right chloride ion}} = -\frac{2e^2}{4\pi\epsilon_o r_o} \tag{4.1.13E.1}$$

- **Next Nearest Neighbors (second shell)**: Similarly the repulsive energy due to the next two positive sodium ions at a distance of $2r_0$ is

$$\underbrace{\frac{+e^2}{4\pi\epsilon_o (2r_o)}}_{\text{left sodium ion}} + \underbrace{\frac{+e^2}{4\pi\epsilon_o (2r_o)}}_{\text{right sodium ion}} = +\frac{2e^2}{4\pi\epsilon_o (2r_o)} \tag{4.1.13E.2}$$

- **Next Next Nearest Neighbors (third shell)**: The attractive Coulomb energy due to the next two chloride ions neighbors at a distance $3r_0$ is

$$\underbrace{\frac{-e^2}{4\pi\epsilon_o (3r_o)}}_{\text{left chloride ion}} + \underbrace{\frac{-e^2}{4\pi\epsilon_o (3r_o)}}_{\text{right chloride ion}} = -\frac{2e^2}{4\pi\epsilon_o (3r_o)} \tag{4.1.13E.3}$$

and so on. Thus the total energy due to all the ions in the linear array is

$$E = -\frac{2e^2}{4\pi\epsilon_o r_o} + \frac{2e^2}{4\pi\epsilon_o (2r_o)} - \frac{2e^2}{4\pi\epsilon_o (3r_o)} - \ldots \tag{4.1.13E.4}$$

or

$$E = \frac{e^2}{4\pi\epsilon_o r_o}\left[2\left(1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + ...\right)\right] \tag{4.1.13E.5}$$

We can use the following Maclaurin expansion

$$\ln(1+x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^3}{4} + \cdots \tag{4.1.13E.6}$$

to simplify the sum in the parenthesis of Equation 4.1.13E.5 as $\ln(1+1)$ to obtain

$$E = \frac{e^2}{4\pi\epsilon_o r_o}\left[2\ln 2\right] \tag{4.1.13E.7}$$

$$= \frac{e^2}{4\pi\epsilon_o} M \tag{4.1.13E.8}$$

The first factor of Equation 4.1.13E.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 Medelung 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 1*r*, 12 Na^+ ions at a distance 2*r*, eight Cl^- ions at 3*r*, six Na^+ ions at 4*r*, 24 Na^+ ions at 5*r*, 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:

$$E_{ion-lattice} = \frac{Z^2 e^2}{4\pi\epsilon_o r} M \tag{4.1.13E.9}$$

For NaCl is a poorly converging series of interaction energies:

$$M = \frac{6}{1} - \frac{12}{2} + \frac{8}{3} - \frac{6}{4} + \frac{24}{5}... \tag{4.1.13E.10}$$

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).

The Madelung constant depends on the structure type and Equation 4.1.13E.10 is applicable only for the sodium chloride (ei.g, rock salt) lattice geometry. Other values for other structural types are given in Table $4.1.13E.2$. A is the number of anions coordinated to cation and C is the numbers of cations coordinated to anion.

Table $4.1.13E.2$: 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		

Compound	Crystal Lattice	M	A : C	Type
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.				

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 4.1.13E.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

$$U = \frac{N_A M Z^2 e^2}{4\pi\epsilon_o r}\left(1 - \frac{1}{n}\right) \tag{4.1.13E.11}$$

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 $4.1.13E.3$).

Table $4.1.13E.1$: 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

Example $4.1.13E.1$: NaCl

Estimate the lattice energy for NaCl.

Solution
Using the values giving in the discussion above, the estimation is given by

$$U_{NaCl} = \frac{(6.022 \times 10^{23}/mol)(1.74756)(1.6022 \times 10^{-19})^2(1.747558)}{4\pi\,(8.854 \times 10^{-12}C^2/m)(282 \times 10^{-12}\ m)}\left(1 - \frac{1}{9.1}\right)$$
$$= -756\,kJ/mol$$

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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4.1.13F: Refinements to the Born-Lande Equation

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4.1.13G: Overview

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4.1.14: 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.

Introduction

This module will introduce the idea of lattice energy, as well as one process that allows us to calculate it: the Born-Haber Cycle. In order to use the Born-Haber Cycle, there are several concepts that we must understand first.

Lattice Energy

Lattice Energy is a type of potential energy that may be defined in two ways. In one definition, 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. The other definition says that lattice energy is the reverse process, meaning it 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.

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.

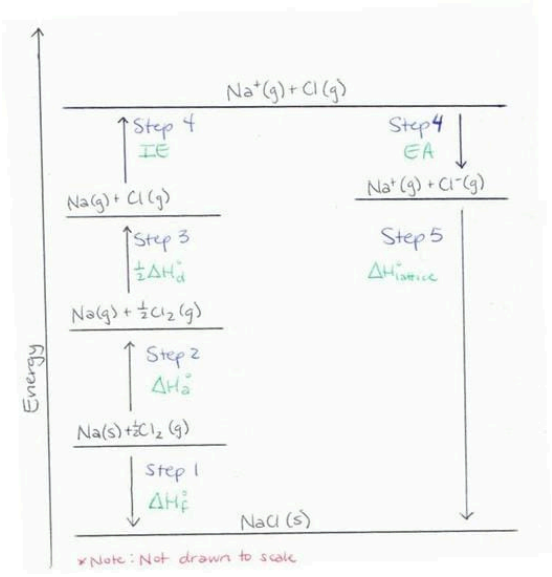
Born-Haber Cycle

There are several important concept to understand before the Born-Haber Cycle can be applied 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.
- Sublimation 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 energy of atomization.
- **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.

Using the Born-Haber Cycle

The values used in the Born-Haber Cycle are all predetermined changes in enthalpy for the processes described in the section above. Hess' Law allows us to add or subtract these values, which allows us to determine the lattice energy.



Step 1

Determine the energy of the metal and nonmetal in their elemental forms. (Elements in their natural state have an energy level of zero.) Subtract from this the heat of formation of the ionic solid that would be formed from combining these elements in the appropriate ration. This is the energy of the ionic solid, and will be used at the end of the process to determine the lattice energy.

Step 2

The Born-Haber Cycle requires that the elements involved in the reaction are in their gaseous forms. Add the changes in enthalpy to turn one of the elements into its gaseous state, and then do the same for the other element.

Step 3

Metals exist in nature as single atoms and thus no dissociation energy needs to be added for this element. However, many nonmetals will exist as polyatomic species. For example, Cl exists as Cl_2 in its elemental state. The energy required to change Cl_2 into 2Cl atoms must be added to the value obtained in Step 2.

Step 4

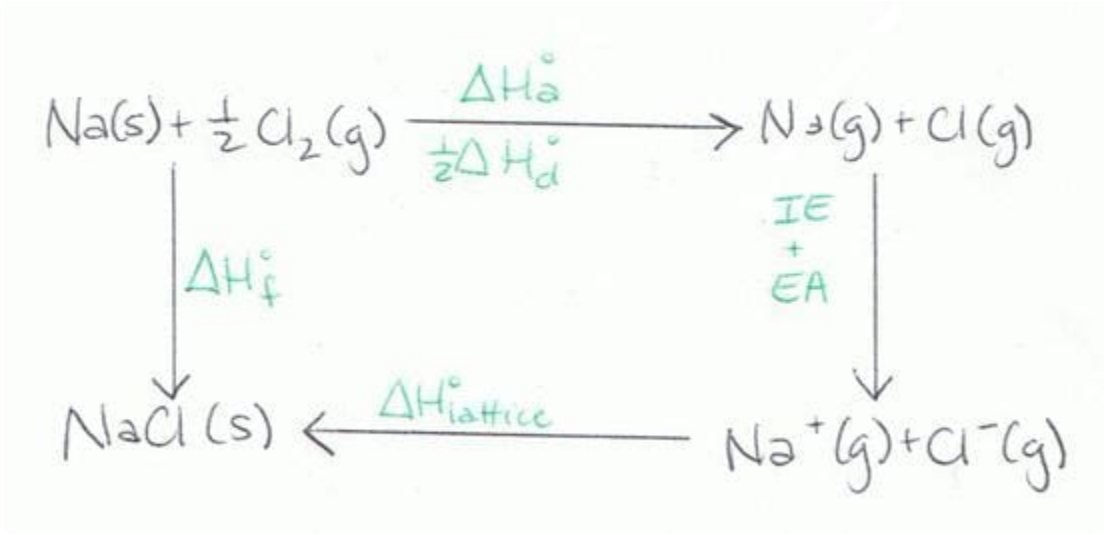
Both the metal and nonmetal now need to be changed into their ionic forms, as they would exist in the ionic solid. To do this, the ionization energy of the metal will be added to the value from Step 3. Next, the electron affinity of the nonmetal will be subtracted from the previous value. It is subtracted because it is a release of energy associated with the addition of an electron.

*This is a common error due to confusion caused by the definition of electron affinity, so be careful when doing this calculation.

Step 5

Now the metal and nonmetal will be combined to form the ionic solid. This will cause a release of energy, which is called the lattice energy. The value for the lattice energy is the difference between the value from Step 1 and the value from Step 4.

The diagram below is another representation of the Born-Haber Cycle.



Equation

The Born-Haber Cycle can be reduced to a single equation:

Heat of formation= Heat of atomization+ Dissociation energy+ (sum of Ionization energies)+ (sum of Electron affinities)+ Lattice energy

*Note: In this general equation, the electron affinity is added. However, when plugging in a value, determine whether energy is released (exothermic reaction) or absorbed (endothermic reaction) for each electron affinity. If energy is released, put a negative sign in front of the value; if energy is absorbed, the value should be positive.

Rearrangement to solve for lattice energy gives the equation:

Lattice energy= Heat of formation- Heat of atomization- Dissociation energy- (sum of Ionization energies)- (sum of Electron Affinities)

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Problems

1. Define lattice energy, ionization energy, and electron affinity.
2. What is Hess' Law?
3. Find the lattice energy of KF(s).
   Note: Values can be found in standard tables.
4. Find the lattice energy of $MgCl_2$(s).
5. Which one of the following has the greatest lattice energy?
   a. A) MgO

   b. B) NaC
   c. C) LiCl
   d. D) $MgCl_2$
6. Which one of the following has the greatest Lattice Energy?
   a. NaCl
   b. $CaCl_2$
   c. $AlCl_3$
   d. KCl

Solutions

1. Lattice energy: The difference in energy between the expected experimental value for the energy of the ionic solid and the actual value observed. More specifically, this is the energy gap between the energy of the separate gaseous ions and the energy of the ionic solid.
   Ionization energy: The energy change associated with the removal of an electron from a neutral atom or ion.
   Electron affinity: The release of energy associated with the addition of an electron to a neutral atom or ion.
2. Hess' Law states that the overall energy of a reaction may be determined by breaking down the process into several steps, then adding together the changes in energy of each step.
3. Lattice Energy= [-436.68-89-(0.5*158)-418.8-(-328)] kJ/mol= **-695.48 kJ/mol**
4. Lattice Energy= [-641.8-146-243-(737.7+1450.6)-(2*-349)] kJ/mol= **-2521.1 kJ/mol**
5. MgO. It has ions with the largest charge.
6. $AlCl_3$. According to the periodic trends, as the radius of the ion increases, lattice energy decreases.

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4.1.15: Lattice Energy - Calculated vs. Experimental Values

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4.1.16: APPLICATION OF LATTICE ENERGIES

- Topic hierarchy

4.1.16A: Estimation of Electron Affinities

4.1.16B: Fluoride Affinities

4.1.16C: Estimation of Standard Enthalpies of Formation and Disproportionation

4.1.16D: The Kapustinskii Equation

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4.1.16A: Estimation of Electron Affinities

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4.1.16B: Fluoride Affinities

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4.1.16C: Estimation of Standard Enthalpies of Formation and Disproportionation

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4.1.16D: The Kapustinskii Equation

9.05: Kapustinskii equation

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4.1.17: DEFECTS IN SOLID STATE LATTICES

- Topic hierarchy

4.1.17.E: Defects in Solid State Lattices (Exercises)

4.1.17A: Schottky Defect

4.1.17B: Frenkel Defect

4.1.17C: Experimental Observations of Schottky and Frenkel Defects

4.1.17D: Non-Stoichiometric Compounds

4.1.17E: Color Centers (F-Centers)

4.1.17F: Thermodynamic Effects of Crystal Defects

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4.1.17.E: Defects in Solid State Lattices (Exercises)

Crystal Defects and Solids

Problems

All diagrams must be hand drawn, no photocopies or computer images will be accepted.

1. Nonstoichiometric compounds
2. Stoichiometric titanium (II) oxide and magnesium oxides have densities of 4.93 and 3.58 g cm^{-3} respectively. X-ray diffraction studies have shown that both have the NaCl structure, with unit cell edges of 416.2 and 421.2 pm respectively. Assume that the presence of vacancies does not affect the cell edge lengths. Estimate the percentage of vacancies in these solids.
3. Explain the Pilling-Bedworth principle regarding the protective behaviour of oxide films of metal (Swaddle: p103-104). From the following densities (d), evaluate the molar volumes (V^o = molar mass/d) of the metals and of the oxides. Suggest which oxides forms protective layers?

Metal	d(metal)	Oxide	d(oxide)	V^o(metal)	V^o(oxide)	Protective?
Be	1.85	BeO	3.01			
Ca	1.54	CaO	3.25-3.38			
Al	2.70	Al_2O_3	3.97			
Fe	7.86	FeO	5.7			
		Fe_2O_3	5.24			
		Fe_3O_4	5.18			
Ti	4.50	TiO_2	4.26			

FeO, wuestite; Fe_2O_3, hematite; Fe_3O_4, magnetite;
TiO_2, rutile.

What advantages and disadvantages do Al and Ti have in their application as material for tableware? This is an open ended question, and give a common-sense type discussion.

4. y = 1.6 nm after 1 day
y = 3.5 nm after 1 year Estimate *c* and *k*. What are the thickness of the oxide layer at *t* = 5, 10, and 20 years?

What effect does moisture have on the oxidation of iron?

Contributors and Attributions

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4.1.17A: Schottky Defect

Lattice structures are not perfect; in fact most of the time they experience defects. Lattice structures (or crystals) are prone to defects especially when their temperature is greater than 0 K [1]. One of these defects is known as the Schottky defect, which occurs when oppositely charged ions vacant their sites [1].

Introduction

Like the human body, lattice structures (most commonly known as crystals) are far from perfection. Our body works hard to keep things proportional but occasionally our right foot is bigger than our left; similarly, crystals may try to arrange it's ions under a strict layout, but occasionally an ion slips to another spot or simply goes missing. Realistically speaking, it should be expected that crystals will depart itself from order (not surprising considering defects occurs at temperature greater than 0 K). There are many ways a crystal can depart itself from order (thus experiences defects); these defects can be grouped in different categories such as Point Defects, Line Defects, Planar Defects, or Volume or Bulk Defects [2]. We will focus on Point Defects, specifically the defect that occurs in ionic crystal structures (i.e. NaCl) called the Schottky Defect.

Point Defects

Lattice structures (or crystals) undergoing point defects experience one of two types:

1. atoms or ions leaving their spot (thus creating vacancies).
2. atoms or ions slipping into the little gaps in between other atoms or ions; those little gaps are known as interstitials--since atoms or ions in the crystals are occupying interstitials, they inherently become (create) interstitials.

By the simplest definition, the Schottky defect is defined by type one, while type two defects are known as the Frenkel defect. The Schottky defect is often visually demonstrated using the following layout of anions and cations:

+	-	+	-	+	-	+	-	+	-	+
-	+	-	+	-	+	-	+	(vacant)	+	-
+	-	+	-	+	-	+	-	+	-	+
-	+	-	(vacant)	-	+	-	+	-	+	-
+	-	+	-	+	-	+	-	+	-	+
-	+	-	+	-	+	-	+	-	+	-

Figure $4.1.17A.1$*: The positive symbols represents cations (i.e. Na^+) and the negative symbol represents anions (i.e. Cl^-).*

In addition, this layout is applicable only for ionic crystal compounds of the formula MX--layout for ionic crystals with formula MX_2 and M_2X_3 will be discussed later--where M is metal and X is nonmetal. Notice the figure has exactly one cation and one anion vacating their sites; that is what defines a (one) Schottky Defect for a crystal of MX formula--for every cation that vacant its site, the same number of anion will follow suit; essentially the vacant sites come in pairs. This also means the crystal will neither be too positive or too negative because the crystal will always be in equilibrium in respect to the number of anions and cations.

It is possible to approximate the number of Schottky defects (n_s) in a MX ionic crystal compound by using the equation:

$$N = \exp^{-\frac{\Delta H}{2RT}} \tag{4.1.17A.1}$$

where

- ΔH is the enthalpy of defect formation,
- R is the gas constant,

- T is the absolute temperature (in K), and

N can be calculated by:

$$N = \frac{\text{density of the ionic crystal compound} \times N_A}{\text{molar mass of the ionic crystal compound}} \tag{4.1.17A.2}$$

From Equation 4.1.17A.1, it is also possible to calculate the fraction of vacant sites by using the equation:

$$\frac{n_s}{N} = \exp^{-\frac{\Delta H}{2RT}} \tag{4.1.17A.3}$$

Schottky defects for MX_2 and M_2X_3

As mentioned earlier, a Schottky defect will always result a crystal structure in equilibrium--where no crystal is going to be too positive or too negative; thus in the case of:

- MX_2: one Schottky defect equals one cation and two anion vacancy.
- M_2X_3: one Schottky defect equals two cation and three anion vacancy.

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Problems

1. How does an ionic crystal structure maintain electrical neutrality despite undergoing a Schottky defect?
2. How is a Schottky defect defined for a compound with a MX formula? MX_2? M_2X_3?
3. Given that the enthalpy of defect formation for LiCl is 3.39 x 10^{-19} J and the density of LiCl is 2.068 g/cm^{-3}. Calculate the number of Schottky defect at 873 K.
4. Using the number of Schottky defect solved for question 3, determine the fraction of vacant site for LiCl.
5. If a anion and a cation vacant its site and occupies a space between other anions and cations, is it still a Schottky defect?

Answers

1. For a MX compound: one anion and one cation vacant their sites, so the overall charge will remain balanced. This is the same for MX_2 and M_2X_3 because appropriate numbers of anions and cations vacant their site thus leaving the overall charge neutral.
2. MX compound: one Schottky defect is when one anion and one cation leave their sites. MX_2 compound: one Schottky defect is when one anion and two cations leave their sites. M_2X_3 is when two anions and three cations leave their sites.

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4.1.17B: Frenkel Defect

The **Frenkel defect** (also known as the Frenkel pair/disorder) is a defect in the lattice crystal where an atom or ion occupies a normally vacant site other than its own. As a result the atom or ion leaves its own lattice site vacant.

The Frenkel Defect in a Molecule

The Frenkel Defect explains a defect in the molecule where an atom or ion (normally the cation) leaves its own lattice site vacant and instead occupies a normally vacant site (Figure $4.1.17B.1$). The cation leaves its own lattice site open and places itself between the area of all the other cations and anions. This defect is only possible if the cations are smaller in size when compared to the anions.

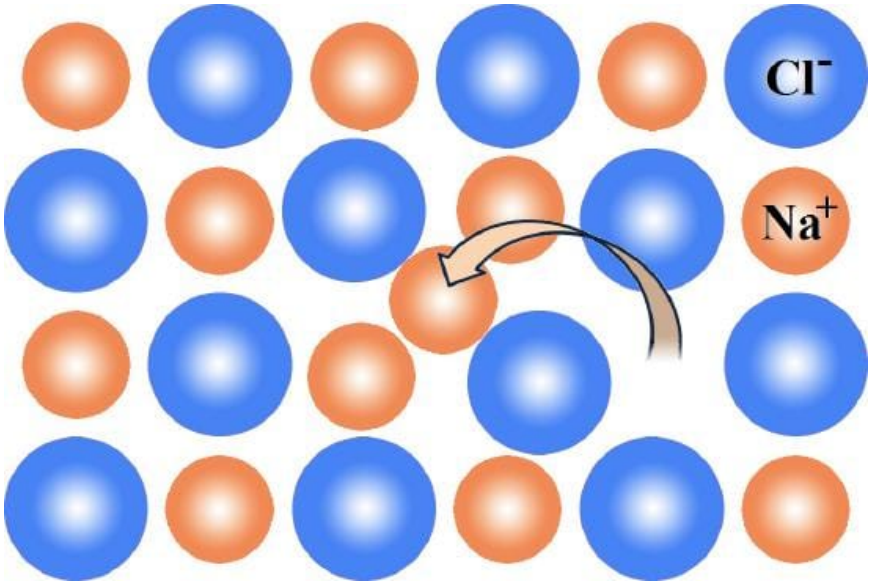


Figure $4.1.17B.1$: The Frenkel defect within the NaCl structure. (CC BY-SA 3.0; VladVD via Wikipedia)

The number of Frenkel Defects can be calculated using the equation:

$$\sqrt{NN^*}\, e^{\frac{\Delta H}{2RT}}$$

where N is the number of normally occupied positions, N^* is the number of available positions for the moving ion, the ΔH of formation is the enthalpy formation of one Frenkel defect, and R is the gas constant. Frenkel defects are intrinsic defects because the existence causes the Gibbs energy of a crystal to decrease, which means it is favorable to occur.

Solids Found with a Frenkel Defect

The crystal lattices are relatively open and the coordination number is low.

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1. Housecroft, Catherine E., and Alan G. Sharpe. *Inorganic Chemistry*. 3rd ed. Harlow: Pearson Education, 2008. Print.
2. Tilley, Richard. *Understanding Solids*. John Wiley & Sons, LTD. 2004.

Problems

1. What requirements are needed in order for the Frenkel defect to occur in an atom?

2. What are the differences between the Schottky defect and the Frenkel defect?

Answers

1. A low coordination number as well as having the crystal lattices open for the molecule.
2. The Frenkel defect causes an cation to leave its own lattice and go to another, while Sckhotty defect depicts that an equal number of cations and anions must be absent to maintain charge neutraility.

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4.1.17C: Experimental Observations of Schottky and Frenkel Defects

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4.1.17D: Non-Stoichiometric Compounds

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4.1.17F: Thermodynamic Effects of Crystal Defects

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4.2: THE CRYSTALLINE SOLID STATE

4.2.1: Molecular Orbitals and Band Structure

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4.2.1.2: Metal-Insulator Transitions

4.2.1.3: Periodic Trends- Metals, Semiconductors, and Insulators

4.2.1.4: Semiconductors- Band Gaps, Colors, Conductivity and Doping

4.2.1.5: Semiconductor p-n Junctions

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4.2.1.8: Discussion Questions

4.2.1.9: Problems

4.2.1.10: References

4.2.2: Formulas and Structures of Solids

4.2.2.1: The Solid State of Matter

4.2.2.2: Lattice Structures in Crystalline Solids

4.2.3: Superconductivity

4.2.3.1: Superconductors

4.2.4: Bonding in Ionic Crystals

4.2.5: Imperfections in Solids

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4.2.7: Thermodynamics of Ionic Crystal Formation

4.2.7.1: Lattice Energy

4.2.7.2: Lattice Energy - The Born-Haber cycle

4.2.7.3: Lattice Enthalpies and Born Haber Cycles

4.2.7.4: The Born-Lande' equation

4.2.P: Problems

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4.2.1: MOLECULAR ORBITALS AND BAND STRUCTURE

Learning Objectives

- Explain the physical basis of the Hubbard and Mott models of metal-insulator transitions.
- Understand why good superconductors derive from bad metals.
- Know the structures and the periodic trends in band gaps and colors of semiconductors.
- Obtain the band gap of an intrinsic semiconductor from the temperature dependence of the conductivity.
- Predict the doping type when impurities or defects are introduced into a semiconductor.
- Correlate the band picture and Fermi level with n- or p-type doping.
- Understand the physical principles of operation of diodes, LEDs, solar cells, and FETs.
- Explain the differences in structures and electronic properties of crystalline and amorphous semiconductors.

The band model (like MO theory) is based on a *one-electron* model. This was an approximation we made at the very beginning of our discussion of MO theory: we used hydrogen-like (one-electron) solutions to the Schrödinger equation to give us the shapes of s, p, d, and f atomic orbitals. In a one-electron atom, these orbitals are degenerate within a given shell, and the energy differences between, e.g., 2s and 2p orbitals arise only when we consider the energy of an electron in the field of other electrons in the atom. Moving from atoms to molecules, we made linear combinations to generate one-electron molecular orbitals (and, in solids, one-electron energy bands). But as in multi-electron atoms, life is not so simple for real molecules and solids that contain many electrons. Electrons repel each other, and so their movement in molecules and in solids is ***correlated***.

4.2.1.1: Prelude to Electronic Properties of Materials - Superconductors and Semiconductors

4.2.1.2: Metal-Insulator Transitions

4.2.1.3: Periodic Trends- Metals, Semiconductors, and Insulators

4.2.1.4: Semiconductors- Band Gaps, Colors, Conductivity and Doping

4.2.1.5: Semiconductor p-n Junctions

4.2.1.6: Diodes, LEDs and Solar Cells

4.2.1.7: Amorphous Semiconductors

4.2.1.8: Discussion Questions

4.2.1.9: Problems

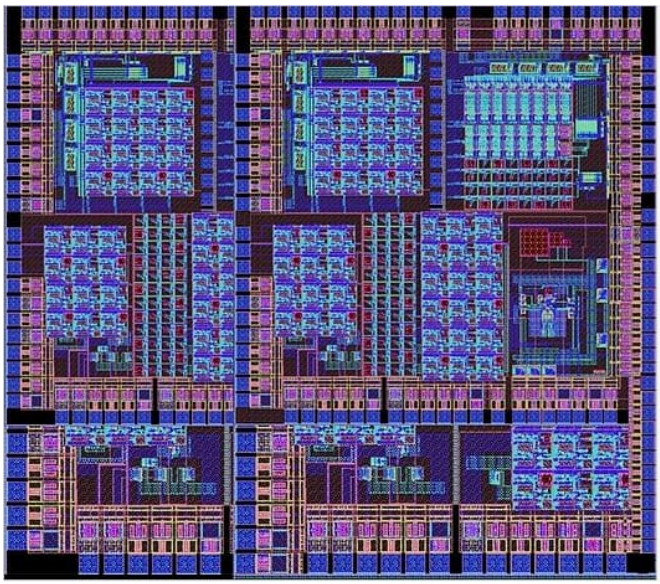
4.2.1.10: References

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4.2.1.1: Prelude to Electronic Properties of Materials - Superconductors and Semiconductors

In Chapter 6 we developed an energy band picture for metals, starting from atomic orbitals and building up the molecular orbitals of the solid metallic crystal. This treatment gave us a useful picture of how electrons behave in metals, moving at very fast speed between scattering events, and migrating in an electric field at a slow drift velocity. It also taught us that a metal is something with a partially filled band, meaning that the Fermi level cuts through one of its bands of orbitals. An insulator or a semiconductor has a similar band picture, except that the bands are either completely full or completely empty. In this case the Fermi level lies in the gap between fully occupied and unoccupied bands. We will see in this chapter that the properties of semiconductors (along with their useful electronic applications) depend on the addition of small amounts of impurities ("dopants") that change the position of the Fermi level, resulting in conduction by electrons or "holes."



Modern integrated circuits contain billions of nanoscale transistors and diodes that are essential for logic and memory functions. Both kinds of devices rely on junctions between crystalline silicon regions that contain a few parts per million of boron or phosphorus impurities.

While the band picture works well for most crystalline materials, it does not tell us the whole story of conduction in solids. That is because the band model (like MO theory) is based on a *one-electron* model. This was an approximation we made at the very beginning of our discussion of MO theory: we used hydrogen-like (one-electron) solutions to the Schrödinger equation to give us the shapes of s, p, d, and f atomic orbitals. In a one-electron atom, these orbitals are degenerate within a given shell, and the energy differences between, e.g., 2s and 2p orbitals arise only when we consider the energy of an electron in the field of other electrons in the atom. Moving from atoms to molecules, we made linear combinations to generate one-electron molecular orbitals (and, in solids, one-electron energy bands). But as in multi-electron atoms, life is not so simple for real molecules and solids that contain many electrons. Electrons repel each other and so their movement in molecules and in solids is ***correlated***. While this effect is weak in a "good" metal such as sodium - where the wavefunctions are highly delocalized - it can be quite important in other materials such as transition metal oxides. Correlated electron effects give rise to **metal-insulator transitions** that are driven by small changes in temperature, pressure, or composition, as well as to **superconductivity** - the passage of current with zero resistance at low temperatures. In this chapter we will develop some simple models to understand these interesting and important electronic properties of solids.

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4.2.1.2: Metal-Insulator Transitions

In Chapter 6 we learned that metals and insulators not only have different electrical properties but also have very different crystal structures. Metals tend to have high coordination numbers (typically 8 or 12) whereas insulators have low coordination numbers that can be rationalized as "octet" bonding arrangements. For example, in crystalline Si or Ge (diamond structure), each atom has four nearest neighbors. There are two electrons per bond, and thus each atom has eight electrons in its valence shell. Sn, the element below Ge, exists in two different forms, one (gray tin) with the diamond structure that is a brittle narrow-gap semiconductor, and the other (white tin) with a body-centered tetragonal structure that is a malleable metal. These two forms are very close in energy, and in fact metallic white tin transforms to the brittle semiconducting gray form at low temperature. Extremely cold weather in 18th century Europe caused many tin organ pipes to break and eventually turn to dust. This transformation has been called tin blight, tin disease, tin pest or tin leprosy. The dust is actually grey tin, which lacks the malleability of its metallic cousin white tin.

Under experimentally accessible temperatures and pressures, Si and Ge are always semiconducting (i.e., insulating), and Pb is always metallic. Why is Sn different? The reason has to do with orbital overlap. Theory tells us in fact that any (and all) insulators should become metallic at high enough pressure, or more to the point, at high enough density. For most insulators, however, the pressures required are far beyond those that we can achieve in the laboratory.

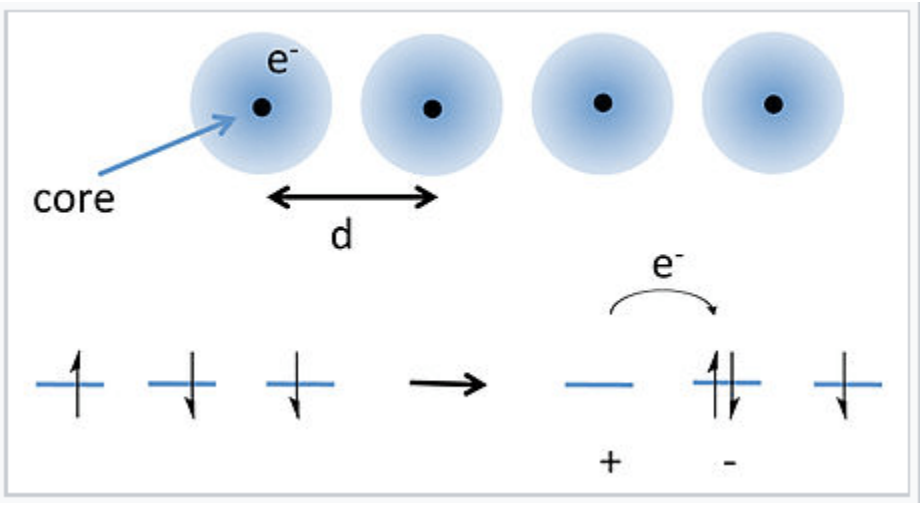


Figure 4.2.1.2.1: Organ pipes destroyed by "tin blight"

How can we rationalize the transition of insulators to the metallic state? Indeed, how can we understand the existence of insulators at all?

The Hubbard Model

Let's consider a chain of a large number (N) of atoms as we did in Chapter 6. For convenience, we can say that these are atoms such as H, Na, or Cs that have one valence electron. The simple band model we developed earlier suggests that the chain should be metallic, because N atoms combine to make N orbitals, and the N valence electrons only fill the band of orbitals halfway. But this conclusion doesn't depend on the density, which creates a paradox. If atoms in the chain are very far apart, we suspect that the electrons should localize on the atoms.

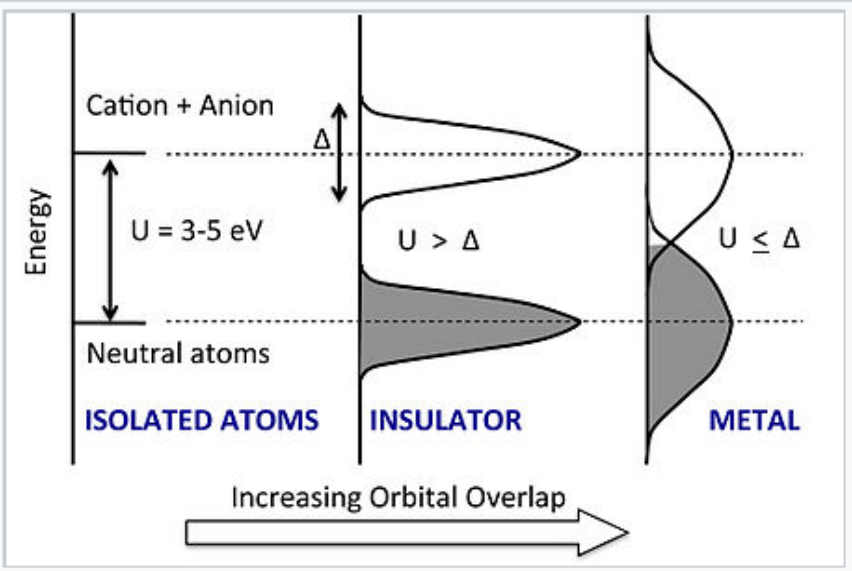


Electron hopping in a 1-D chain of atoms.

A solution to this problem was proposed by J. Hubbard in 1963.[1] Hubbard considered the energy required to transfer an electron from an atom to its nearest neighbor, as shown in the picture at the right. Because each atom already has one electron (with random spin), moving an electron over by one atom requires overcoming the energy of electron-electron repulsion to make a cation-anion pair. For well-separated atoms this energy (U) is given by:

$$U = IP - Ea - \frac{e^2}{4\pi\varepsilon_0 d} \tag{4.2.1.2.1}$$

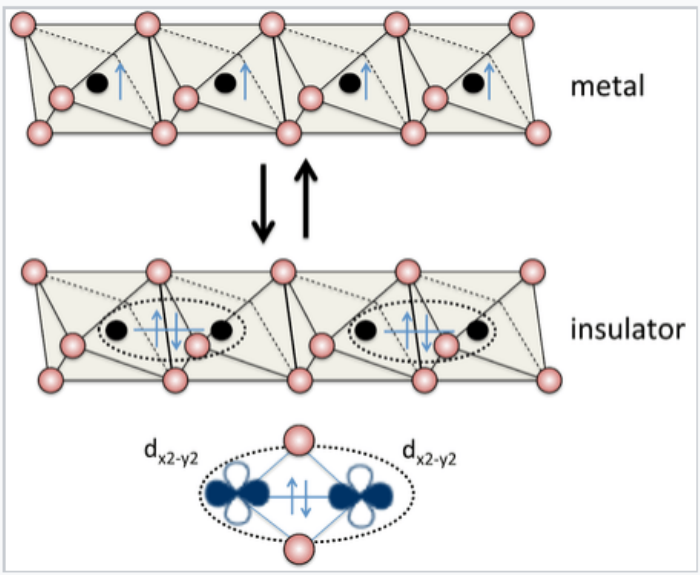
where IP and EA are the ionization energy and electron affinity, ε_0 is the permittivity of free space, and the last term in the equation represents the coulombic attraction between the cation and the anion. For atoms such as alkali metals, U is on the order of 3–5 eV, which is much larger than the thermal energy kT. Thus we expect there to be very few anion-cation pairs at room temperature, and the chain of atoms should be insulating.



Energy vs. DOS for the chain of atoms as the density and degree of orbital overlap between atoms increases. Increasing overlap broadens the neutral atom and anion-cation states into bands, each of which has a bandwidth Δ. A transition to the metallic state occurs abruptly when Δ exceeds the Hubbard gap U.

What happens when we squeeze the atoms together? In the Hubbard model, as the distance between atoms decreases, the energies of both the neutral atom states and the anion-cation states broaden into bands, each of which has a band width Δ. The lower band can accommodate exactly *N* electrons (not *2N* as in the MO picture we developed earlier) because each orbital can only take one electron without spin-pairing. Thus for small Δ the lower band is full and the upper band is empty. However, as we continue to compress the chain, the orbital overlap becomes so strong that Δ ≈ U. At this point, the bands overlap and some of the electrons fill the anion-cation states. The chain then becomes conducting and the material is metallic.

Some materials, such as Sn and VO_2, happen to have just the right degree of orbital overlap to make the Hubbard transition occur by changing the temperature or pressure. Such materials can be very useful for electrical switching, as illustrated at the right for rutile structure VO_2. Most materials are far away from the transition, either on the metallic or insulating side. An interesting periodic trend that illustrates this concept can be seen among the transition metal monoxides, MO (M = Ti, V, Cr, Mn, Fe, Co, Ni), all of which have the NaCl structure. TiO and VO are metallic, because the 3d orbitals have significant overlap in the structure. However, CrO, MnO, FeO, CoO, and NiO are all insulators, because the 3d orbitals contract (and therefore Δ < U) going across the transition metal series. In contrast, the analogous sulfides (TiS, VS,....NiS) are all metallic. The sulfides have the NiAs structure, in which all the metal atoms are eclipsed along the stacking axis (the hexagonal c-axis). The short metal-metal distances along that axis result in strong orbital overlap, making Δ > U.



Vanadium dioxide has the rutile structure, and in its undistorted form it is metallic, with one valence electron per V atom. Distortion of the lattice makes pairs of V atoms, resulting in an electronically insulating state. The metal-insulator transition can be driven reversibly by changing the temperature, pressure, or orbital occupancy. Electrical switching of this transition in VO_2 is being studied for applications in high performance thin film transistors[2]

The Mott Model

A simpler, less atomistic model of the metal-insulator transition was formulated by Neville Mott.[3] The Mott model considers the behavior of an electron in a material as a function of the density of all the other valence electrons. We know for a one-electron hydrogen-like atom (H, Na, Cs, etc.) the Schrödinger equation contains a potential energy term:

$$V(r) = -(\frac{e^2}{4\pi\varepsilon_0 r}) \tag{4.2.1.2.2}$$

This potential energy function gives rise to familiar ladder of allowed energy levels in the hydrogen atom. However, in a metal, this Coulomb potential must be modified to include the screening of nuclear charge by the other electrons in the solid. In this case there is a **screened Coulomb potential**:

$$V(r) = -(\frac{e^2}{4\pi\varepsilon_0 r})exp(-qr) \tag{4.2.1.2.3}$$

where q, which is the inverse of the **screening length**, is given by:

$$q^2 = 4m_e^2(\frac{3n}{\pi})^{\frac{1}{3}}(\frac{2\pi}{h}) \tag{4.2.1.2.4}$$

Here n is the density of atoms (or valence electrons), m_e is the electron mass, and h is Planck's constant. At distances much larger than the screening length q^{-1}, the electron no longer "feels" the charge on the nucleus. Mott showed that there is a critical density of electrons n_c above which the valence electrons are no longer bound by individual nuclei and are free to roam the crystal. This critical density marks the transition to the metallic state, and is given by the Mott criterion:

$$\mathbf{n_c^{\frac{1}{3}} a_H \approx 0.26} \tag{4.2.1.2.5}$$

In this equation, a_H is an effective Bohr radius for the valence electrons in the low-density limit, e.g. the average orbital radius of electrons in the 6s shell of a Cs atom when computing the value for Cs metal.



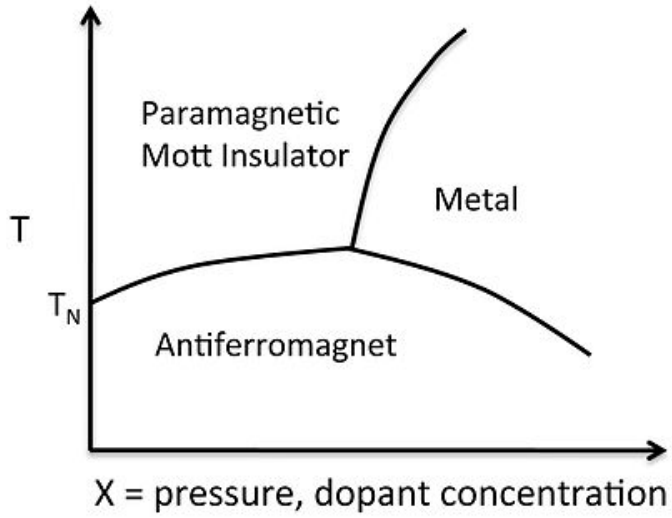
Solutions of lithium metal in liquid ammonia at low (top, ionic conductor) and higher (bottom, metal) Li concentration. From a video by Joshua Judkins

The important concept from the Mott model is that the metal-insulator transition depends very strongly on the **density of valence electrons.** This is consistent with the orbital overlap model of Hubbard, but also more general in the sense that it does not depend on a periodic structure of atoms. The Mott model is thus applicable to such diverse systems as metal atoms dissolved in liquid ammonia, metal atoms trapped in frozen gas matrices, and dopants in semiconductors.[4] In some systems, it is possible to continuously tune the density of valence electrons with rather striking results. For example, dissolving alkali metal (Li, Na, ...) in liquid ammonia (bp -33 ^{o}C) produces a blue liquid. The solvated alkali cations and negatively charged electrons impart ionic conductivity (as in a salt solution) but not electronic conductivity to the blue liquid ammonia solution. But as the concentration of electrons increases, a reflective, bronze-colored liquid phase forms that floats over the blue phase. This bronze phase is metallic and highly conducting. Eventually, with enough alkali metal added, the entire liquid is converted to the electronically conducting bronze phase.

The electrical switching of VO_2 between insulating and metallic phases (see above) can also be rationalized in terms of the Mott transition. Adding more electron density (by chemical or electric field doping) increases the concentration of valence electrons, driving the phase transition to the metallic state.

Thermodynamics and phase transitions

Thermodynamically, the metal-insulator transition is a **first-order phase transition**. In such a transition, the structure and properties change abruptly (think of the breakfast-to-lunch transition at McDonalds - there is just no way to get pancakes after, or hamburgers before 10:30 AM![5]). Thus in the case of Sn metal, the changes in structure (from four- to eight-coordination) and in electronic conductivity (insulator to metal) occur simultaneously. As in other first order phase transitions such as ice to water to steam, there is a latent heat associated with the transition and a discontinuity in derivative properties such as the heat capacity.



A typical phase diagram for a metal-insulator transition is shown at the right for V_2O_3. The octahedrally coordinated V^{3+} ion has a d^2 electron count, so there are two unpaired spins per atom, and at low temperature the spins in the lattice order antiferromagnetically. As we learned in Chapter 8, above the Néel temperature an antiferromagnet becomes a paramagnet, which is also a Mott insulator. Increasing the pressure, or doping with electrons (e.g., by substituting some d^3 Cr^{3+} for V^{3+}) pushes the electron density over the Mott transition, the spins pair, and the solid becomes metallic.

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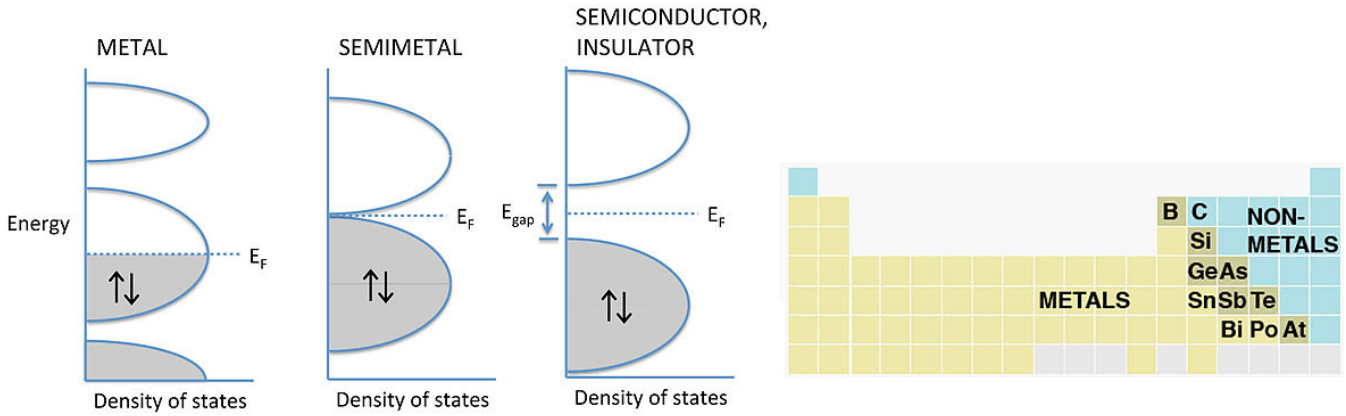
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4.2.1.3: Periodic Trends- Metals, Semiconductors, and Insulators

As we consider periodic trends in the electronic properties of materials, it is important to review some of the key bonding trends we have learned in earlier chapters:

- Going down the periodic table, atoms in solids tend to adopt structures with higher coordination numbers.
- The second row of the periodic table is special, with strong s-p hybridization and π-bonding between atoms.
- Electrons in higher quantum shells are less strongly bound, so the energy difference between bonding and antibonding orbitals becomes smaller for heavier atoms.

We also know that most of the elements in the periodic table are metals, but the elements in the top right corner are insulating under ordinary conditions (1 atm. pressure) and tend to obey the octet rule in their compounds.



At the transition between metals and non-metals in the periodic table we encounter a crossover in electronic properties, as well as in other properties such as the acidity of the oxides (see Ch. 3). The group of elements at the border is loosely referred to as the metalloids. Several of these elements (such as C, Sn, and As) can exist as different allotropes that can be metals, insulators, or something in between.

A more rigorous delineation of the electronic properties of these elements (and of many compounds) can be made by considering their band structures and the **temperature dependence of the electronic conductivity**. As we have previously discussed, metals have partially filled energy bands, meaning that the Fermi level intersects a partially filled band. With increasing temperature, metals become poorer conductors because lattice vibrations (which are called phonons in the physics literature) scatter the mobile valence electrons. In contrast, semiconductors and insulators, which have filled and empty bands, become better conductors at higher temperature, since some electrons are thermally excited to the lowest empty band. The distinction between insulators and semiconductors is arbitrary, and from the point of view of metal-insulator transitions, all semiconductors are insulators. We typically call an insulator a semiconductor if its band gap (E_{gap}) is less than about 3 eV. A semimetal is a material that has a band gap near zero, examples being single sheets of sp^2-bonded carbon (graphene) and elemental Bi. Like a narrow gap semiconductor, a semimetal has higher conductivity at higher temperature.

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4.2.1.4: Semiconductors- Band Gaps, Colors, Conductivity and Doping

Semiconductors, as we noted above, are somewhat arbitrarily defined as insulators with **band gap energy ≤ 3.0 eV** (~290 kJ/mol). This cutoff is chosen because, as we will see, the conductivity of undoped semiconductors drops off exponentially with the band gap energy and at 3.0 eV it is very low. Also, materials with wider band gaps (e.g. $SrTiO_3$, E_{gap} = 3.2 eV) do not absorb light in the visible part of the spectrum

There are a number of places where we find semiconductors in the periodic table:

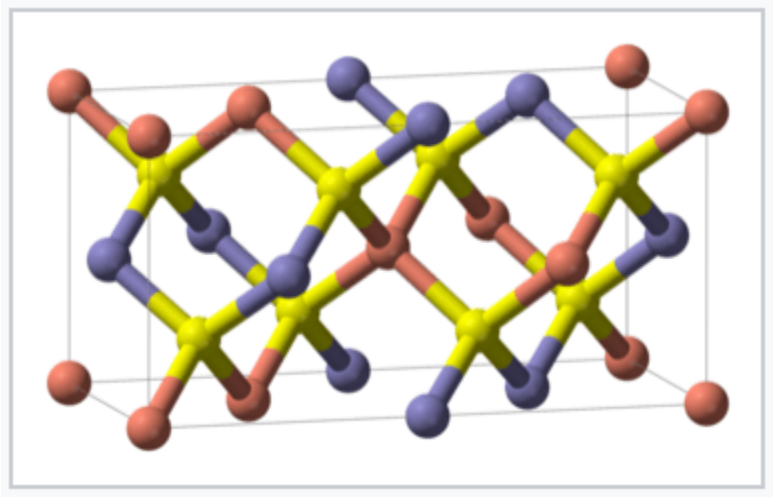
- Early transition metal oxides and nitrides, especially those with d^0 electron counts such as TiO_2, TaON, and WO_3
- Oxides of later 3d elements such as Fe_2O_3, NiO, and Cu_2O
- Layered transition metal chalcogenides with d^0, d^2 and d^6 electron counts including TiS_2, ZrS_2, MoS_2, WSe_2, and PtS_2
- d^{10} copper and sliver halides, e.g., CuI, AgBr, and AgI
- Zincblende- and wurtzite-structure compounds of the p-block elements, especially those that are isoelectronic with Si or Ge, such as GaAs and CdTe. While these are most common, there are other p-block semiconductors that are not isoelectronic and have different structures, including GaS, PbS, and Se.



A 2" wafer cut from a GaAs single crystal. GaAs, like many p-block semiconductors, has the zincblende structure.

The **p-block octet semiconductors** are by far the most studied and important for technological applications, and are the ones that we will discuss in detail.

Zincblende- and wurtzite-structure semiconductors have 8 valence electrons per 2 atoms. These combinations include 4-4 (Si, Ge, SiC,...), 3-5 (GaAs, AlSb, InP,...), 2-6 (CdSe, HgTe, ZnO,...), and 1-7 (AgCl, CuBr,...) semiconductors. Other variations that add up to an octet configuration are also possible, such as $Cu^{I}In^{III}Se_2$, which has the **chalcopyrite** structure, shown at the right.



The **chalcopyrite structure** is adopted by ABX_2 octet semiconductors such as $Cu^{I}In^{III}Se_2$ and $Cd^{II}Sn^{IV}P_2$. The unit cell is doubled relative to the parent **zincblende structure** because of the ordered arrangement of cations. Each anion (yellow) is coordinated by two cations of each type (blue and red).

How does the **band gap energy** vary with **composition**? There are two important trends

(1) Going **down a group** in the periodic table, the gap **decreases**:

C (diamond) > Si > Ge > α-Sn

E_{gap} (eV): 5.4 1.1 0.7 0.0

This trend can be understood by recalling that E_{gap} is related to the **energy splitting between bonding and antibonding orbitals**. This difference decreases (and bonds become weaker) as the principal quantum number increases.

(2) For isoelectronic compounds, **increasing ionicity** results in a **larger band gap**.

Ge < GaAs < ZnSe

0.7 1.4 2.8 eV

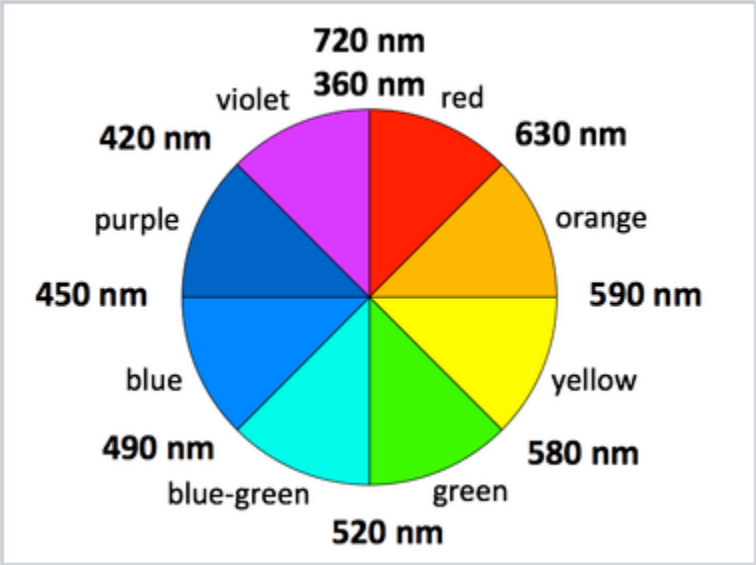
Sn < InSb < CdTe < AgI

0.0 0.2 1.6 2.8 eV

This trend can also be understood from a simple MO picture, as we discussed in Ch. 2. As the electronegativity difference $\Delta\chi$ increases, so does the energy difference between bonding and antibonding orbitals.

The band gap is a very important property of a semiconductor because it determines its color and conductivity. Many of the applications of semiconductors are related to band gaps:

- Narrow gap materials ($Hg_xCd_{1-x}Te$, VO_2, InSb, Bi_2Te_3) are used as infrared photodetectors and thermoelectrics (which convert heat to electricity).
- Wider gap materials (Si, GaAs, GaP, GaN, CdTe, $CuIn_xGa_{1-x}Se_2$) are used in electronics, light-emitting diodes, and solar cells.



Color wheel showing the colors and wavelengths of emitted light.

Semiconductor solid solutions such as $GaAs_{1-x}P_x$ have band gaps that are intermediate between the end member compounds, in this case GaAs and GaP (both zincblende structure). Often, there is a linear relation between composition and band gap, which is referred to as **Vegard's Law**. This "law" is often violated in real materials, but nevertheless offers useful guidance for designing materials with specific band gaps. For example, red and orange light-emitting diodes (LED's) are made from solid solutions with compositions of $GaP_{0.40}As_{0.60}$ and $GaP_{0.65}As_{0.35}$, respectively. Increasing the mole fraction of the lighter element (P) results in a larger band gap, and thus a higher energy of emitted photons.

Colors of semiconductors

The color of absorbed and emitted light both depend on the band gap of the semiconductor. Visible light covers the range of approximately 390-700 nm, or 1.8-3.1 eV. The **color of emitted light** from an LED or semiconductor laser corresponds to the band gap energy and can be read off the color wheel shown at the right.



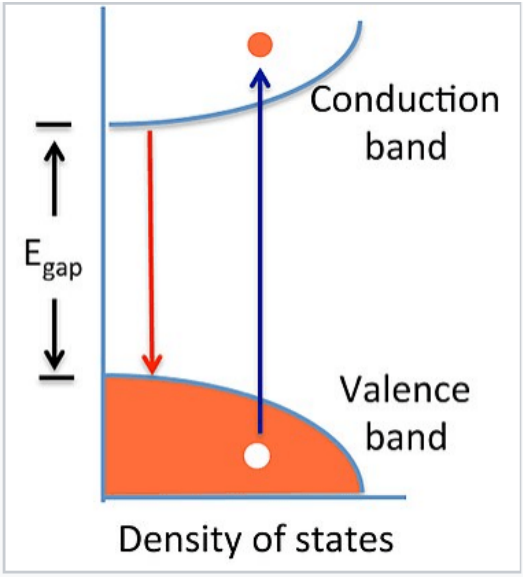
Fe_2O_3 powder is reddish orange because of its 2.2 eV band gap

The color of **absorbed light** includes the band gap energy, but also all colors of higher energy (shorter wavelength), because electrons can be excited from the valence band to a range of energies in the conduction band. Thus semiconductors with band gaps in the infrared (e.g., Si, 1.1 eV and GaAs, 1.4 eV) appear black because they absorb all colors of visible light. Wide band gap semiconductors such as TiO_2 (3.0 eV) are white because they absorb only in the UV. Fe_2O_3 has a band gap of 2.2 eV and thus absorbs light with $\lambda < 560$ nm. It thus appears reddish-orange (the colors of light reflected from Fe_2O_3) because it absorbs green, blue, and violet light. Similarly, CdS (E_{gap} = 2.6 eV) is yellow because it absorbs blue and violet light.

Electrons and holes in semiconductors

Pure (undoped) semiconductors can conduct electricity when electrons are promoted, either by heat or light, from the valence band to the conduction band. The promotion of an **electron** (e^-) leaves behind a **hole** (h^+) in the valence band. The hole, which is the absence of an electron in a bonding orbital, is also a mobile charge carrier, but with a positive charge. The motion of holes in the lattice can be pictured as analogous to the movement of an empty seat in a crowded theater. An empty seat in the middle of a row can move to the end of the row (to accommodate a person arriving late to the movie) if everyone moves over by one seat. Because the movement of the hole is in the opposite direction of electron movement, it acts as a positive charge carrier in an electric field.

The opposite process of excitation, which creates an electron-hole pair, is their recombination. When a conduction band electron drops down to recombine with a valence band hole, both are annihilated and energy is released. This release of energy is responsible for the emission of light in LEDs.



An electron-hole pair is created by adding heat or light energy E ≥ E_{gap} to a semiconductor (blue arrow). The electron-hole pair recombines to release energy equal to E_{gap} (red arrow).

At equilibrium, the creation and annihilation of electron-hole pairs proceed at equal rates. This dynamic equilibrium is analogous to the dissociation-association equilibrium of H^+ and OH^- ions in water. We can write a mass action expression:

$$n \times p = K_{eq} = n_i^2$$

where n and p represent the number density of electrons and holes, respectively, in units of cm^{-3}. The intrinsic carrier concentration, n_i, is equal to the number density of electrons or holes in an undoped semiconductor, where n = p = n_i.

Note the similarity to the equation for water autodissociation:

$$[H^+][OH^-] = K_w$$

By analogy, we will see that when we increase n (e.g., by doping), p will decrease, and vice-versa, but their product will remain constant at a given temperature.

Temperature dependence of the carrier concentration. Using the equations $K_{eq} = e^{(\frac{-\Delta G^o}{RT})}$ and $\Delta G^o = \Delta H^o - T\Delta S^o$, we can write:

$$n \times p = n_i^2 = e^{(\frac{\Delta S^o}{R})} e^{(\frac{-\Delta H^o}{RT})} \tag{4.2.1.4.1}$$

The entropy change for creating electron hole pairs is given by:

$$\Delta S^o = Rln(N_V) + Rln(N_V) = Rln(N_C N_V) \tag{4.2.1.4.2}$$

where N_V and N_C are the effective density of states in the valence and conduction bands, respectively.

and thus we obtain

$$n_i^2 = N_C N_V e^{(-\Delta H^o RT)} \tag{4.2.1.4.3}$$

Since the volume change is negligible, $\Delta H^o \approx \Delta E^o$, and therefore $\frac{\Delta H^o}{R} \approx \frac{E_{gap}}{k}$, from which we obtain

$$n_i^2 = N_C N_V e^{(\frac{-E_{gap}}{kT})} \tag{4.2.1.4.4}$$

and finally

$$\mathbf{n = p = n_i = (N_C N_V)^{\frac{1}{2}} e^{(\frac{-E_{gap}}{2kT})}} \tag{4.2.1.4.5}$$

For pure Si (E_{gap} = 1.1 eV) with N ≈ 10^{22}/cm^3, we can calculate from this equation a carrier density n_i of approximately 10^{10}/cm^3 at 300 K. This is about 12 orders of magnitude lower than the valence electron density of Al, the element just to the left of Si in the periodic table. Thus we expect the conductivity of pure semiconductors to be many orders of magnitude lower than those of metals.

Conductivity of intrinsic semiconductors

The conductivity (σ) is the product of the number density of carriers (n or p), their charge (e), and their mobility (μ). Recall from Chapter 6 that μ is the ratio of the carrier drift velocity to the electric field and has units of cm^2/Volt-second. Typically electrons and holes have somewhat different mobilities (μ_e and μ_h, respectively) so the conductivity is given by:

$$\sigma = ne\mu_e + pe\mu_h \tag{4.2.1.4.6}$$

For either type of charge carrier, we recall from Ch. 6 that the mobility μ is given by:

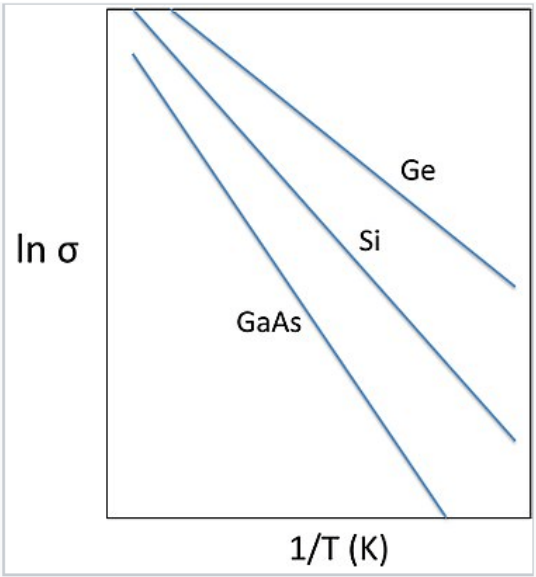
$$\mu = \frac{v_{drift}}{E} = \frac{e\tau}{m} \tag{4.2.1.4.7}$$

where e is the fundamental unit of charge, τ is the scattering time, and m is the effective mass of the charge carrier.

Taking an average of the electron and hole mobilities, and using n = p, we obtain

$$\sigma = \sigma_o e^{(\frac{-E_{gap}}{2kT})},\ where\ \sigma_o = 2(N_C N_V)^{\frac{1}{2}} e\mu \tag{4.2.1.4.8}$$

By measuring the conductivity as a function of temperature, it is possible to obtain the activation energy for conduction, which is E_{gap}/2. This kind of plot, which resembles an Arrhenius plot, is shown at the right for three different undoped semiconductors. The slope of the line in each case is -E_{gap}/2k.



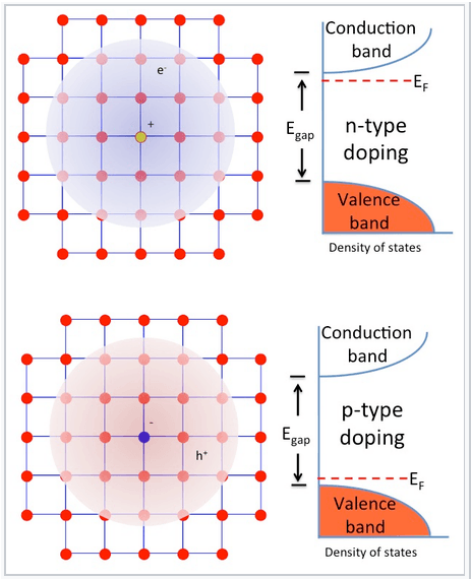
Plots of ln(σ) vs. inverse temperature for intrinsic semiconductors Ge (E_{gap} = 0.7 eV), Si (1.1 eV) and GaAs (1.4 eV). The slope of the line is -E_{gap}/2k.

Doping of semiconductors. Almost all applications of semiconductors involve controlled **doping**, which is the substitution

of impurity atoms, into the lattice. Very small amounts of dopants (in the parts-per-million range) dramatically affect the conductivity of semiconductors. For this reason, very pure semiconductor materials that are carefully doped - both in terms of the concentration and spatial distribution of impurity atoms - are needed.

n- and p-type doping. In crystalline Si, each atom has four valence electrons and makes four bonds to its neighbors. This is exactly the right number of electrons to completely fill the valence band of the semiconductor. Introducing a phosphorus atom into the lattice (the positively charged atom in the figure at the right) adds an extra electron, because P has five valence electrons and only needs four to make bonds to its neighbors. The extra electron, at low temperature, is bound to the phosphorus atom in a hydrogen-like molecular orbital that is much larger than the 3s orbital of an isolated P atom because of the high dielectric constant of the semiconductor. In silicon, this "expanded" Bohr radius is about 42 Å, i.e., 80 times larger than in the hydrogen atom. The energy needed to ionize this electron – to allow it to move freely in the lattice - is only about 40–50 meV, which is not much larger the thermal energy (26 meV) at room temperature. Therefore the Fermi level lies just below the conduction band edge, and a large fraction of these extra electrons are promoted to the conduction band at room temperature, leaving behind fixed positive charges on the P atom sites. The crystal is **n-doped**, meaning that the majority carrier (electron) is negatively charged.

Alternatively, boron can be substituted for silicon in the lattice, resulting in **p-type** doping, in which the majority carrier (hole) is positively charged. Boron has only three valence electrons, and "borrows" one from the Si lattice, creating a positively charged hole that exists in a large hydrogen-like orbital around the B atom. This hole can become delocalized by promoting an electron from the valence band to fill the localized hole state. Again, this process requires only 40–50 meV, and so at room temperature a large fraction of the holes introduced by boron doping exist in delocalized valence band states. The Fermi level (the electron energy level that has a 50% probability of occupancy at zero temperature) lies just above the valence band edge in a p-type semiconductor.



n- and p-type doping of semiconductors involves substitution of electron donor atoms (light orange) or acceptor atoms (blue) into the lattice. These substitutions introduce extra electrons or holes, respectively, which are easily ionized by thermal energy to become free carriers. The Fermi level of a doped semiconductor is a few tens of mV below the conduction band (n-type) or above the valence band (p-type).

As noted above, the doping of semiconductors dramatically changes their conductivity. For example, the intrinsic carrier concentration in Si at 300 K is about 10^{10} cm^{-3}. The mass action equilibrium for electrons and holes also applies to doped semiconductors, so we can write:

$$n \times p = n_i^2 = 10^{20} cm^{-6} \; at \; 300K \tag{4.2.1.4.9}$$

If we substitute P for Si at the level of one part-per-million, the concentration of electrons is about 10^{16} cm^{-3}, since there are approximately 10^{22} Si atoms/cm^3 in the crystal. According to the mass action equation, if n = 10^{16}, then p = 10^4 cm^{-3}. There are

three consequences of this calculation:

- The density of carriers in the doped semiconductor (10^{16} cm^{-3}) is much higher than in the undoped material (~10^{10} cm^{-3}), so the conductivity is also many orders of magnitude higher.
- The activation energy for conduction is only 40–50 meV, so the conductivity does not change much with temperature (unlike in the intrinsic semiconductor)
- The minority carriers (in this case holes) do not contribute to the conductivity, because their concentration is so much lower than that of the majority carrier (electrons).

Similarly, for p-type materials, the conductivity is dominated by holes, and is also much higher than that of the intrinsic semiconductor.

Chemistry of semiconductor doping. Sometimes it is not immediately obvious what kind of doping (n- or p-type) is induced by "messing up" a semiconductor crystal lattice. In addition to substitution of impurity atoms on normal lattice sites (the examples given above for Si), it is also possible to dope with vacancies - missing atoms - and with interstitials - extra atoms on sites that are not ordinarily occupied. Some simple rules are as follows:

- For substitutions, adding an **atom to the right** in the periodic table results in **n-type** doping, and an atom to the **left** in **p-type** doping.

  For example, when TiO_2 is doped with Nb on some of the Ti sites, or with F on O sites, the result is n-type doping. In both cases, the impurity atom has one more valence electron than the atom for which it was substituted. Similarly, substituting a small amount of Zn for Ga in GaAs, or a small amount of Li for Ni in NiO, results in p-type doping.

- **Anion vacancies** result in **n-type** doping, and **cation vacancies** in **p-type** doping.

  Examples are anion vacancies in CdS_{1-x} and WO_{3-x}, both of which give n-type semiconductors, and copper vacancies in $Cu_{1-x}O$, which gives a p-type semiconductor.

- **Interstitial cations** (e.g. Li) donate electrons to the lattice resulting in **n-type** doping. Interstitial anions are rather rare but would result in p-type doping.

Sometimes, there can be both p- and n-type dopants in the same crystal, for example B and P impurities in a Si lattice, or cation and anion vacancies in a metal oxide lattice. In this case, the two kinds of doping **compensate** each other, and the doping type is determined by the one that is in higher concentration. A dopant can also be present on more than one site. For example, Si can occupy both the Ga and As sites in GaAs, and the two substitutions compensate each other. Si has a slight preference for the Ga site, however, resulting in n-type doping.

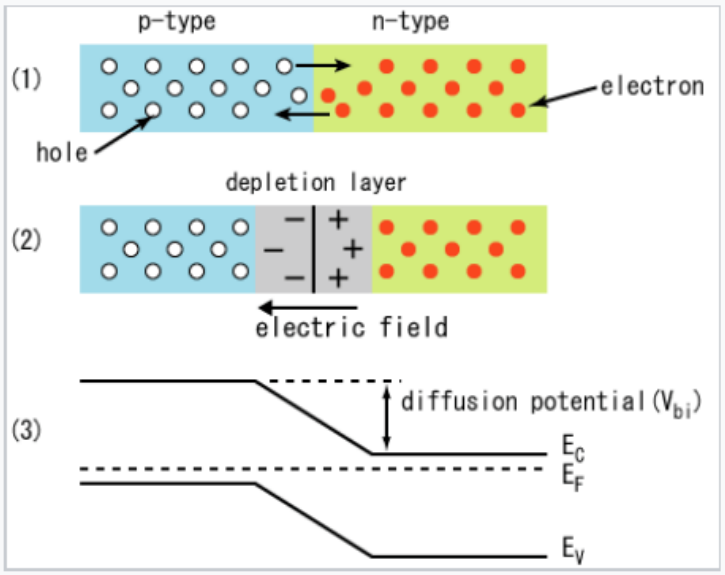
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4.2.1.5: Semiconductor p-n Junctions

Semiconductor p-n junctions are important in many kinds of electronic devices, including diodes, transistors, light-emitting diodes, and photovoltaic cells. To understand the operation of these devices, we first need to look at what happens to electrons and holes when we bring p-type and n-type semiconductors together. At the junction between the two materials, mobile electrons and holes annihilate each other, leaving behind the fixed + and - charges of the electron donor and electron acceptor dopants, respectively. For example, on the n-side of a silicon p-n junction, the positively charged dopants are P^+ ions and on the p-side the negatively charged dopants are B^-. The presence of these uncompensated electrical charges creates an electric field, the **built-in field** of the p-n junction. The region that contains these charges (and a very low density of mobile electrons or holes) is called the **depletion region**.

The electric field, which is created in the depletion region by electron-hole recombination, repels both the electrons (on the n-side) and holes (on the p-side) away from the junction. The concentration gradient of electrons and holes, however, tends to move them in the opposite direction by diffusion. At equilibrium, the flux of mobile carriers is zero because the field-driven migration flux is equal and opposite to the concentration-driven diffusion flux.



When p-type and n-type semiconductors are joined, electrons and holes are annihilated at the interface, leaving a depletion region that contains positively and negatively charged donor and acceptor atoms, respectively. At equilibrium, the Fermi level (E_F) is uniform throughout the junction. E_F lies just above the valence band on the p-type side of the junction and just below the conduction band on the n-type side.

The width of the depletion layer depends on the screening length in the semiconductor, which in turn depends on the dopant density. At high doping levels, the depletion layer is narrow (tens of nanometers across), whereas at low doping density it can be as thick as 1 µm. The depletion region is the only place where the electric field is nonzero, and the only place where the bands bend. Elsewhere in the semiconductor the field is zero and the bands are flat.

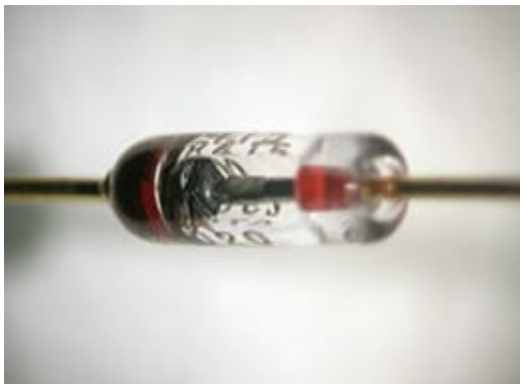
In the middle of p-n junction, the Fermi level energy, E_F, is halfway between the valence band, VB, and the conduction band, CB, and the semiconductor is intrinsic ($n = p = n_i$)

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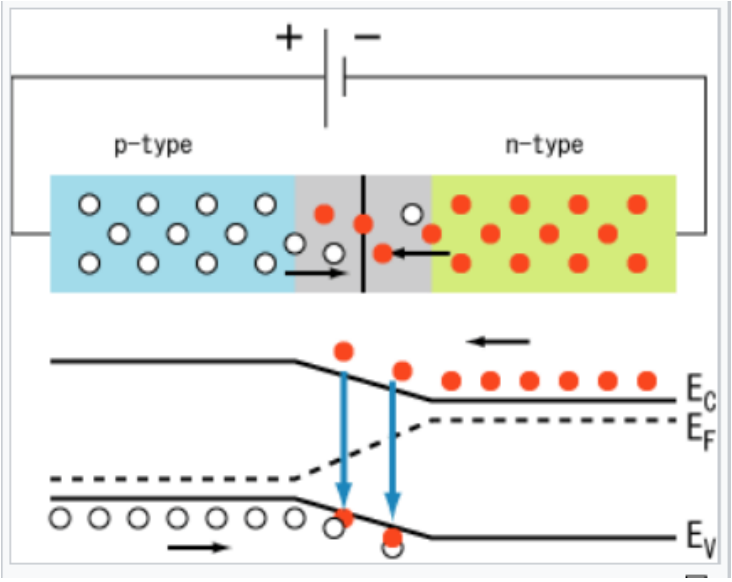
4.2.1.6: Diodes, LEDs and Solar Cells

Diodes are semiconductor devices that allow current to flow in only one direction. Diodes act as rectifiers in electronic circuits, and also as efficient light emitters (in LEDs) and solar cells (in photovoltaics). The basic structure of a diode is a junction between a p-type and an n-type semiconductor, called a p-n junction. Typically, diodes are made from a single semiconductor crystal into which p- and n- dopants are introduced.



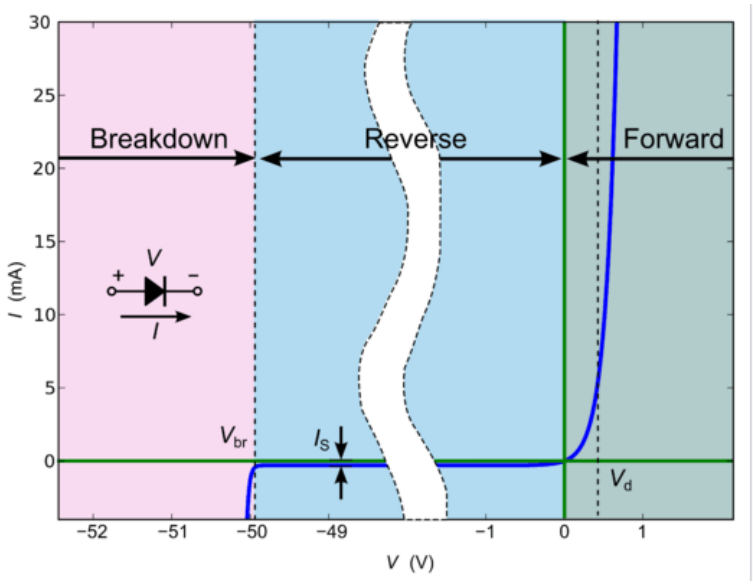
Closeup of a diode, showing the square-shaped semiconductor crystal *(black object on left)* (John Maushammer, Wikipedia, CC-BY-SA)

If the n-side of a diode is biased at positive potential and the p-side is biased negative, electrons are drawn to the n-side and holes to the p-side. This reinforces the built in potential of the p-n junction, the width of the depletion layer increases, and very little current flows. This polarization direction is referred to as "back bias." If the diode is biased the other way, carriers are driven into the junction where they recombine. The electric field is diminished, the bands are flattened, and current flows easily since the applied bias lowers the built-in potential. This is called "forward bias."



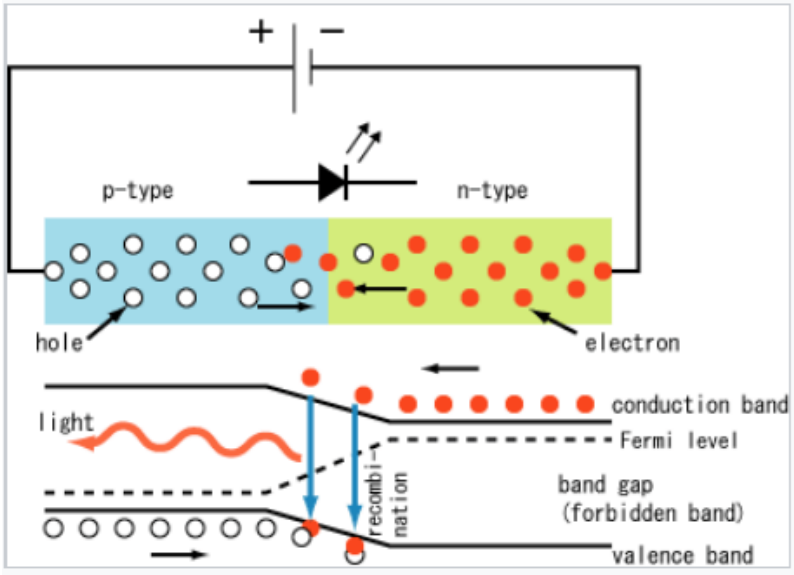
Electrons (red) and holes (white) in a forward-biased diode. (S-kei. Wikipedia, CC-BY-SA)

The figure on the left illustrates a forward-biased diode, through which current flows easily. As electrons and holes are driven into the junction (black arrows in lower left figure), they recombine (downward blue arrows), producing light and/or heat. The Fermi level in the diode is indicated as the dotted line. There is a drop in the Fermi level (equal to the applied bias) across the depletion layer. The corresponding diode i-V curve is shown on the right. The current rises exponentially with applied voltage in the forward bias direction, and there is very little leakage current under reverse bias. At very high reverse bias (typically tens of volts) diodes undergo avalanche breakdown and a large reverse current flows.



Diode i-V curve

A **light-emitting diode** or **LED** is a kind of diode that converts some of the energy of electron-hole recombination into light. This radiative recombination process always occurs in competition with non-radiative recombination, in which the energy is simply converted to heat. When light is emitted from an LED, the photon energy is equal to the bandgap energy. Because of this, LED lights have pure colors and narrow emission spectra relative to other light sources, such as incandescent and fluorescent lights. LED lights are energy-efficient and thus are typically cool to the touch.



Light-emitting diode (LED). (S-kei. Wikipedia, CC-BY-SA)

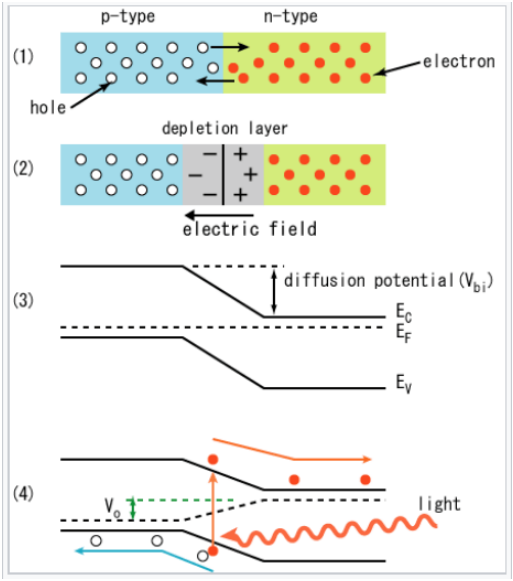
Direct-gap semiconductors such as GaAs and GaP have efficient luminescence and are also good light absorbers. In direct gap semiconductors, there is no momentum change involved in electron-hole creation or recombination. That is, the electrons and holes originate at the same value of the momentum wavevector **k**, which we encountered in Ch. 6. **k** is related to the momentum (also a vector quantity) by $\mathbf{p} = h\mathbf{k}/2\pi$. In a direct-gap semiconductor, the top of the valence band and the bottom of the conduction band most typically both occur at $\mathbf{k} = 0$. Since the momentum of the photon is close to zero, photon absorption and emission are strongly allowed (and thus kinetically fast). Polar semiconductors such as GaAs, GaN, and CdSe are typically direct-gap materials. **Indirect-gap** semiconductors such as Si and Ge absorb and emit light very weakly because the valence band maximum and conduction band minimum do not occur at the same point in k-space. This means that a lattice vibration (a phonon) must also be created or annihilated in order to conserve momentum. Since this "three body" (electron, hole, phonon) process has low probability, the radiative recombination of electrons and holes is slow relative to non-radiative decay - the thermalization of electron-hole energy as lattice vibrations - in indirect-gap semiconductors. The momentum selection rule thus prevents light absorption/emission and there are no pure Si LEDs or Si-based lasers.



Prof. Shuji Nakamura holding a blue LED.

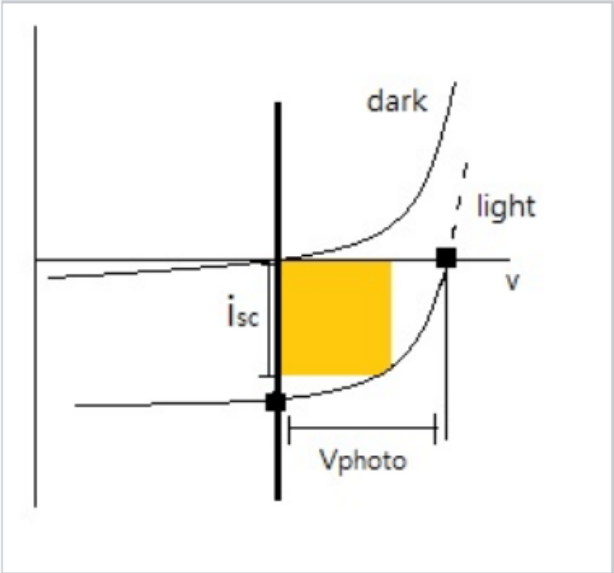
While red, orange, yellow, and green LEDs can be fabricated relatively easily from AlP-GaAs solid solutions, it was initially very difficult to fabricate blue LEDs because the best direct gap semiconductor with a bandgap in the right energy range is a nitride, GaN, which is difficult to make and to dope p-type. Working at Nichia Corporation in Japan, Shuji Nakamura succeeded in developing a manufacturable process for p-GaN, which is the basis of the blue LED. Because of the importance of this work in the development of information storage (Blu-Ray technology) and full-spectrum, energy-efficient LED lighting, Nakamura shared the 2014 Nobel Prize in Physics with Isamu Asaki and Hiroshi Amano, both of whom had made earlier contributions to the development of GaN diodes.

A **Solar cell**, or photovoltaic cell, converts light absorbed in a p-n junction directly to electricity by the photovoltaic effect. Photovoltaics is the field of technology and research related to the development of solar cells for conversion of solar energy to electricity. Sometimes the term solar cell is reserved for devices intended specifically to capture energy from sunlight, whereas the term photovoltaic cell is used when the light source is unspecified.



Photovoltaic effect in a semiconductor p-n junction. (S-kei. Wikipedia, CC-BY-SA)

Photocurrent in p-n junction solar cells flows in the diode reverse bias direction. In the dark, the solar cell simply acts as a diode. In the light, the photocurrent can be thought of as a constant current source, which is added to the i-V characteristic of the diode. The relationship between the dark and light current in a photovoltaic cell is shown in the diagram at the left.

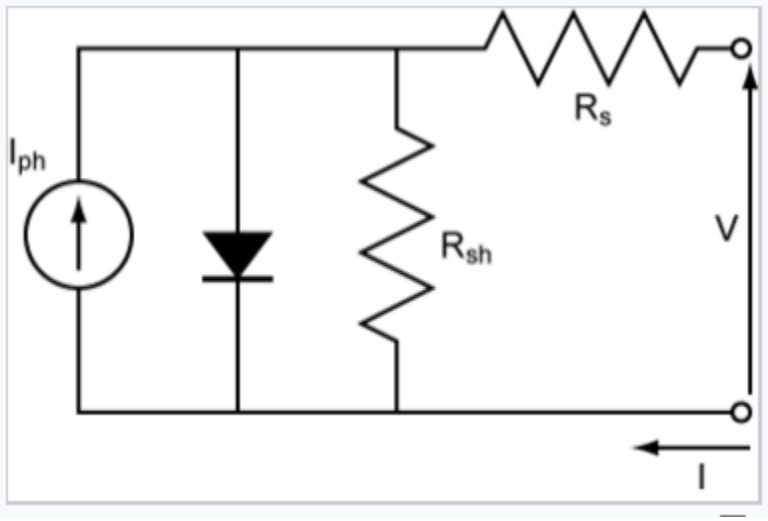


Current-voltage characteristic of a solar cell in the dark and under illumination with band gap light. The short-circuit photocurrent is indicated as i_{sc}, and the open-circuit photovoltage is V_{photo}. The maximum power generated by the solar cell is determined by the area of the orange box.

The built-in electric field of the p-n junction separates e^- h^+ pairs that are formed by absorption of bandgap light in the depletion region. The electrons flow downhill, towards the n-type side of the junction, the holes flow uphill towards the p-side. If $h\nu \geq E_{gap}$, light can be absorbed by promoting an electron from the valence band to the conduction band. Any excess energy is rapidly

thermalized. Light with hν > E_g thus can store only E_g worth of energy in an e^- h^+ pair. If light is absorbed outside of depletion region, i.e., on the n- or p-side of the junction where there is no electric field, minority carriers must diffuse into the junction in order to be collected. This process occurs in competition with electron-hole recombination. Because impurity atoms and lattice defects make efficient recombination centers, semiconductors used in solar cells (especially indirect-gap materials such as Si, which must be relatively thick in order to absorb most of the solar spectrum) must be very pure. Most of the cost of silicon solar cells is associated with the process of purifying elemental silicon and growing large single crystals from the melt.

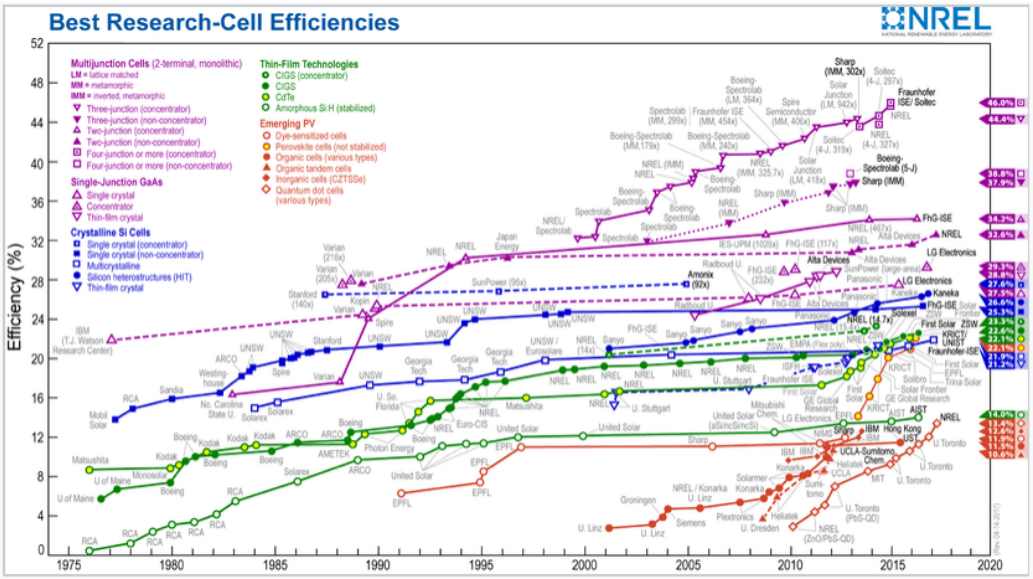
In the photodiode i-V curve above, V_{photo} is typically only about 70% of the bandgap energy E_{gap}. The photocurrent is limited by the photon flux, the recombination rate, and the re-emission of absorbed light.[6] The area of the orange rectangle indicates the power generated by the solar cell, which can be calculated as P = i x V. In good single crystal or polycrystalline solar cells made of Si, GaAs, CdTe, $CuIn_xGa_{1-x}Se_2$, or $(CH_3NH_3)PbI_3$ the quantum yield (the ratio of short circuit photocurrent to photon flux) is close to unity.



The equivalent circuit of a p-n junction solar cell, which results in the "light" i-V curve shown in the figure above. The solar cell is effectively a diode with a reverse-bias current source provided by light-generated electrons and holes. The shunt resistance (R_{sh}) in the equivalent circuit represents parasitic electron-hole recombination. A high shunt resistance (low recombination rate) and low series resistance (R_s) are needed for high solar cell efficiency.

Solar cells have many current applications. Individual cells are used for powering small devices such as electronic calculators. Photovoltaic arrays generate a form of renewable electricity, particularly useful in situations where electrical power from the grid is unavailable such as in remote area power systems, Earth-orbiting satellites and space probes, remote radio-telephones and water pumping applications. Photovoltaic electricity is also increasingly deployed in grid-tied electrical systems.

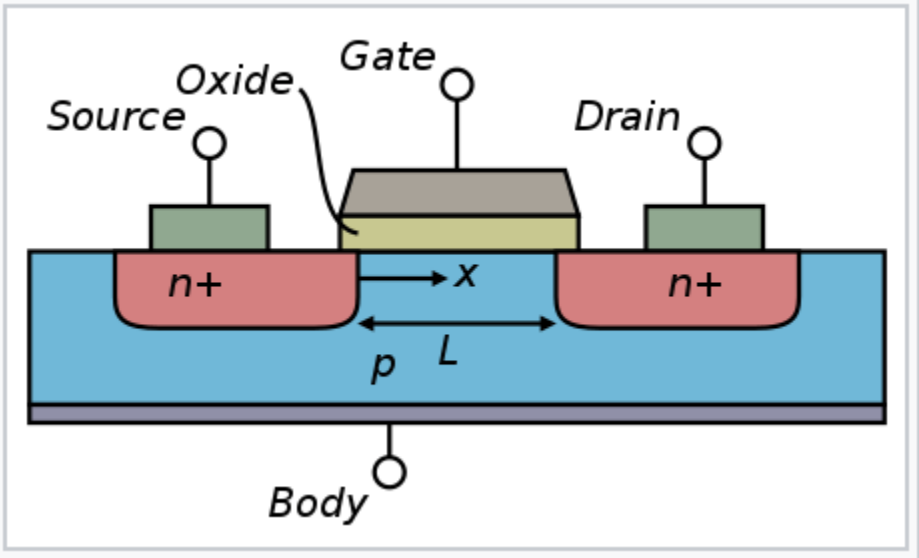
The cost of installed photovoltaics (calculated on a per-watt basis) has dropped over the past decade at a rate of about 13% per year, and has already reached grid parity in Germany and a number of other countries.[7] Photovoltaic grid parity is anticipated in U.S. power markets in the 2020 timeframe.[8] A major driver in the progressively lower cost of photovoltaic power is the steadily increasing efficiency of solar cells, which is shown in the graphic at the right. Higher efficiency solar cells require less area to deliver the same amount of power, and this lowers the "balance of system" costs such as wiring, roof mounting, etc., which scale as the area of the solar panels. Progress towards higher efficiency reflects improved processes for making photovoltaic materials such as silicon and gallium arsenide, as well as the discovery of new materials. Silicon solar cells are a mature technology, so they are now in the flat part of the learning curve and are approaching their maximum theoretical efficiencies. Newer technologies such as organic photovoltaics, quantum dot solar cells, and lead halide perovskite cells are still in the rising part of the learning curve.



Reported timeline of solar cell energy conversion efficiencies since 1976 (National Renewable Energy Laboratory)

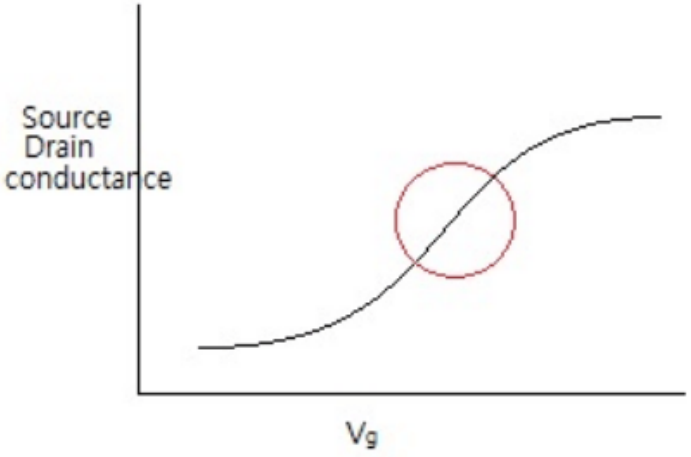
A **field effect transistor (FET)** is a transistor that uses an electric field to control the width of a conducting channel and thus the current in a semiconductor material. It is classified as unipolar transistor, in contrast to bipolar transistors.

Field effect transistors function as current amplifiers. The typical structure of Si-based FETs is one in which two n-type regions (the source and the drain) are separated by a p-type region. An oxide insulator over the p-type region separates a metal gate lead from the semiconductor. This structure is called a metal-oxide-semiconductor FET (or MOSFET). When voltage is applied between source and drain, current cannot flow because either the n-p or the p-n junction is back-biased. When a positive potential is applied to the gate, however, electrons are driven towards the gate, and locally the semiconductor is "inverted" to n-type. Then the current flows easily between the n-type source and drain through the n-channel. The current flow between the source and drain is many times larger than the current through the gate, and thus the FET can act as an amplifier. Current flow can also represent a logical "1," so FETs are also used in digital logic.



Cross section of an n-type MOSFET

In electronic devices such as microprocessors, field-effect transistors are kept in the off-state most of the time in order to minimize background current and power consumption. The FET shown above, which has n-type source and drain regions, is called an NMOS transistor. In a PMOS transistor, the source and drain regions are p-type and the gate is n-type. In **CMOS** (complementary metal-oxide semiconductor) integrated circuits, both NMOS and PMOS transistors are used. CMOS circuits are constructed in such a way that all PMOS transistors must have either an input from the voltage source or from another PMOS transistor. Similarly, all NMOS transistors must have either an input from ground or from another NMOS transistor. This arrangement results in low static power consumption.



Transistors are most useful in the range of gate voltage (indicated by the red circle in the figure at the left) where the source-drain current changes rapidly. In this region it is possible to effect a large change in current between source and drain when a small signal is applied to the gate. An important figure of merit for FETs is the **subthreshold slope**, which is the slope a plot of log(current) vs. V_{gate}. An ideal subthreshold slope is one decade of current per 60 mV of gate bias. Typically, a decade change in source-drain current can be achieved with a change in gate voltage of ~70 mV. The performance of FETs as switches and amplifiers is limited by the subthreshold slope, which in turn is limited by the capacitance of the gate. It is desirable to have

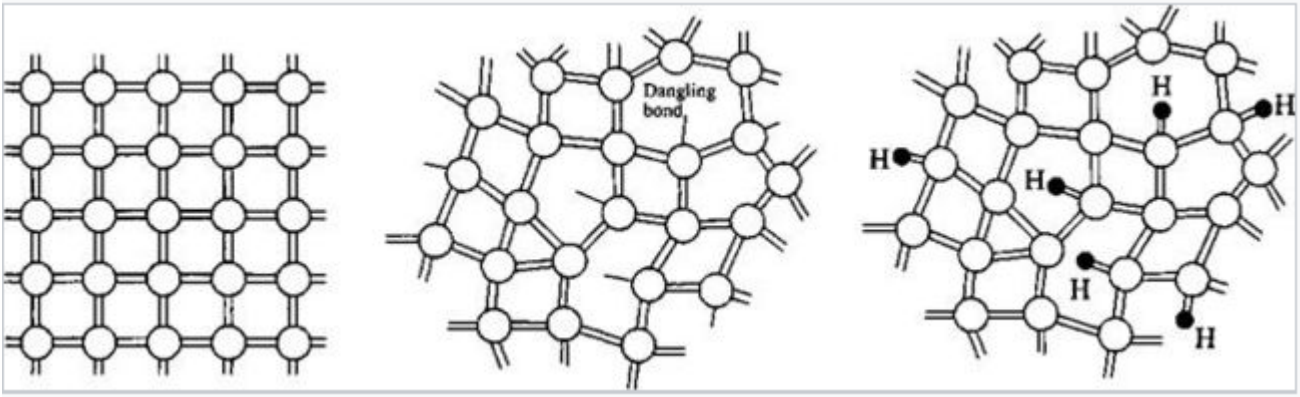
a very high gate capacitance, which requires a thin insulating oxide, but also to have a small leakage current, which requires a thick oxide. A current challenge in the semiconductor industry is to continue to scale FETs to even smaller nanoscale dimensions while maintaining acceptable values of these parameters. This is being done by developing new gate insulator materials that have higher dielectric constants than silicon oxide and do not undergo redox reactions with silicon or with metal gate leads. Only a few known materials (such as hafnium oxynitride and hafnium silicates) currently meet these stringent requirements.

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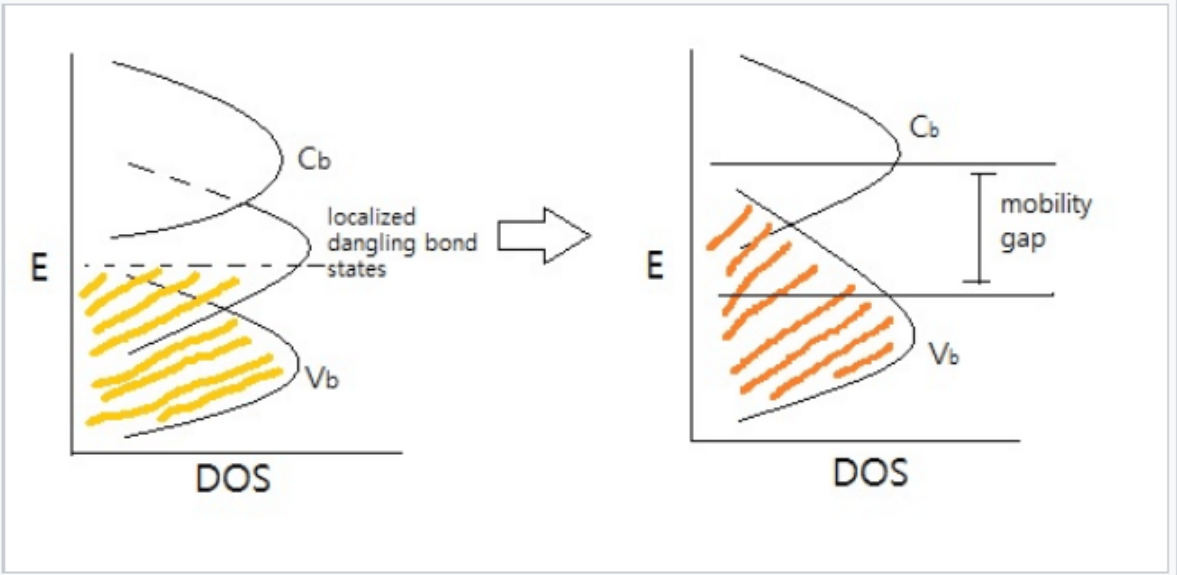
4.2.1.7: Amorphous Semiconductors

Amorphous semiconductors are disordered or glassy forms of crystalline semiconductor materials. Like non-conducting glasses, they are network structures with primarily covalent bonding. Crystalline silicon, which has the diamond structure, is an ordered arrangement of fused six-membered silicon rings, all in the "chair" conformation, as we saw in Ch. 8. The local bonding environment of the silicon atoms is tetrahedral. The silicon atoms in amorphous silicon (a-Si) are also predominantly tetrahedrally coordinated, but there is no long-range order in the structure. In addition to six-membered rings, there are five- and seven-membered rings, as well as some "dangling bond" sites in which Si atoms have only three nearest neighbors.



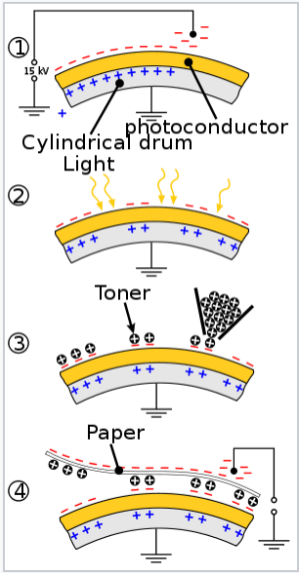
Schematic illustration of the structures of crystalline silicon (left), amorphous silicon (middle), and amorphous hydrogenated silicon (right)

Two of the most widely studied amorphous semiconductors are a-Si and amorphous selenium, a-Se. Si and Se can both be made in glassy form, usually by sputtering or evaporation at relatively low temperature. In a-Se, as in a-Si, locally, most of the atoms have their "normal" valence, but there are many defects and irregularities in the structure. Dangling bonds in amorphous semiconductors have orbital energies in the middle of gap, and electrons in these states are effectively non-bonding. Because these dangling bond sites are far apart from each other, there is little orbital overlap between them, and they also exist over a range of energies. Electrons in these mid-gap states are therefore **localized**, a phenomenon known as Anderson localizaton. Amorphous Si is insulating because electrons the Fermi level (in the middle of the gap) are not mobile in the lattice. These localized states create a mobility gap, and only electrons in states that are strongly bonding or antibonding are delocalized. Therefore, unmodified a-Si is not very useful as a semiconductor. However, by hydrogenating the material as it is formed (typically in a plasma of H atoms), the under-coordinated Si atoms are bonded to hydrogen atoms. This generates filled bonding and empty antibonding orbitals, the energies of which are outside the mobility gap. Hydrogenation thus lowers the density of states in the mobility gap. Hydrogenated amorphous silicon (a-Si:H) is insulating in the dark, but is a good photoconductor because light absorption creates electrons and holes in mobile states that are outside the mobility gap.



Energy vs. DOS for an amorphous semiconductor. Disorder and dangling bonds result in localized mid-gap states.

The photoconductivity of **amorphous Se** is exploited in xerography. A conductive drum coated with a-Se, which is insulating, is charged with static electricity by corona discharge from a wire. When the drum is exposed to a pattern of light and dark (the image to be duplicated), the illuminated a-Se areas become conductive and the static charge is dissipated from those parts of the drum. Carbon-containing toner particles then adhere via static charge to the areas that were not exposed to light, and are transferred and bonded to paper to make the copy. The speed of the process and the high resolution of pattern transfer depend on the very low conductivity of a-Se in the dark and its high conductivity under illumination.



Charging of amorphous Se and pattern transfer in the xerographic cycle.

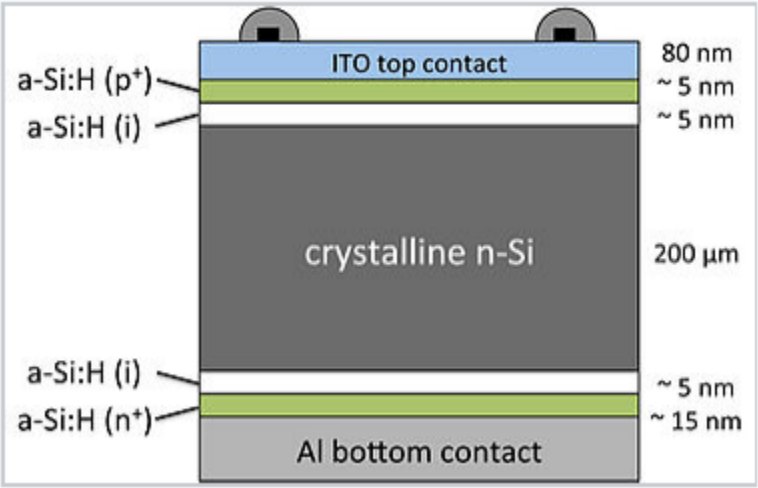
Amorphous hydrogenated Si is used in inexpensive thin film solar cells. The mobility gap is about 1.7 eV, which is larger than the bandgap crystalline of Si (1.1 eV). a-Si:H is a direct-gap material, and therefore thin films are good light absorbers. a-Si:H solar

cells can be vapor-deposited in large-area sheets. p^+Si-a-Si:H-n^+Si cells have around 10% power conversion efficiency. However amorphous Si solar cells gradually lose efficiency as they are exposed to light. The mechanism of this efficiency loss, called the Staebler-Wronski effect,[9], involves photogenerated electron-hole pairs which have sufficient energy to cause chemical changes in the material. While the exact mechanism is still unclear, it has been proposed that the energy of electron-hole recombination breaks a weak Si-Si bond, and that one of the resulting dangling bonds abstracts a H atom, leaving a passivated Si-H center and a permanent dangling bond. The effect is minimized by hydrogenating a-Si and can be partially reversed by annealing.



A calculator that runs on solar and battery power

Thin layers of amorphous silicon are used in conjunction with crystalline silicon in heterojunction intrinsic thin-layer (HIT) solar cells.[10] Because the mobility gap of a-Si is wider than the bandgap of c-Si, there is a potential energy barrier at the amorphous-crystalline interface that reflects electrons and holes away from that interface. At the p^+ contact, only holes can tunnel through the barrier, whereas only electrons can tunnel through the barrier to the n^+ contact. The passivation of surface defects that are sites of electron-hole recombination prevents a major loss mechanism in solar cells, increasing both the photovoltage and the photocurrent relative to conventional c-Si p-n junction cells. Panasonic and Sanyo have announced the production of HIT cells with power conversion efficiencies as high as 23%.



Layered structure of a HIT solar cell. The layers are not drawn to scale. A thick crystalline n-silicon layer is the light absorber, and photogenerated holes, which are the minority carriers, are reflected away from the aluminum back contact by the thin intrinsic a-Si layer there.

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4.2.1.8: Discussion Questions

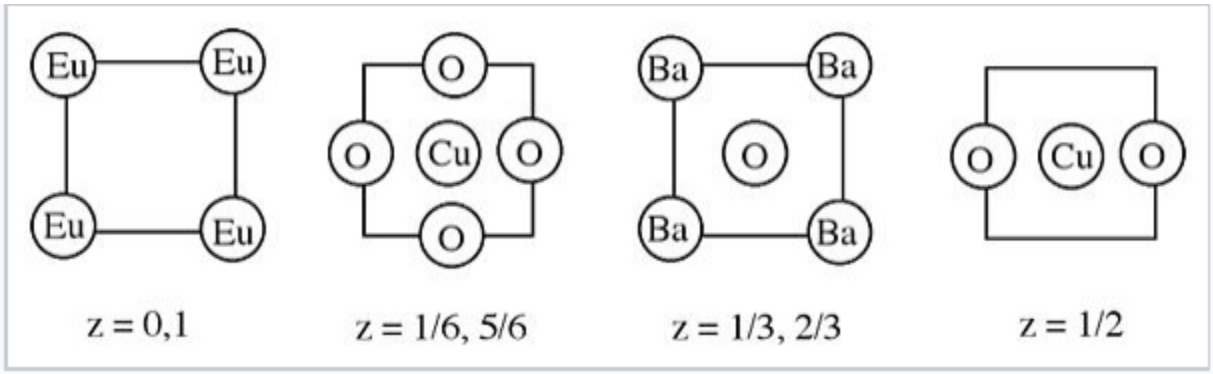
- How is magnetic ordering in the 3d transition metals (Fe, Co, Ni) and the absence of magnetism in the elements just below them (Ru, Ir, Pd) related to the metal-insulator transition?
- Why are good metals bad superconductors and vice-versa?
- Discuss why semiconducting oxides of early transition metals such as TiO_2 and Nb_2O_5 can be doped n-type but not p-type. Conversely, semiconducting late transition metal oxides such as NiO and Cu_2O can be doped p-type but not n-type.

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4.2.1.9: Problems

1. The structure of a high temperature superconductor containing barium, europium, copper, and oxygen is shown below. What are the coordination environments of Cu in this compound? This structure is actually closely related to perovskite, ABO_3. Explain the relationship between this structure and the ideal perovskite structure.



2. VO_2 can exist in insulating or metallic form, depending on temperature and pressure. Which form would be stabilized by increasing the temperature? Explain your answer.

3. Explain briefly how and why the bandgaps for octet p-block semiconductors vary (1) with the average principal quantum number, and (2) with the electronegativity difference between anion and cation.

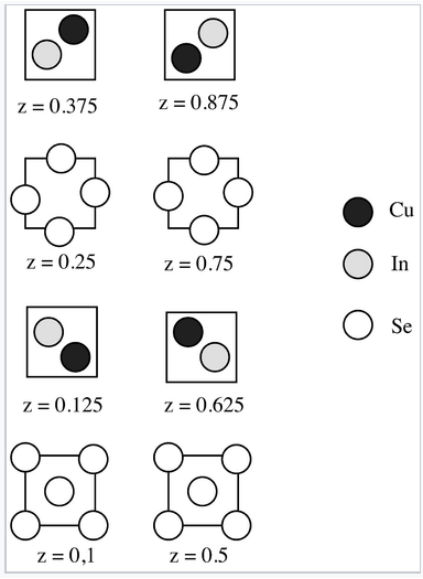
4. Indicate the type of conduction (n or p) in the following: (a) Se-doped GaAs, (b) $InAs_{1-x}$, where x << 1, (c) $Li_{0.05}Ni_{0.95}O$, (d) Li_xWO_3, where x << 1.

5. The structure of copper indium selenide, a semiconductor used in thin film solar cells, is shown below in sections.

(a) What is the stoichiometry of the compound?

(b) What kind of doping (n or p) will occur if a small amount of iodine is substituted for selenium?

(c) What kind of doping (n or p) will occur if a small fraction of the indium sites are occupied by copper atoms?

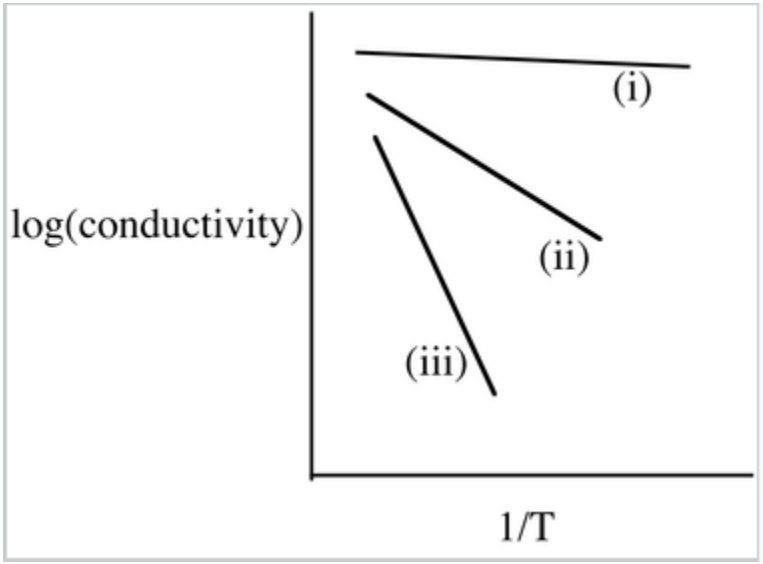


6. Using 1 eV = 1240 nm, predict the colors of anatase TiO_2 (Eg = 3.1 eV), SiC (2.0 eV), $ZnSnP_2$ (1.7 eV), $ZnGeP_2$ (1.9 eV), and InP (1.27 eV).

7. The conductivity of a certain intrinsic (undoped) semiconductor increases by a factor of two when the temperature is raised from 300 to 330 K. What is the bandgap (in eV)? R = 8.314 J/mol-K, 1 eV/atom = 96.52 kJ/mole.

8. Pure Ge is much more conductive than pure Si. Given their bandgaps (0.74 and 1.15 eV, respectively), estimate the ratio of their conductivities at room temperature.

9. The figure below illustrates the trends in conductivity vs. inverse temperature for Si, Ge, and As-doped Ge. Identify lines (i), (ii), and (iii) with the appropriate materials. Explain why the slope of line (i) is close to zero.



10. Sketch a silicon p-n junction, showing the depletion region, band bending, and the Fermi level in the absence of light or applied potential. In the dark, the p-n junction acts as a rectifier. (a) Which way do electrons and holes flow most easily in the dark? (b) Does the built in electric field increase or decrease under forward bias? (c) In the light, the junction acts as a photodiode. In this case, under short circuit conditions, do electrons flow in the same direction or in the opposite direction as in (a)? Explain.

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4.2.2: Formulas and Structures of Solids

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4.2.2.1: The Solid State of Matter

Learning Objectives

- Define and describe the bonding and properties of ionic, molecular, metallic, and covalent network crystalline solids
- Describe the main types of crystalline solids: ionic solids, metallic solids, covalent network solids, and molecular solids
- Explain the ways in which crystal defects can occur in a solid

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 4.2.2.1.1).

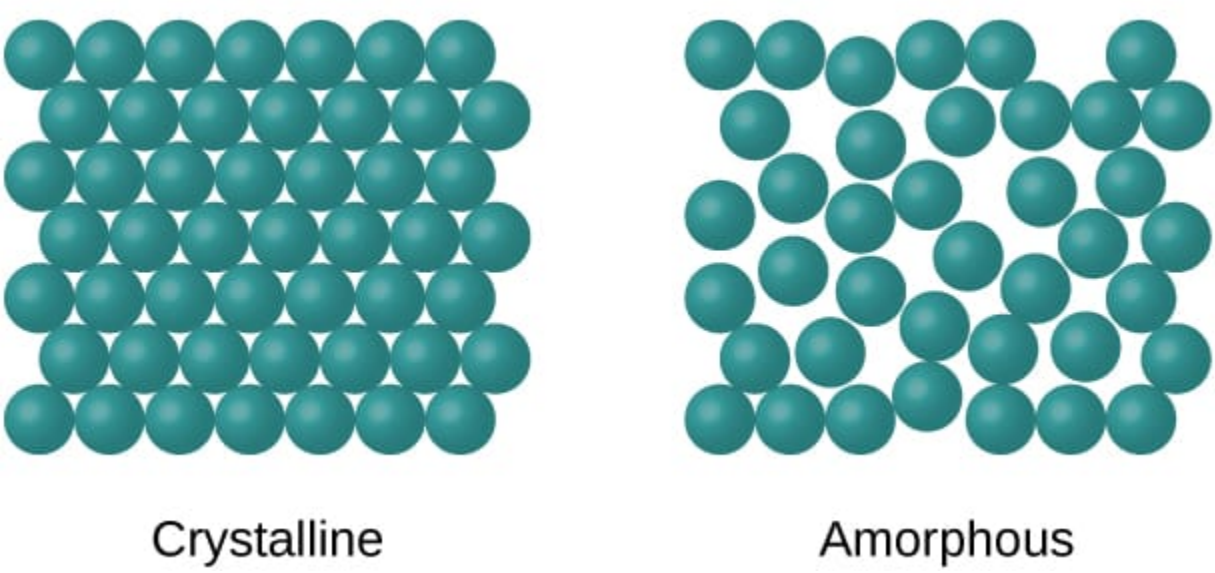


Figure 4.2.2.1.1: The entities of a solid phase may be arranged in a regular, repeating pattern (crystalline solids) or randomly (amorphous).

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 4.2.2.1.2), 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.

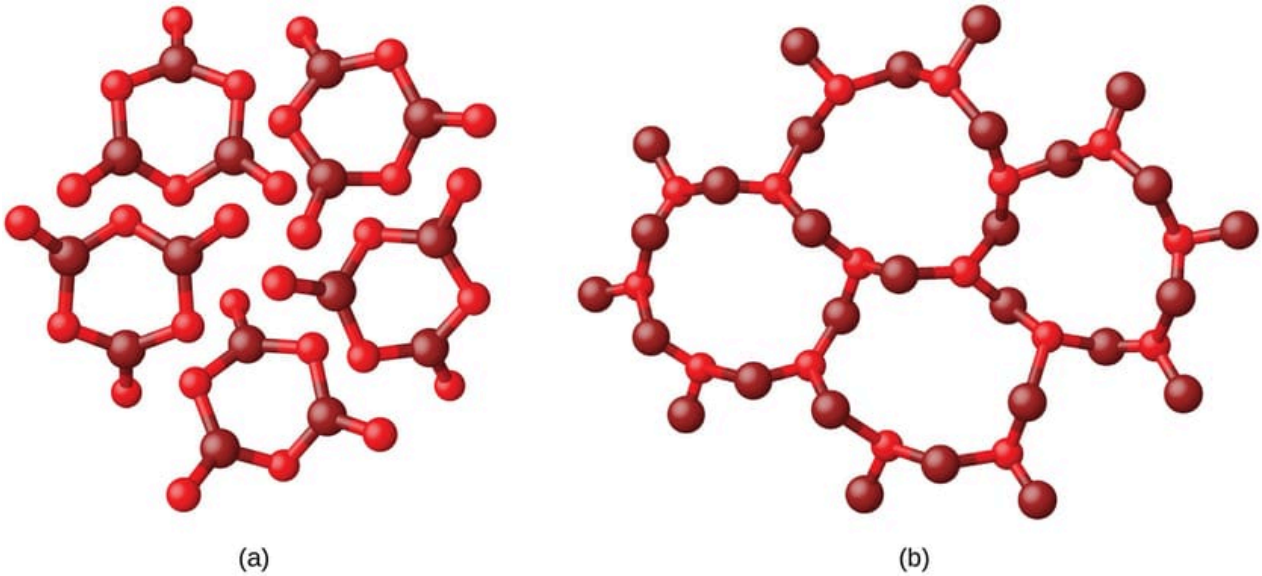


Figure 4.2.2.1.2: (a) Diboron trioxide, B_2O_3, is normally found as a white, amorphous solid (a glass), which has a high degree of disorder in its structure. (b) By careful, extended heating, it can be converted into a crystalline form of B_2O_3, which has a very ordered arrangement.

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.

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 4.2.2.1.3). 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.

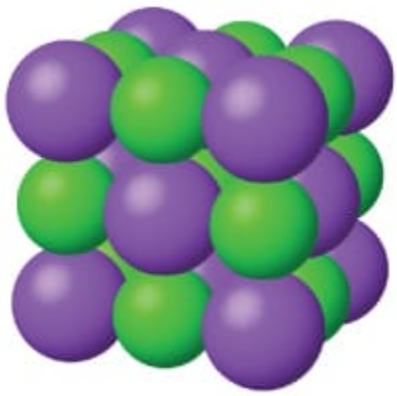


Figure 4.2.2.1.3: Sodium chloride is an ionic solid.

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.

Metallic Solids

Metallic solids such as crystals of copper, aluminum, and iron are formed by metal atoms Figure 4.2.2.1.4. 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.

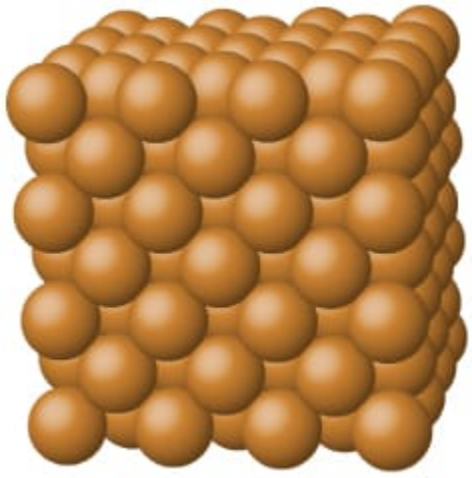


Figure 4.2.2.1.4: Copper is a metallic solid.

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 4.2.2.1.5. 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.

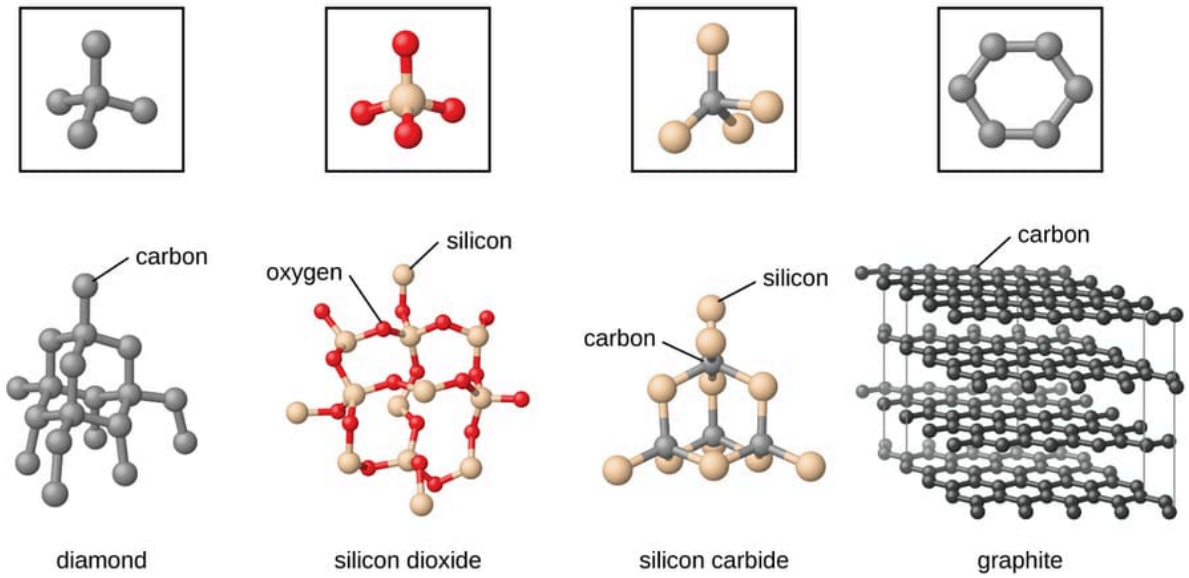


Figure 4.2.2.1.5. A covalent crystal contains a three-dimensional network of covalent bonds, as illustrated by the structures of diamond, silicon dioxide, silicon carbide, and graphite. Graphite is an exceptional example, composed of planar sheets of covalent crystals that are held together in layers 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 4.2.2.1.6, 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).

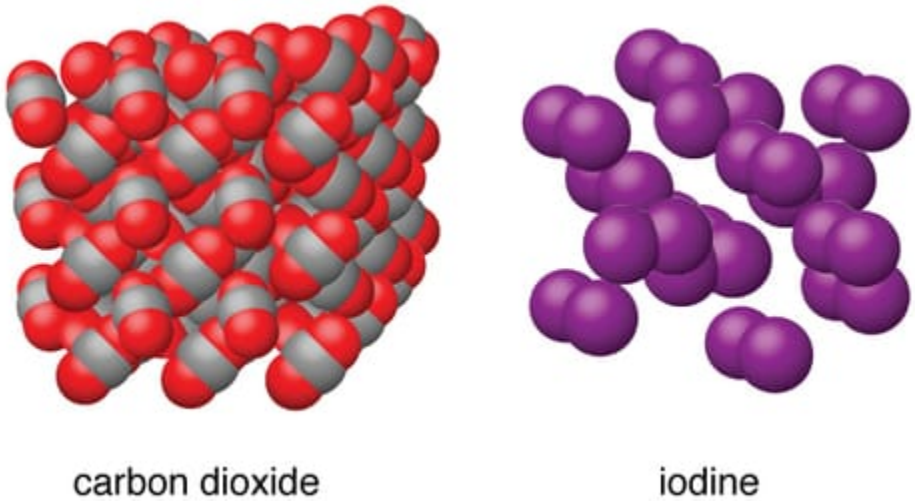


Figure 4.2.2.1.6: Carbon dioxide (CO_2) consists of small, nonpolar molecules and forms a molecular solid with a melting point of –78 °C. Iodine (I_2) consists of larger, nonpolar molecules and forms a molecular solid that melts at 114 °C.

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 4.2.2.1.1 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 4.2.2.1.1: Types of Crystalline Solids and Their Properties

Type of Solid	Type of Particles	Type of Attractions	Properties	Examples
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
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
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 4.2.2.1.7. 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.

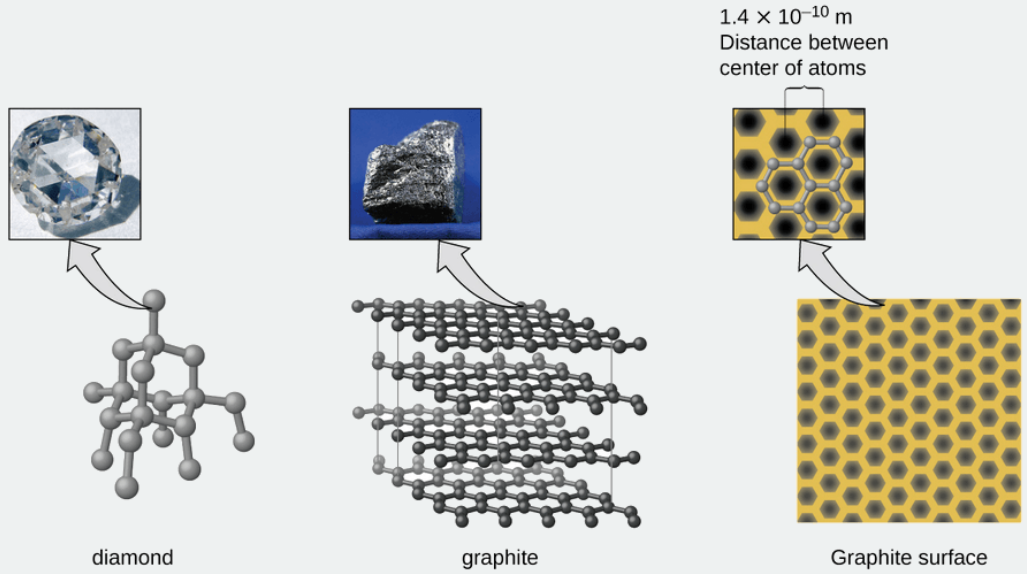


Figure 4.2.2.1.7: Diamond is extremely hard because of the strong bonding between carbon atoms in all directions. Graphite (in pencil lead) rubs off onto paper due to the weak attractions between the carbon layers. An image of a graphite surface shows the distance between the centers of adjacent carbon 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 4.2.2.1.8, 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.

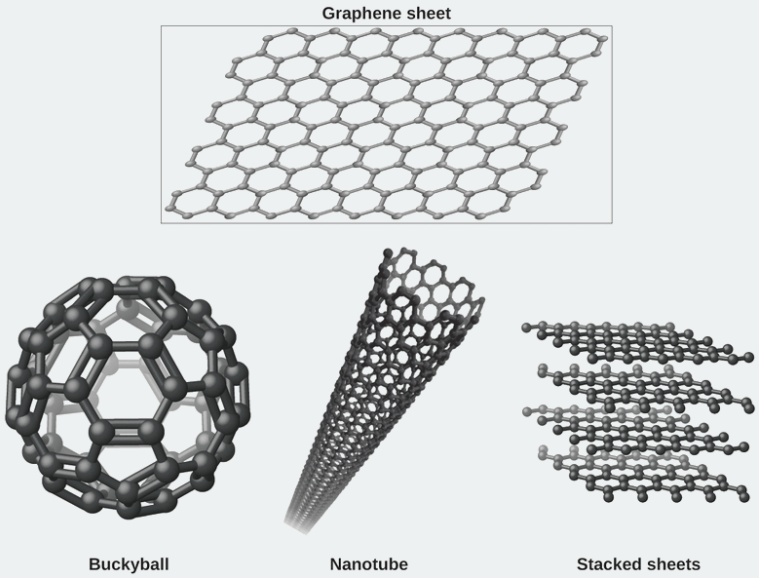


Figure 4.2.2.1.8: Graphene sheets can be formed into buckyballs, nanotubes, and stacked layers.

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.

Crystal Defects

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 4.2.2.1.9. Vacancies are defects that occur when positions that should contain atoms or ions are vacant. Less commonly, some atoms or ions in a crystal may occupy positions, called interstitial sites, located between the regular positions for atoms. Other distortions are found in impure crystals, as, for example, when the cations, anions, or molecules of the impurity are too large to fit into the regular positions without distorting the structure. 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.

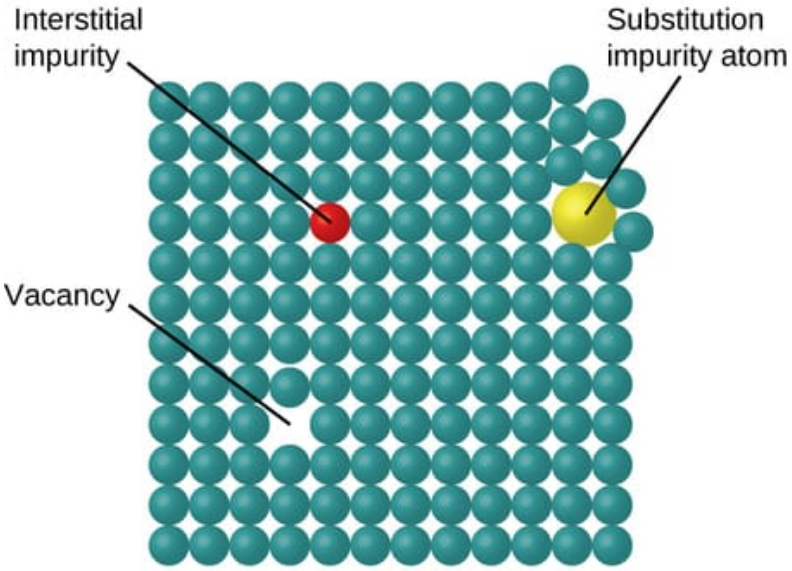


Figure 4.2.2.1.9: Types of crystal defects include vacancies, interstitial atoms, and substitutions impurities.

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. Some crystalline solids have defects in the definite repeating pattern of their particles. These defects (which include vacancies, atoms or ions not in the regular positions, and impurities) change physical properties such as electrical conductivity, which is exploited in the silicon crystals used to manufacture computer chips.

Glossary

amorphous solid
: (also, noncrystalline solid) solid in which the particles lack an ordered internal structure

covalent network solid
: solid whose particles are held together by covalent bonds

crystalline solid
: solid in which the particles are arranged in a definite repeating pattern

interstitial sites
: spaces between the regular particle positions in any array of atoms or ions

ionic solid
: solid composed of positive and negative ions held together by strong electrostatic attractions

metallic solid
: solid composed of metal atoms

molecular solid
: solid composed of neutral molecules held together by intermolecular forces of attraction

vacancy
: defect that occurs when a position that should contain an atom or ion is vacant

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4.2.2.2: Lattice Structures in Crystalline Solids

Learning Objectives

- Describe the arrangement of atoms and ions in crystalline structures
- Compute ionic radii using unit cell dimensions
- Explain the use of X-ray diffraction measurements in determining crystalline structures

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.

The Structures of Metals

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 4.2.2.2.1.

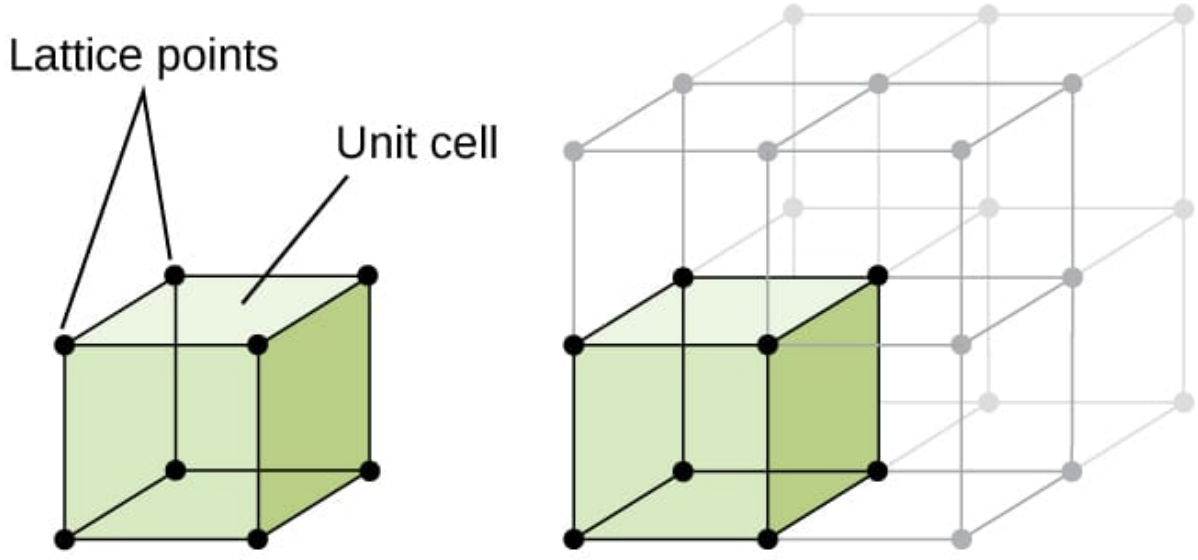


Figure 4.2.2.2.1: A unit cell shows the locations of lattice points repeating in all directions.

A diagram of two images is shown. In the first image, a cube with a sphere at each corner is shown. The cube is labeled “Unit cell” and the spheres at the corners are labeled “Lattice points.” The second image shows the same cube, but this time it is one cube amongst eight that make up a larger cube. The original cube is shaded a color while the other cubes are not.

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 4.2.2.2.2. This arrangement is called simple cubic structure, and the unit cell is called the simple cubic unit cell or primitive cubic unit cell.

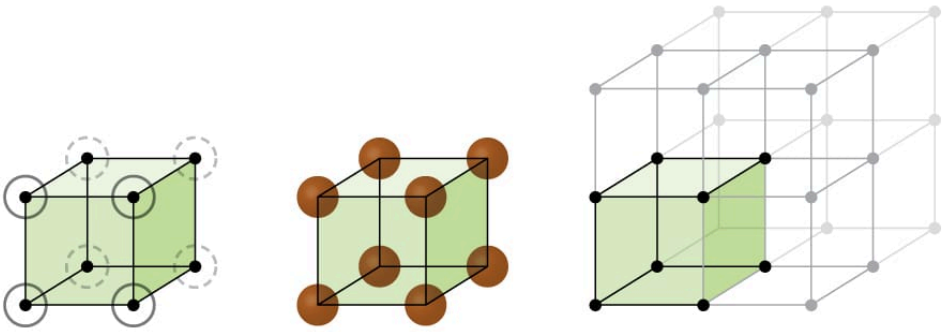


Figure 4.2.2.2.2: .When metal atoms are arranged with spheres in one layer directly above or below spheres in another layer, the lattice structure is called simple cubic. Note that the spheres are in contact.

A diagram of three images is shown. In the first image, a cube with a sphere at each corner is shown. The spheres at the corners are circled. The second image shows the same cube, but this time the spheres at the corners are larger and shaded in. In the third image, the cube is one cube amongst eight that make up a larger cube. The original cube is shaded a color while the other cubes are not.

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 4.2.2.2.3, 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.

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" height="200" width="463" src="/@api/deki/files/61021/CNX_Chem_10_06_SimpleCub2.jpg">

Figure 4.2.2.2.3: 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 4.2.2.2.4. 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.

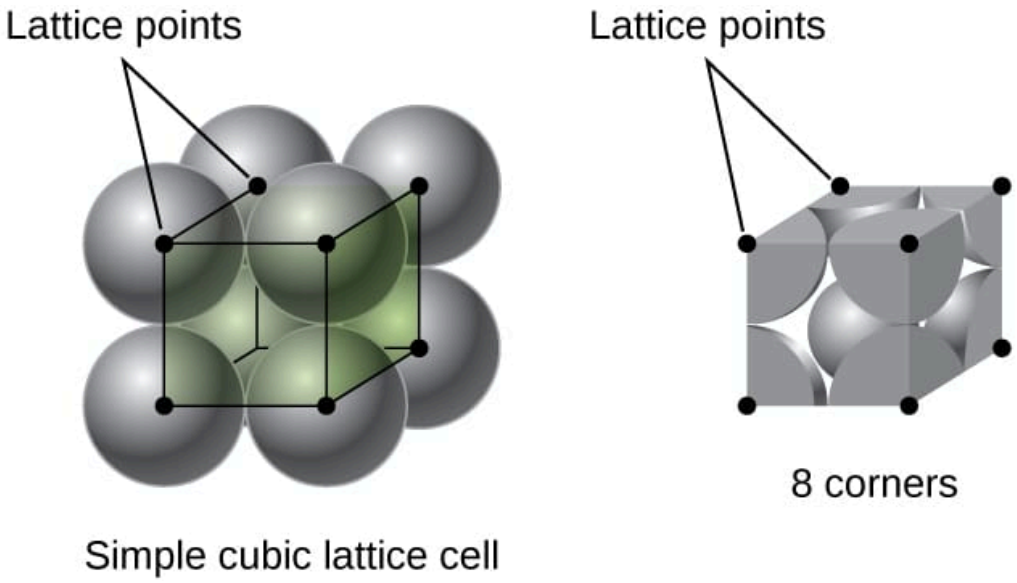


Figure 4.2.2.2.4: A simple cubic lattice unit cell contains one-eighth of an atom at each of its eight corners, so it contains one atom total.

A diagram of two images is shown. In the first image, eight spheres are stacked together to form a cube and dots at the center of each sphere are connected to form a cube shape. The dots are labeled “Lattice points” while a label under the image reads “Simple cubic lattice cell.” The second image shows the portion of each sphere that lie inside the cube. The corners of the cube are shown with small circles labeled “Lattice points” and the phrase “8 corners” is written below the image.

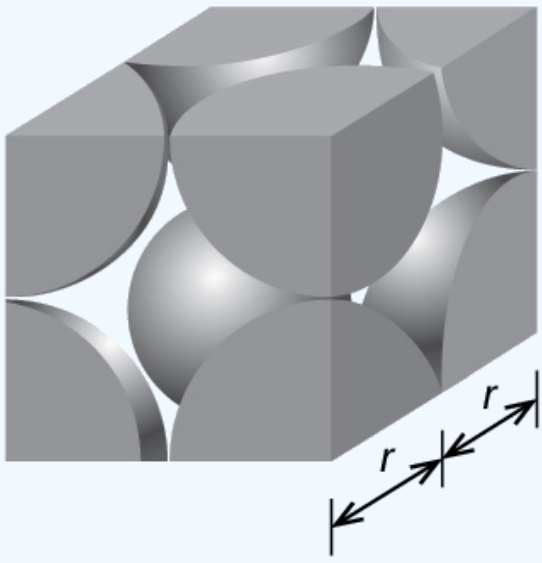
Example 4.2.2.2.1: Calculating Atomic Radius and Density for Metals (Part 1)

The edge length of the unit cell of alpha polonium is 336 pm.

a. Determine the radius of a polonium atom.
b. Determine the density of alpha polonium.

Solution

Alpha polonium crystallizes in a simple cubic unit cell:



(a) 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

$$r = \frac{l}{2} = \frac{336\ \text{pm}}{2} = 168\ \text{pm}$$

(b) 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

$$\text{Po} = \frac{3.471 \times 10^{-22}\ \text{g}}{3.79 \times 10^{-23}\ \text{cm}^3} = 9.16\ \text{g/cm}^3$$

Exercise 4.2.2.2.1

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 available at the end of this section.

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 (which we have already seen), body-centered cubic unit cell, and face-centered cubic unit cell—all of which are illustrated in Figure 4.2.2.2.5. (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. We leave the more complicated geometries for later in this module.)

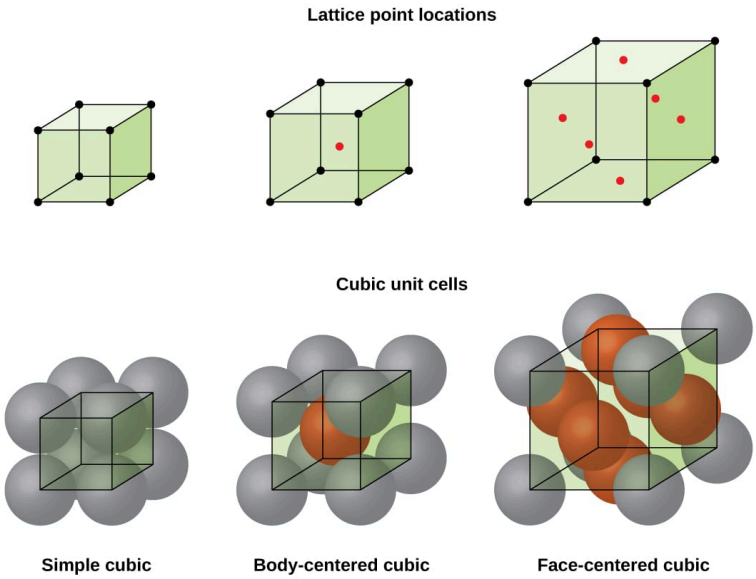


Figure 4.2.2.2.5: Cubic unit cells of metals show (in the upper figures) the locations of lattice points and (in the lower figures) metal atoms located in the unit cell.

Three pairs of images are shown. The first three images are in a row and are labeled “Lattice point locations” while the second three images are in a row labeled “Cubic unit cells.” The first image in the top row shows a cube with black dots at each corner while the first image in the second row is composed of eight spheres that are stacked together to form a cube and dots at the center of each sphere are connected to form a cube shape. The name under this image reads “Simple cubic.” The second image in the top row shows a cube with black dots at each corner and a red dot in the center while the second image in the second row is composed of eight spheres that are stacked together to form a cube with one sphere in the center of the cube and dots at the center of each corner sphere connected to form a cube shape. The name under this image reads “Body-centered cubic.” The third image in the top row shows a cube with black dots at each corner and red dots in the center of each face while the third image in the second row is composed of eight spheres that are stacked together to form a cube with six more spheres located in the center of each face of the cube. Dots at the center of each corner sphere are connected to form a cube shape. The name under this image reads “Face-centered cubic.”

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 4.2.2.2.6. 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.

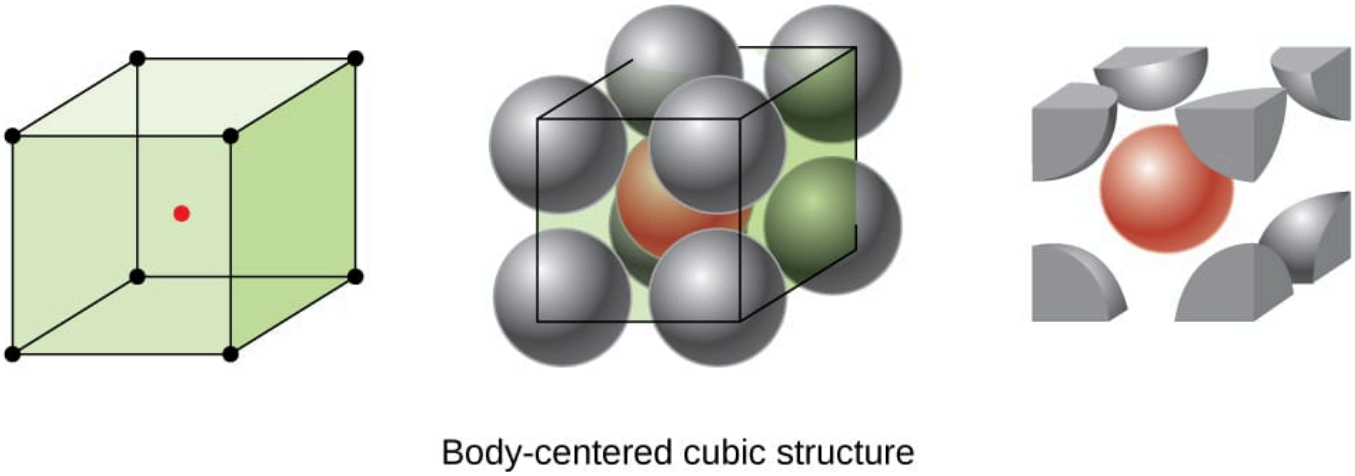


Figure 4.2.2.2.6: In a body-centered cubic structure, atoms in a specific layer do not touch each other. Each atom touches four atoms in the layer above it and four atoms in the layer below it.

Three images are shown. The first image shows a cube with black dots at each corner and a red dot in the center while the second image is composed of eight spheres that are stacked together to form a cube with one sphere in the center of the cube and dots at the center of each corner sphere connected to form a cube shape. The name under this image reads “Body-centered cubic structure.” The third image is the same as the second, but only shows the portions of the spheres that lie inside the cube shape.

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.)

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 4.2.2.2.7. 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.

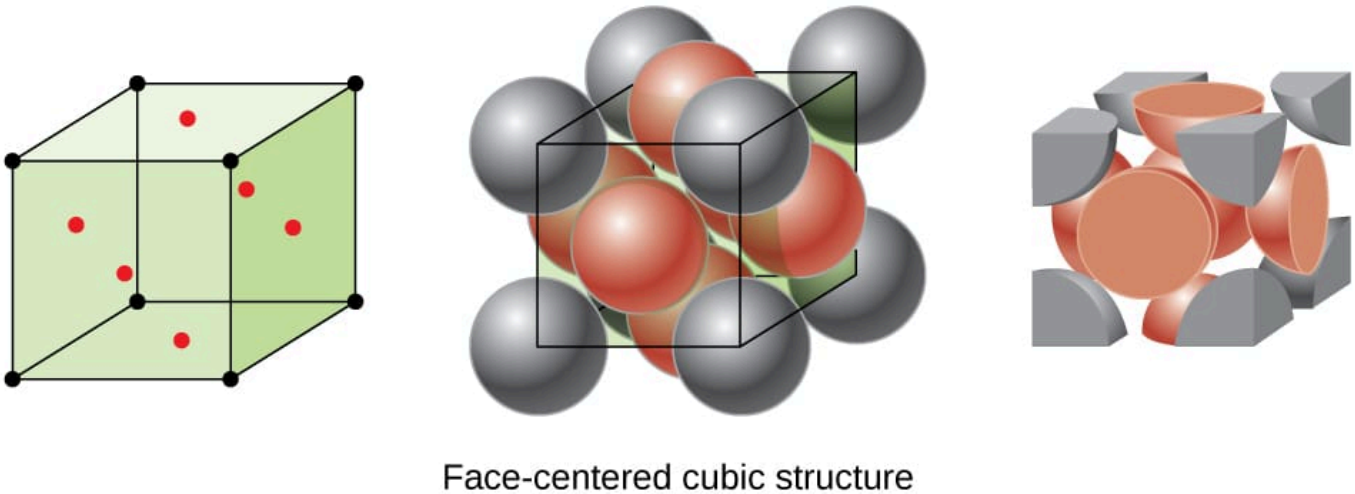


Figure 4.2.2.2.7:A face-centered cubic solid has atoms at the corners and, as the name implies, at the centers of the faces of its unit cells.

Three images are shown. The first image shows a cube with black dots at each corner and red dots in the center of each face of the cube while the second image is composed of eight spheres that are stacked together to form a cube with six more spheres, one located on each face of the structure. Dots at the center of each corner sphere are connected to form a cube shape. The name under this image reads “Face-centered cubic structure.” The third image is the same as the second, but only shows the portions of the spheres that lie inside the cube shape.

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 4.2.2.2.8.

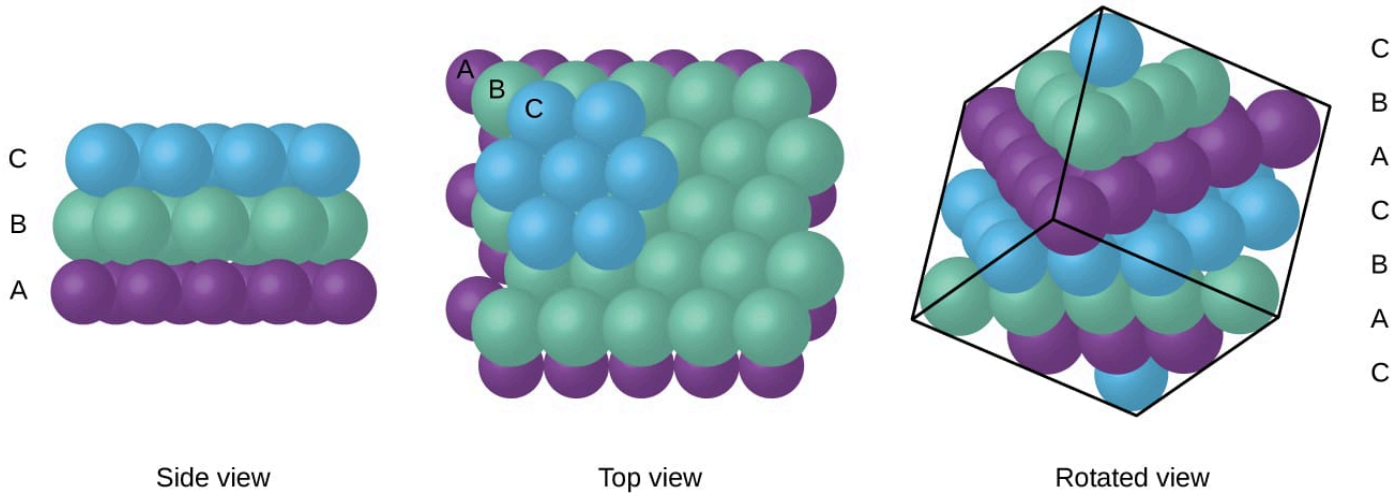


Figure 4.2.2.2.8: A CCP arrangement consists of three repeating layers (ABCABC...) of hexagonally arranged atoms. Atoms in a CCP structure have a coordination number of 12 because they contact six atoms in their layer, plus three atoms in the layer above and three atoms in the layer below. By rotating 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.

Three images are shown. In the first image, a side view shows a layer of blue spheres, labeled “C” stacked on top of, and sitting in between the gaps in a second layer that is composed of green spheres, labeled “B,” which are sitting atop a purple layer of spheres labeled “A.” A label below this image reads “Side view.” The second image shows a top view of the same layers of spheres, where the top layer is “C,” the second layer is “B” and the lowest layer is “C.” This image is labeled “Top view” and written under this is the phrase “Cubic closest packed structure.” The third image shows an upper view of the side of a cube composed of two sets of the repeating layers shown in the other images. The layers are arranged “C, B, A, C, B, A, C” and the phrase written under this image reads “Rotated view.”

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 4.2.2.2.9. 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$\cdots$). 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$\cdots$). 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.

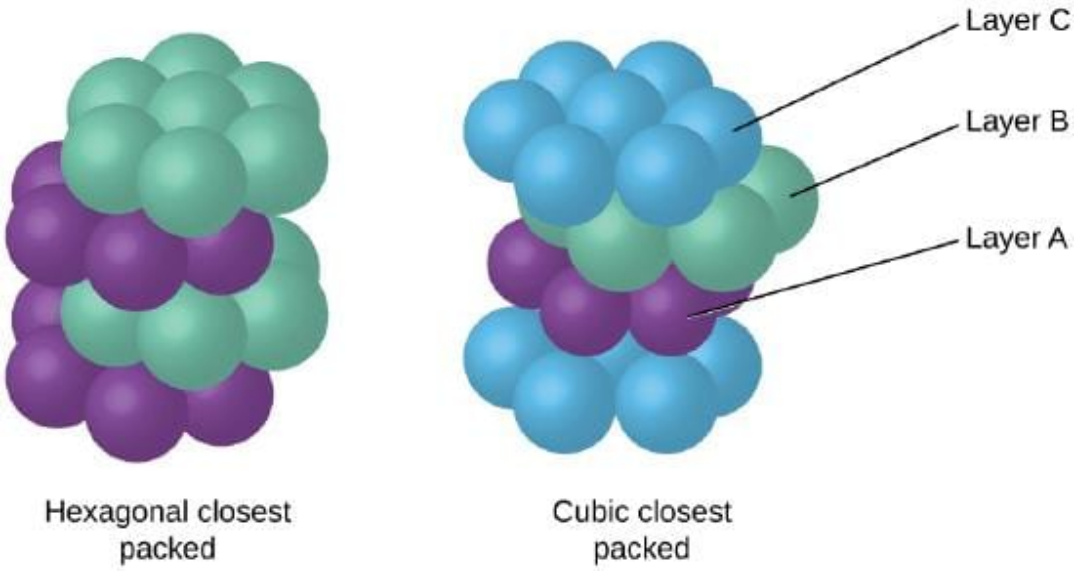


Figure 4.2.2.2.9: In both types of closest packing, atoms are packed as compactly as possible. Hexagonal closest packing consists of two alternating layers (ABABAB...). Cubic closest packing consists of three alternating layers (ABCABCABC...).

Two images are shown. The first image, labeled “Hexagonal closest packed,” shows seven green spheres arranged in a circular sheet lying atop another sheet that is the same except the spheres are purple. The second sheet is offset just a bit so that the spheres of the top sheet lie in the grooves of the second sheet. Two more alternating green and purple layers of spheres lie below the first pair. The second image shows seven blue spheres, labeled “Layer C,” arranged in a circular sheet laying atop another sheet, labeled “Layer B” that is the same except the spheres are green. The second sheet is offset just a bit so that the spheres of the top sheet lie in the grooves of the second sheet. Two more alternating purple and then blue layers of spheres lie below the first pair. The purple layer is labeled “Layer A” and the phrase written below this image reads “Cubic closest packed.”

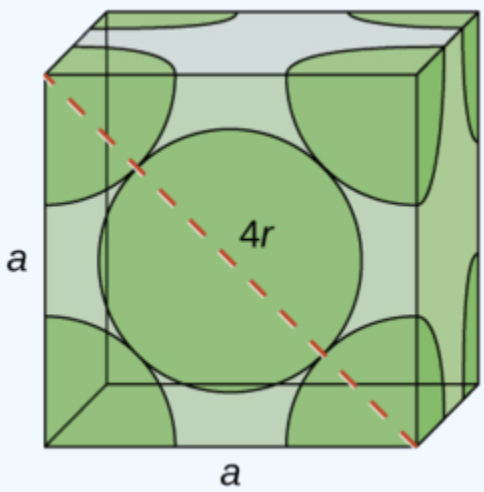
Example 4.2.2.2.2: Calculating Atomic Radius and Density for Metals (Part 2)

Calcium crystallizes in a face-centered cubic structure. The edge length of its unit cell is 558.8 pm.

a. What is the atomic radius of Ca in this structure?
b. Calculate the density of Ca.

Solution

(a) 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 = 4*r*).



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

$$r = \sqrt{\frac{(558.8\text{ pm})^2 + (558.5\text{ pm})^2}{16}} = 197.6\text{ pmg for a Ca radius.}$$

(b) Density is given by $\text{density} = \frac{\text{mass}}{\text{volume}}$. 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 ($8 \times \frac{1}{8} = 1$atom) and one-half of an atom on each of the six faces $6 \times \frac{1}{2} = 3$ 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 4.2.2.2.2

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 available at the end of this section.

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 4.2.2.2.10. The axes are defined as being the lengths between points in the space lattice. Consequently, unit cell axes join points with identical environments.

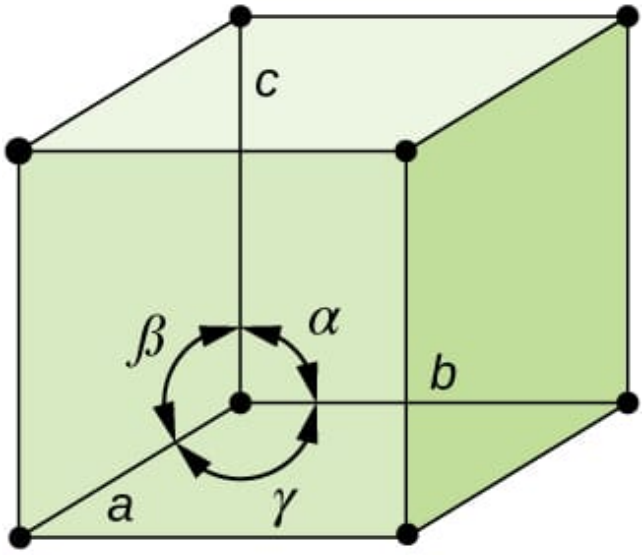


Figure 4.2.2.2.10: A unit cell is defined by the lengths of its three axes (a, b, and c) and the angles (α, β, and γ) between the axes.

A cube is shown where each corner has a black dot drawn on it. A circle in the bottom of the cube is composed of three double-ended arrows. The left top of this circle is labeled “alpha,” the top right is labeled “beta” and the bottom is labeled “gamma.” The bottom left corner of the cube is labeled “a” while the bottom of the back face is labeled “b” and the top, back, left corner is labeled “c.”

There are seven different lattice systems, some of which have more than one type of lattice, for a total of fourteen different unit cells, which have the shapes shown in Figure 4.2.2.2.11.

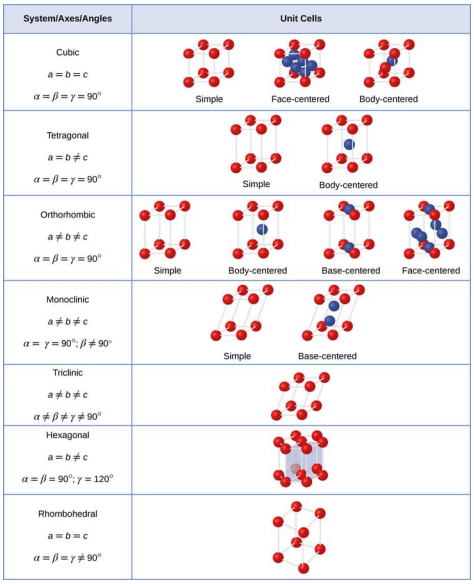


Figure 4.2.2.2.11:There are seven different lattice systems and 14 different unit cells.

A table is composed of two columns and eight rows. The header row reads “System / Axes / Angles” and “Unit Cells .” The first column reads “Cubic, a equals b equals c, alpha equals beta equals gamma equals 90 degrees,” “Tetragonal, a equals b does not equal c, alpha equals beta equals gamma equals 90 degrees,” “Orthorhombic, a does not equal b does not equal c, alpha equals beta equals gamma equals 90 degrees,” “Monoclinic, a does not equal b does not equal c, alpha equals gamma equals 90 degrees, beta does not equal 90 degrees,” “Triclinic, a does not equal b does not equal c, alpha does not equal beta does not equal gamma does not equal 90 degrees,” “Hexagonal, a equals b does not equal c, alpha equals beta equals 90 degrees, gamma equals 120 degrees,” “Rhombohedral, a equals b equals c, alpha equals beta equals gamma does not equal 90 degrees.” The second column is composed of diagrams. The first set of diagrams in the first cell show a cube with spheres at each corner labeled “Simple,” a cube with spheres in each corner and on each face labeled “Face-centered” and a cube with spheres in each corner and one in the center labeled “Body-centered.” The second set of diagrams in the second cell show a vertical rectangle with spheres at each corner labeled “Simple” and a vertical rectangle with spheres in each corner and one in the center labeled “Body-centered.” The third set of diagrams in the third cell show a vertical rectangle with spheres at each corner labeled “Simple,” a vertical rectangle with spheres in each corner and one in the center labeled “Body-centered,” a vertical rectangle with spheres in each corner and one on the top and bottom faces labeled “Base-centered,” and a vertical rectangle with spheres in each corner and one on each face labeled “Face-centered.” The fourth set of diagrams in the fourth cell show a vertical rectangle with spheres at each corner that is slanted to one side labeled “Simple” and a vertical rectangle with spheres in each corner that is slanted to one side and has two spheres in the center is labeled “Body-centered.” The fifth diagrams in the fifth cell show a cube that is slanted with spheres at each corner while the sixth diagram in the sixth cell shows a pair of hexagonal rings that are connected together to form a six-sided shape with spheres at each corner. The seventh diagram in the seventh cell shows a rectangle that is slanted with spheres at each corner.

The Structures of Ionic Crystals

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.

In simple ionic structures, we usually find the anions, which are normally larger than the cations, arranged in a closest-packed array. (As seen previously, additional electrons attracted to the same nucleus make anions larger and fewer electrons attracted to the same nucleus make cations smaller when compared to the atoms from which they are formed.) The smaller cations commonly occupy one of two types of holes (or interstices) remaining between the anions. The smaller of the holes 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 4.2.2.2.12 illustrates both of these types of holes.

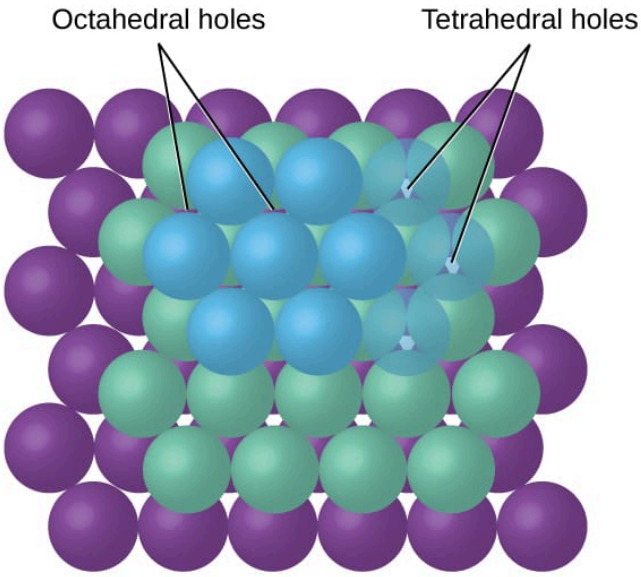


Figure 4.2.2.2.12: Cations may occupy two types of holes between anions: octahedral holes or tetrahedral holes.

An image shows a top-view of a layer of blue spheres arranged in a sheet lying atop another sheet that is the same except the spheres are green. The second sheet is offset just a bit so that the spheres of the top sheet lie in the grooves of the second sheet. A third sheet composed of purple spheres lies at the bottom. The spaces created between the spheres in each layer are labeled “Octahedral holes” and “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 4.2.2.2.13. 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.

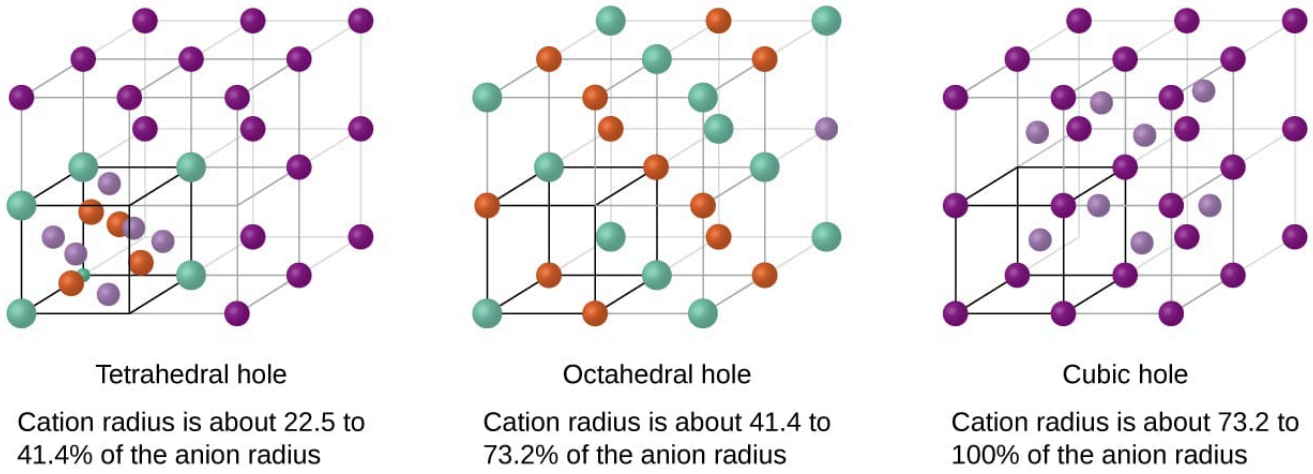


Figure 4.2.2.2.13:A cation’s size and the shape of the hole occupied by the compound are directly related.

A diagram of three images is shown. In the first image, eight stacked cubes, with purple spheres at each corner, that make up one large cube are shown. The bottom left cube is different. It has green spheres at each corner and has four orange and six light purple spheres located on the faces of the cube. Labels below this structure read “Tetrahedral hole” and “Cation radius is about 22.5 to 41.4 percent of the anion radius. In the second image, eight stacked cubes, with alternating orange and green spheres at each corner, make up one large cube that is shown. The bottom left cube has darker lines that connect the spheres together. Labels below this structure read “Octahedral hole” and “Cation radius is about 41.4 to 73.2 percent of the anion radius. In the third image, eight stacked cubes, with purple spheres at each corner and light purple spheres on their interior faces, make up one large cube that is shown. Labels below this structure read “Cubic hole” and “Cation radius is about 73.2 to 100 percent of the anion radius.”

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.

Example 4.2.2.2.3: 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.

Exercise 4.2.2.2.3: 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 available at the end of this section.

The ratio of octahedral holes to anions in either an HCP or CCP structure is 1:1. 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.

Example 4.2.2.2.4: 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 $\mathrm{Al}_{2/3}\mathrm{O}$. The simplest whole number ratio is 2:3, so the formula is Al_2O_3.

Exercise 4.2.2.2.4

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 available at the end of this section.

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.

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.

Unit Cells of Ionic Compounds

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 4.2.2.2.14) 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 4.2.2.2.14: 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.

Three images are shown. The first image shows a cube with black dots at each corner and a red dot in the center. This cube is stacked with seven others that are not colored to form a larger cube. The second image is composed of eight spheres that are grouped together to form a cube with one smaller sphere in the center. The name under this image reads “Body-centered simple cubic structure.” The third image shows five horizontal layers of purple spheres with layers of smaller green spheres in between.

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.

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 4.2.2.2.15. 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 4.2.2.2.15: 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.

Three images are shown. The first image shows a cube with black dots at each corner and a red dot in the center. This cube is stacked with seven others that are not colored to form a larger cube. The second image is composed of eight spheres that are grouped together to form a cube with one much larger sphere in the center. The name under this image reads “Body-centered simple cubic structure.” The third image shows seven horizontal layers of alternating purple and green spheres that are slightly offset with one another and form a large cube.

The cubic form of zinc sulfide, zinc blende, also crystallizes in an FCC unit cell, as illustrated in Figure 4.2.2.2.16. 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.

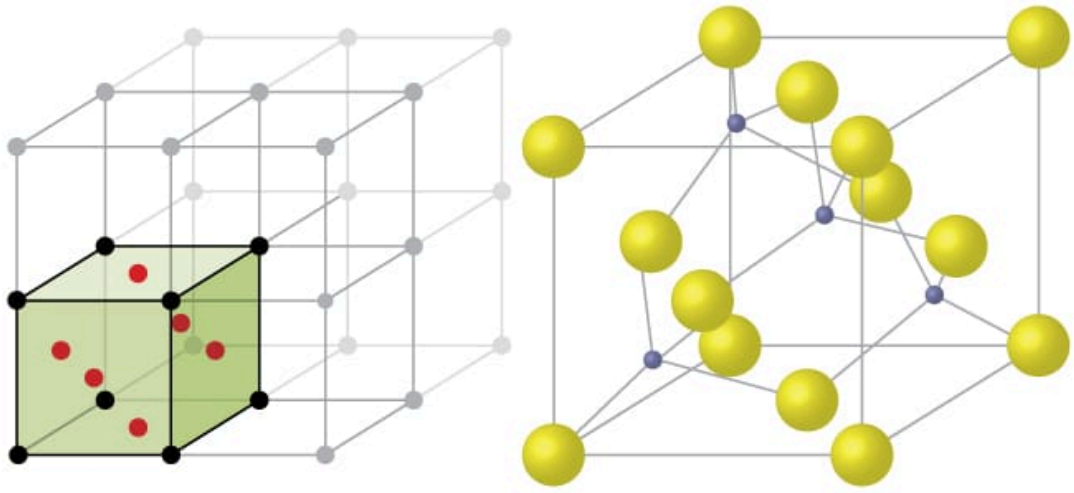


Figure 4.2.2.2.16: ZnS, zinc sulfide (or zinc blende) forms an FCC unit cell with sulfide ions at the lattice points and much smaller zinc ions occupying half of the tetrahedral holes in the structure.

Two images are shown. The first image shows a cube with black dots at each corner and a red dot in the center of each face of the cube. This cube is stacked with seven others that are not colored to form a larger cube. The second image is composed of eight spheres that form the corners of a cube with six other spheres located in the face of the cube. The spheres are connected to one another by lines. The name under this image reads “Z n S, face-centered unit cell.”

A calcium fluoride unit cell, like that shown in Figure 4.2.2.2.17, 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 4.2.2.2.17 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.

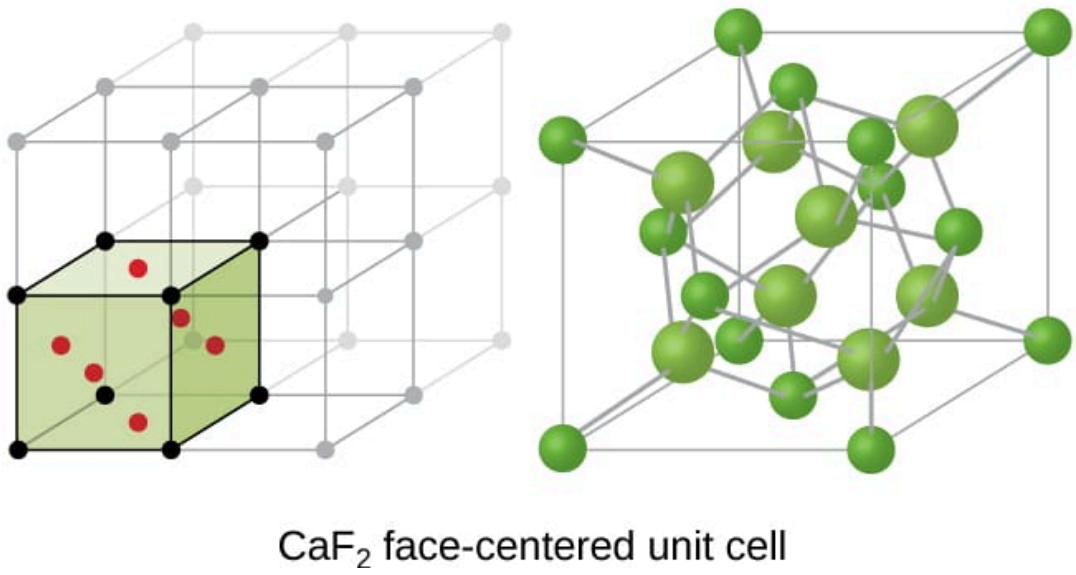


Figure 4.2.2.2.17: Calcium fluoride, CaF_2, forms an FCC unit cell with calcium ions (green) at the lattice points and fluoride ions (red) occupying all of the tetrahedral sites between them.

Two images are shown. The first image shows a cube with black dots at each corner and a red dot in the center of each face of the cube. This cube is stacked with seven others that are not colored to form a larger cube. The second image is composed of eight small green spheres that form the corners of a cube with six other small green spheres located in the faces of the cube. Eight larger green spheres are spaced inside the cube and all of the spheres are connect to one another by lines. The name under this image reads “C a F, subscript 2, face-centered unit cell.”

Calculation of Ionic Radii

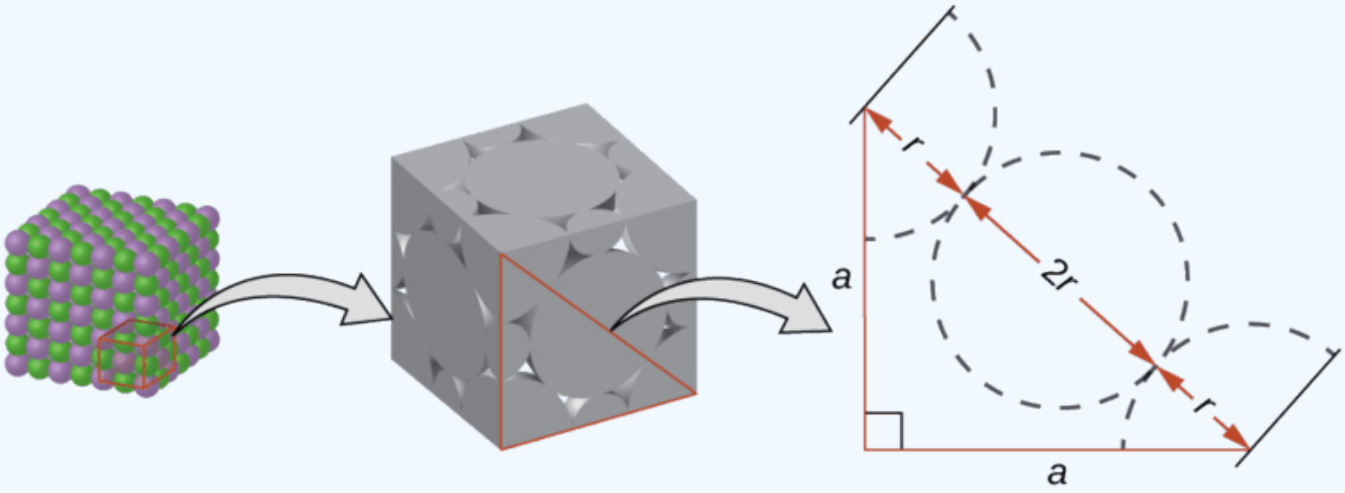
If we know the edge length of a unit cell of an ionic compound and the position of the ions in the cell, we can calculate ionic radii for the ions in the compound if we make assumptions about individual ionic shapes and contacts.

Example 4.2.2.2.5: 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:

$$r = \sqrt{\frac{(0.514\ \text{nm})^2 + (0.514\ \text{nm})^2}{16}} = 0.182\ \text{nm}\ (1.82\ \text{Å})\ \text{for a}\ \text{Cl}^-\ \text{radius.}$$

Exercise 4.2.2.2.6

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 available at the end of this section.

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.

X-Ray Crystallography

The size of the unit cell and the arrangement of atoms in a crystal may be determined from measurements of the *diffraction* of X-rays by the crystal, termed X-ray crystallography. Diffraction is the change in the direction of travel experienced by an electromagnetic wave when it encounters a physical barrier whose dimensions are comparable to those of the wavelength of the light. X-rays are electromagnetic radiation with wavelengths about as long as the distance between neighboring atoms in crystals (on the order of a few Å).

When a beam of monochromatic X-rays strikes a crystal, its rays are scattered in all directions by the atoms within the crystal. When scattered waves traveling in the same direction encounter one another, they undergo *interference*, a process by which the waves combine to yield either an increase or a decrease in amplitude (intensity) depending upon the extent to which the

combining waves' maxima are separated (Figure 4.2.2.2.18).

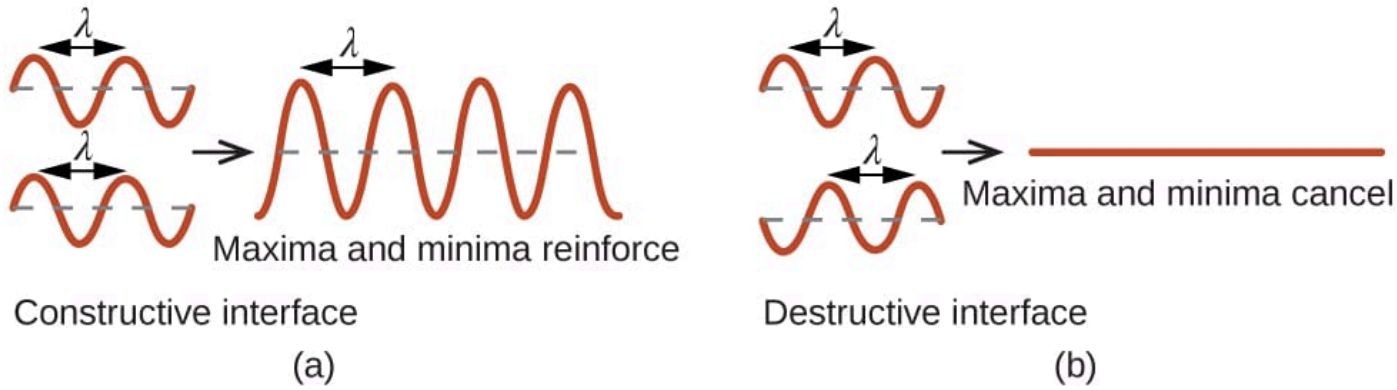


Figure 4.2.2.2.18: Light waves occupying the same space experience interference, combining to yield waves of greater (a) or lesser (b) intensity, depending upon the separation of their maxima and minima.

A pair of images is shown that has four sections. In the first section, two sinusoidal waves are shown, one drawn above the other, and a section from the top of one curve to the top of the next curve is labeled "lambda." The curves align with one another. The phrase below this reads "Constructive interference." A right facing arrow leads from the first section to the second, which shows one larger sinusoidal curve that has higher and lower peaks and troughs. A section from the top of one curve to the top of the next curve is labeled "lambda" and the phrase below this reads "Maxima and minima reinforce." In the second section, two sinusoidal waves are shown, one drawn above the other, and a section from the top of one curve to the top of the next curve is labeled "lambda." The curves do not align with one another. The phrase below this reads "Destructive interference." A right facing arrow leads from the first section to the second, which shows one flat line. The phrase below this reads "Maxima and minima cancel."

When X-rays of a certain wavelength, λ, are scattered by atoms in adjacent crystal planes separated by a distance, d, they may undergo constructive interference when the difference between the distances traveled by the two waves prior to their combination is an integer factor, n, of the wavelength. This condition is satisfied when the angle of the diffracted beam, θ, is related to the wavelength and interatomic distance by the equation:

$$n\lambda = 2d\sin\theta \tag{4.2.2.2.1}$$

This relation is known as the Bragg equation in honor of W. H. Bragg, the English physicist who first explained this phenomenon. Figure 4.2.2.2.18 illustrates two examples of diffracted waves from the same two crystal planes. The figure on the left depicts waves diffracted at the Bragg angle, resulting in constructive interference, while that on the right shows diffraction and a different angle that does not satisfy the Bragg condition, resulting in destructive interference.

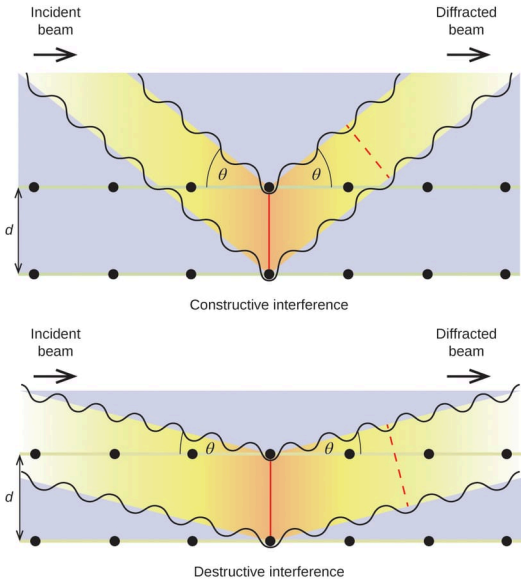


Figure 4.2.2.2.19: The diffraction of X-rays scattered by the atoms within a crystal permits the determination of the distance between the atoms. The top image depicts constructive interference between two scattered waves and a resultant diffracted wave of high intensity. The bottom image depicts destructive interference and a low intensity diffracted wave.

Two similar figures are shown. The first figure, labeled “Constructive Interference,” shows two horizontal rows of seven black dots with a line passing through them. The fourth dots of each row have a vertical line connecting them. The distance between these rows is labeled “d.” A beam labeled “Incident beam” descends at an angle labeled “theta” until it hits the line connecting the fourth dots, after which a diffracted beam ascends at the same angle “theta.” A dotted line is drawn across the diffracted beam. The second figure, labeled “Destructive interference,” is very similar, except that the angles “theta” are far more acute, making the slopes of the beams more shallow.

An X-ray diffractometer, such as the one illustrated in Figure 4.2.2.2.20, may be used to measure the angles at which X-rays are diffracted when interacting with a crystal as described earlier. From such measurements, the Bragg equation may be used to compute distances between atoms as demonstrated in the following example exercise.

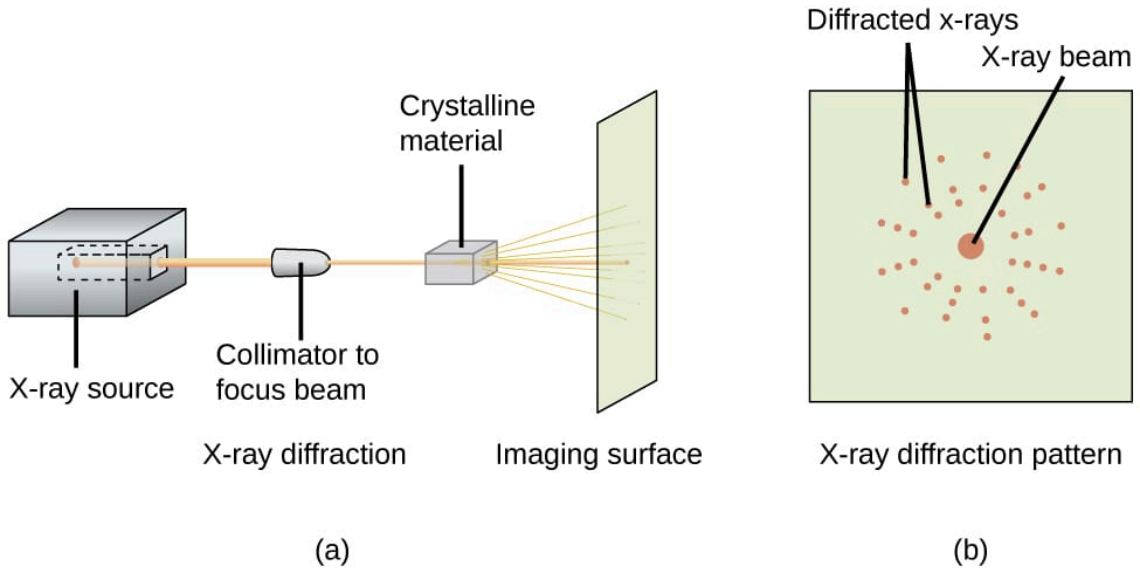


Figure 4.2.2.2.20: (a) In a diffractometer, a beam of X-rays strikes a crystalline material, producing (b) an X-ray diffraction pattern that can be analyzed to determine the crystal structure.

A diagram, labeled “a” shows a cube on the left with a channel bored into its right side labeled “X dash ray source.” A beam is leaving from this channel and traveling in a horizontal line toward an oval-shaped, short tube, labeled “Collimator to focus beam” and “X dash ray diffraction,” where it passes through a cube labeled “Crystalline material” and scatters onto a vertical sheet labeled “Imaging surface.” A second diagram, labeled “b,” shows a square sheet with a large dot in the center labeled “X dash ray beam,” that is surrounded by smaller dots arranged in rings and labeled “Diffracted X dash rays.”

Example 4.2.2.2.6: Using the Bragg Equation

In a diffractometer, X-rays with a wavelength of 0.1315 nm were used to produce a diffraction pattern for copper. The first order diffraction (n = 1) occurred at an angle θ = 25.25°. Determine the spacing between the diffracting planes in copper.

Solution

The distance between the planes is found by solving the Bragg equation (Equation 4.2.2.2.1) for d.

This gives

$$d = \frac{n\lambda}{2\sin\theta} = \frac{1(0.1315\text{ nm})}{2\sin(25.25°)} = 0.154\text{ nm}$$

Exercise 4.2.2.2.6

A crystal with spacing between planes equal to 0.394 nm diffracts X-rays with a wavelength of 0.147 nm. What is the angle for the first order diffraction?

Answer available at the end of this section.

X-ray Crystallographer Rosalind Franklin

The discovery of the structure of DNA in 1953 by Francis Crick and James Watson is one of the great achievements in the history of science. They were awarded the 1962 Nobel Prize in Physiology or Medicine, along with Maurice Wilkins, who provided experimental proof of DNA's structure. British chemist Rosalind Franklin made invaluable contributions to this monumental achievement through her work in measuring X-ray diffraction images of DNA. Early in her career, Franklin's research on the structure of coals proved helpful to the British war effort. After shifting her focus to biological systems in the early 1950s, Franklin and doctoral student Raymond Gosling discovered that DNA consists of two forms: a long, thin fiber formed when wet (type "B") and a short, wide fiber formed when dried (type "A"). Her X-ray diffraction images of DNA provided the crucial information that allowed Watson and Crick to confirm that DNA forms a double helix, and to determine details of its size and structure. Franklin also conducted pioneering research on viruses and the RNA that contains their genetic information, uncovering new information that radically changed the body of knowledge in the field. After developing ovarian cancer, Franklin continued to work until her death in 1958 at age 37. Among many posthumous recognitions of her work, the Chicago Medical School of Finch University of Health Sciences changed its name to the Rosalind Franklin University of Medicine and Science in 2004, and adopted an image of her famous X-ray diffraction image of DNA as its official university logo.

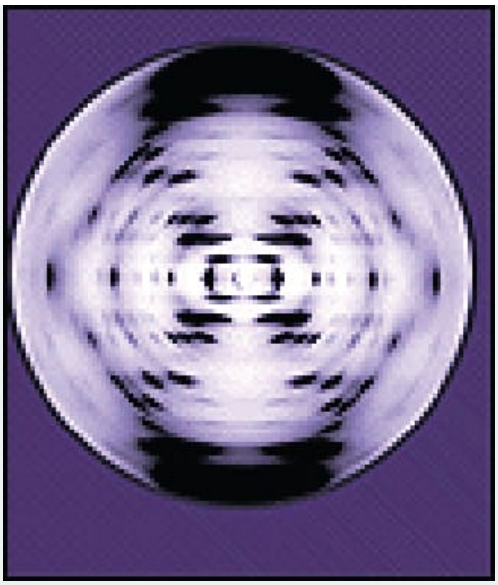


Figure 4.2.2.2.7.This illustration shows an X-ray diffraction image similar to the one Franklin found in her research. (credit: National Institutes of Health)

Key Concepts and 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. 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. The type of structure and dimensions of the unit cell can be determined by X-ray diffraction measurements.

Glossary

body-centered cubic (BCC) solid
: crystalline structure that has a cubic unit cell with lattice points at the corners and in the center of the cell

body-centered cubic unit cell
: simplest repeating unit of a body-centered cubic crystal; it is a cube containing lattice points at each corner and in the center of the cube

Bragg equation
: equation that relates the angles at which X-rays are diffracted by the atoms within a crystal

coordination number
: number of atoms closest to any given atom in a crystal or to the central metal atom in a complex

cubic closest packing (CCP)
: crystalline structure in which planes of closely packed atoms or ions are stacked as a series of three alternating layers of different relative orientations (ABC)

diffraction
: redirection of electromagnetic radiation that occurs when it encounters a physical barrier of appropriate dimensions

face-centered cubic (FCC) solid
: crystalline structure consisting of a cubic unit cell with lattice points on the corners and in the center of each face

face-centered cubic unit cell
simplest repeating unit of a face-centered cubic crystal; it is a cube containing lattice points at each corner and in the center of each face

hexagonal closest packing (HCP)
crystalline structure in which close packed layers of atoms or ions are stacked as a series of two alternating layers of different relative orientations (AB)

hole
(also, interstice) space between atoms within a crystal

isomorphous
possessing the same crystalline structure

octahedral hole
open space in a crystal at the center of six particles located at the corners of an octahedron

simple cubic unit cell
(also, primitive cubic unit cell) unit cell in the simple cubic structure

simple cubic structure
crystalline structure with a cubic unit cell with lattice points only at the corners

space lattice
all points within a crystal that have identical environments

tetrahedral hole
tetrahedral space formed by four atoms or ions in a crystal

unit cell
smallest portion of a space lattice that is repeated in three dimensions to form the entire lattice

X-ray crystallography
experimental technique for determining distances between atoms in a crystal by measuring the angles at which X-rays are diffracted when passing through the crystal

Paul Flowers (University of North Carolina - Pembroke), Klaus Theopold (University of Delaware) and Richard Langley (Stephen F. Austin State University) with contributing authors. Textbook content produced by OpenStax College is licensed under a Creative Commons Attribution License 4.0 license. Download for free at http://cnx.org/contents/85abf193-2bd...a7ac8df6@9.110).

Answers

Exercise 4.2.2.2.1

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 4.2.2.2.2

144 pm

10.5 g/cm^3

Exercise 4.2.2.2.3**: Lithium selenide**

Li_2Se

Exercise 4.2.2.2.4

TiO_2

Exercise 4.2.2.2.6

The radius of the potassium ion is 1.33 Å.

Exercise 4.2.2.2.6

21.9°

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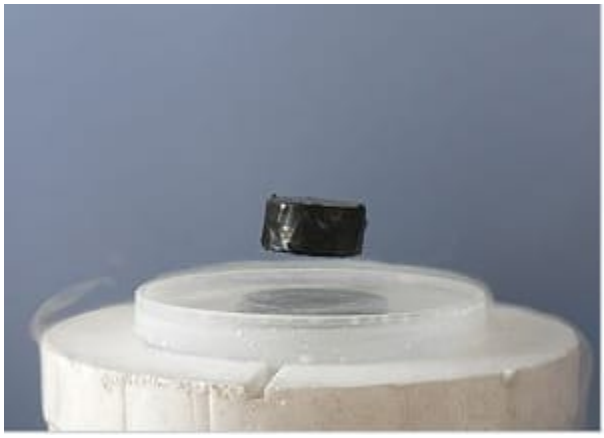
4.2.3: Superconductivity

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4.2.3.1: Superconductors

Superconductivity refers to the flow of electrical current in a material with zero resistance. Such materials are very important for use in electromagnets, e.g., in magnetic resonance imaging (MRI) and nuclear magnetic resonance (NMR) machines, because once the current starts flowing in the coils of these magnets it doesn't stop. Magnetic levitation using superconductors - which, below a critical field strength, are perfect diamagnets that are not penetrated by magnetic flux lines - is also potentially relevant to future technologies such as magnetically levitated trains.

The phenomenon of superconductivity, first discovered in Hg metal in 1911 by Onnes, continues to be only partially understood. It is of great interest to physicists as a macroscopic quantum phenomenon, and to chemists and materials scientists who try to make better superconductors (especially those that superconduct at higher temperatures) and devices derived from them, such as superconducting quantum interference devices (SQUIDs), which are extremely sensitive magnetometers.

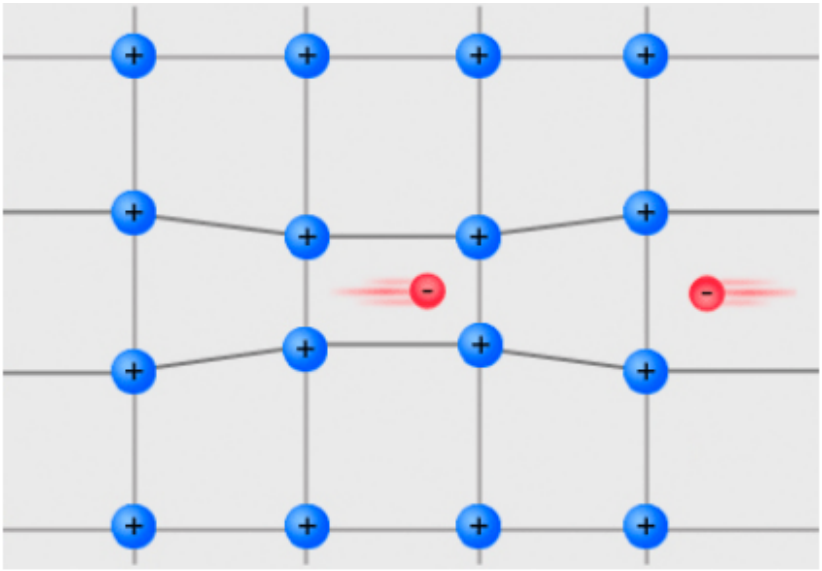


A magnet levitating above a high-temperature superconductor, cooled with liquid nitrogen. Persistent electric current flows on the surface of the superconductor, excluding the magnetic field of the magnet. This current effectively forms an electromagnet that repels the magnet.

Spin pairing and zero resistance

The transition from the metallic to the superconducting state is related to the quantum phenomena of Bose-Einstein condensation and superfluidity. Individual electrons have spin = 1/2, and as such are fermions (particles with half-integer spin). Because of the Pauli exclusion principle, no more than two fermions can occupy the same quantum state (such as an orbital in a molecule or a solid). The familiar consequence of this rule is the aufbau filling of orbitals with spin-paired electrons in each energy level. In contrast, particles with integer spins - which are called bosons - do not have this restriction, and any number of bosons can occupy the same quantized energy level.

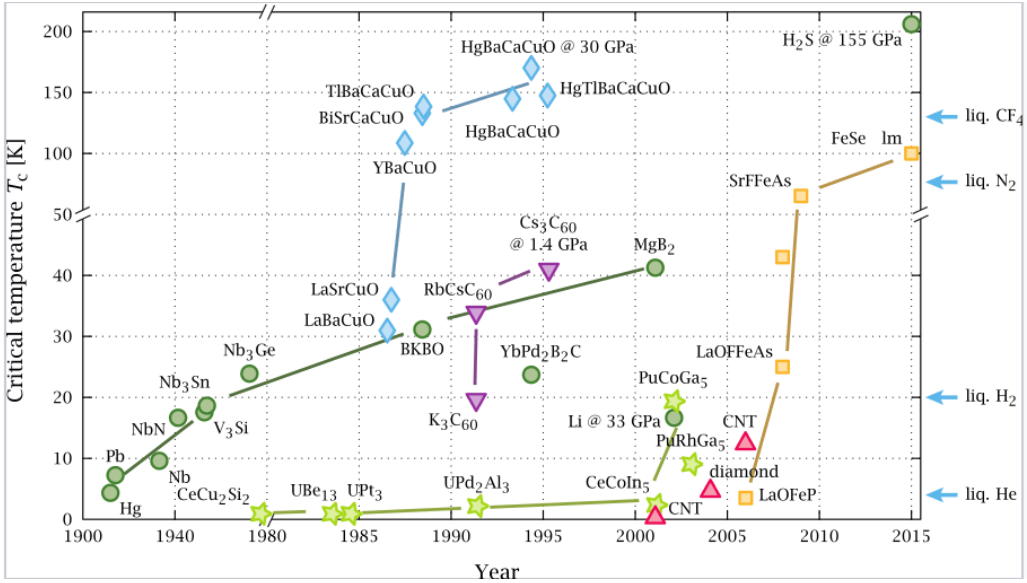
Superconductivity occurs when electrons spin pair into so-called Cooper pairs, which can travel through the lattice together. The electrons in a Cooper pair, although spin-paired, have a long-distance relationship: the spatial extent of a Cooper pair is a few nanometers in cuprate superconductors, and up to one micron in low T_c superconductors such as aluminum. Because its overall spin angular momentum is zero, a Cooper pair is a boson. When the temperature is low enough, the Cooper pairs "condense" into the lowest energy level. The second lowest energy level - which is typically a few meV above the ground state - is not accessible to them as long as the energy gap is larger than the thermal energy, kT. The scattering of electrons by the lattice then becomes forbidden by energy conservation because scattering dissipates energy, and the Cooper pairs cannot change their energy state. Thus the resistance (which arises from scattering, as we learned in Ch. 6) drops abruptly to zero below T_c. However, the Cooper pairs can be broken apart when they move fast, and thus superconductors turn back into normal metals (even below T_c) above some critical current density j_c. This phenomenon is also related to the critical magnetic field, H_c, that quenches superconductivity.



A trampoline for electrons

What causes electrons, which repel each other because of their negative charge, to pair up and travel together in superconductors? The mechanism - which must involve some kind of attractive interaction between electrons - is well understood for "conventional" superconductors which have relatively low transition temperatures, but is not yet known with certainty for high temperature oxide superconductors. In conventional, or BCS superconductors, the spin pairing is mediated by the lattice as shown in the figure at the left. A strong electron-lattice interaction causes a distortion in the lattice as an electron moves through. This elastic deformation is felt as an attractive force by a second electron moving in the opposite direction. This can be thought of as analogous to the interaction of two people jumping on a trampoline. The weight of the first person on the trampoline creates a "well" that attracts the second one, and they tend to move together (even if they don't like each other). Strange as this interaction seems, it is supported experimentally by isotope effects on T_c and by quantitative predictions of T_c values in conventional superconductors.

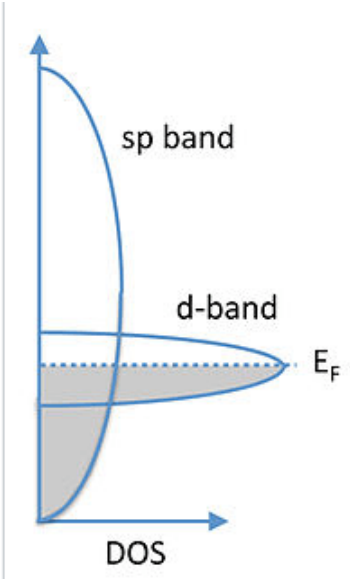
Bad metals make good superconductors. All superconductors are "normal" metals - with finite electrical resistance - above their critical transition temperature, T_c. If you ask where in the periodic table one might look for superconductors, the answer is surprising. The most conductive metals (Ag, Au, Cu, Cs, etc.) make the worst superconductors, i.e., they have the lowest superconducting transition temperatures, in many cases below 0.01 K. Conversely "bad" metals, such as niobium alloys, certain copper oxides, $K_xBa_{1-x}BiO_3$, MgB_2, FeSe, and alkali salts of C_{60}^{n-} anions, can have relatively high transition temperatures.



Timeline of superconducting materials, showing T_c vs. year of discovery.

We observe that most good superconductors appear in composition space very **near a metal-insulator transition**. In terms of our microscopic picture, orbital overlap in superconductors is poor, just barely enough to make them act as metals ($\Delta \approx U$) above T_c. In the normal state, superconductors with high T_c - which can be as high as 150 K - are typically "bad" metals. An important characteristic of such metals is that the **mean free path** of electrons (in the normal state, above T_c) is on the order of the lattice spacing, i.e., **only a few Å**. In contrast, we learned in Ch. 6 that good metals such as Au, Ag, and Cu have electron mean free paths that are two orders of magnitude longer (ca. 40 nm). In a bad metal, the electron "feels" the lattice rather strongly, whereas in a good metal, the electrons are insensitive to small changes in the distance between metals atoms.

What does the band picture look like for a bad metal? The key point is that because orbital overlap is poor, the metal has a **high density of states** at the Fermi level. This is a universal property of high temperature superconductors and provides a clue of where to look for new and improved superconducting materials. Recall that transition elements in the middle of the 3d series (Cr, Fe, Co, Ni) were magnetic because of poor orbital overlap and weak d-d bonding. The elements below these - especially Nb, Ta, and W - have just barely enough d-d orbital overlap to be on the metallic side of the metal-insulator transition and to be "bad" metals. Carbides and nitrides of these elements are typically superconducting, with the carbon and nitrogen atoms serving to adjust the valence electron density, as illustrated in the table below.



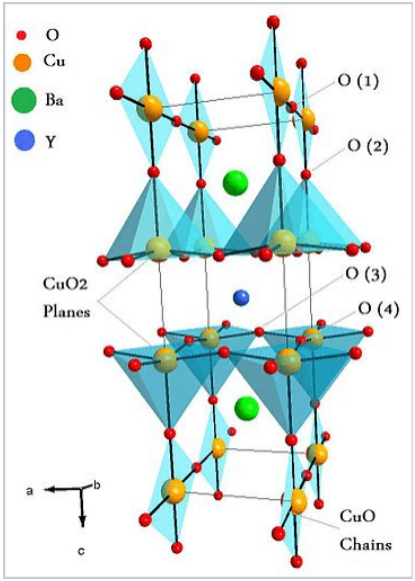
Generic E vs. DOS for a bad metal.

Compound	NbC	Mo_2N	TaC	VN	NbN	TaN	Nb_3Ge
T_c (K)	11.1	5.0	9.7	7.5	15.2	17.8	22.3

High T_c superconductors

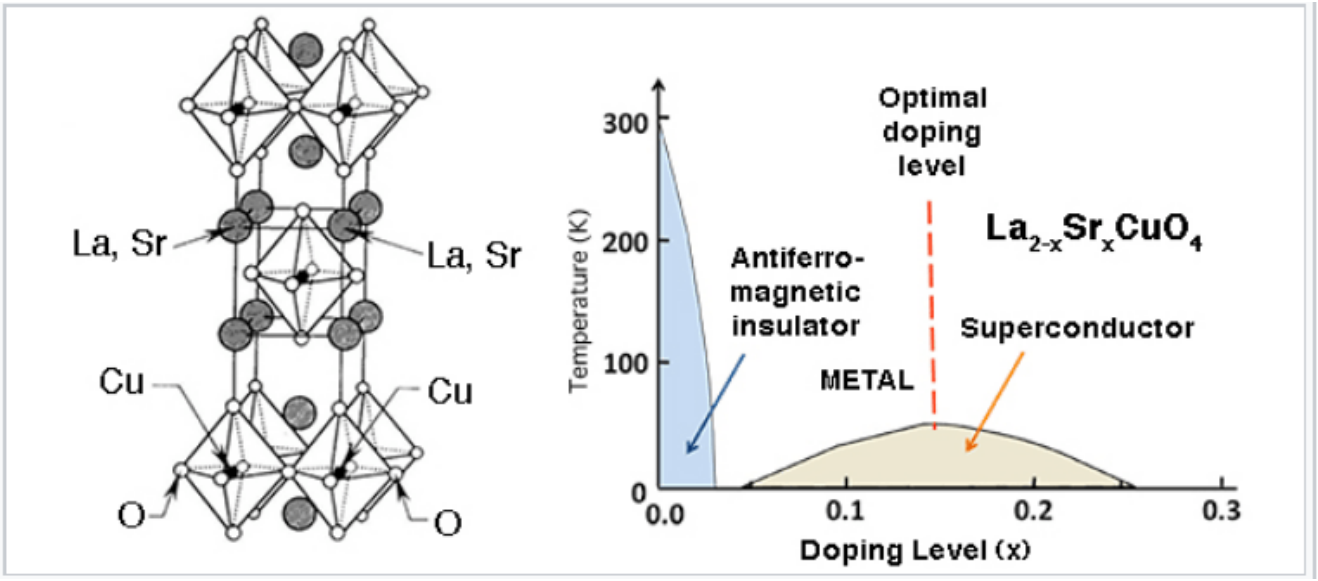
In addition to having weak orbital overlap in the metallic state - which results in a high DOS at E_F - high temperature superconductors also typically contain elements in mixed oxidation states (for example, $Cu^{2+/3+}$ or $Bi^{3+/5+}$) that are close in energy to the O^{2-}/O^- couple in the lattice. At ambient pressure, cuprate superconductors have the highest known T_c values, ranging between about 35 and 150 K. The crystal structures of these materials are almost all variants of the perovskite lattice, as shown at the right for the 1-2-3 superconductor $YBa_2Cu_3O_{7-\delta}$. An ideal perovskite lattice would have formula $ABO_3 = A_3B_3O_9$. In $YBa_2Cu_3O_{7-\delta}$, Y and Ba occupy the A cation sites, Cu occupies the B sites, and two of the nine O atoms are missing.

The $YBa_2Cu_3O_{7-\delta}$ lattice consists of mixed-valent copper(II/III) oxide sheets capped by oxygen atoms to form CuO_5 square pyramids. These sheets encapsulate the Y^{3+} cations. Copper(II) oxide ribbons that share the apical oxygen atoms of the square pyramids run in one direction through the structure. In $YBa_2Cu_3O_{7-\delta}$ and related materials, one component of the structure (here the Cu-O ribbons) acts as a **charge reservoir** to control the doping of the planar CuO_2 sheets, which are the elements of the structure that carry the supercurrent. Cuprate superconductors with Bi, Tl, or Hg-containing charge reservoir layers and multiple, eclipsed CuO_2 sheets in the unit cell tend to have the highest T_c values.



Crystal structure of $YBa_2Cu_3O_{7-\delta}$ (YBCO), the first superconductor with T_c above the boiling point of liquid nitrogen.

The connection between the metal-insulator transtion and superconductivity is nicely illustrated in the phase diagram of $La_{2-x}Sr_xCuO_4$, the first cuprate superconductor, which was discovered in 1986 by Georg Bednorz and K. Alex Müller. This compound has a rather simple structure in which rocksalt La(Sr)O layers are intergrown with perovskite $La(Sr)CuO_3$ layers. Undoped La_2CuO_4 contains only Cu^{2+} ions and is an antiferromagnetic insulator. As a small amount of Sr^{2+} is substituted for La^{3+}, some of the Cu^{2+} is oxidized to Cu^{3+}, and the lattice is doped with holes. As the doping level increases, the antiferromagnetic phase undergoes a first-order phase transition to a "bad" metal, and at slightly higher doping density the superconducting phase appears. The proximity of the superconducting phase to the metal-insulator transition is a hallmark of cuprate superconductors. A maximum T_c of 35K is observed at x = 0.15. Doping at higher levels moves the Fermi level beyond the point of highest DOS in the d-band of Cu and the superconducting phase then gradually disappears. It is interesting to compare this phase diagram with that of V_2O_3 (above), which also undergoes an antiferromagnetic insulator to "bad" metal transition as it is doped.



Crystal structure and phase diagram of the cuprate superconductor $La_{2-x}Sr_xCuO_4$. (LSCO)

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4.2.4: Bonding in Ionic Crystals

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4.2.5: Imperfections in Solids

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4.2.5.1: Imperfections

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4.2.6: Silicates

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4.2.6.1: Silicon

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4.2.7: THERMODYNAMICS OF IONIC CRYSTAL FORMATION

Lattice enthalpy is a measure of the strength of the forces between the ions in an ionic solid. The greater the lattice enthalpy, the stronger the forces. 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.

4.2.7.1: Lattice Energy

4.2.7.2: Lattice Energy - The Born-Haber cycle

4.2.7.3: Lattice Enthalpies and Born Haber Cycles

4.2.7.4: The Born-Lande' equation

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4.2.7.1: Lattice Energy

Discussion Questions

- How is lattice energy estimated using Born-Haber cycle?
- How is lattice energy related to crystal structure?

The Lattice energy, U, is the amount of energy required to separate a mole of the solid (s) into a gas (g) of its ions.

$$\mathrm{M}_a\ \mathrm{L}_b\,(\mathrm{s})\ \rightarrow a\,\mathrm{M}^{b+}\,(\mathrm{g}) + b\,\mathrm{X}^{a-}\,(\mathrm{g}) \tag{4.2.7.1.1}$$

This quantity cannot be experimentally determined directly, but it can be estimated using a Hess Law approach in the form of *Born-Haber cycle*. It can also be calculated from the electrostatic consideration of its crystal structure. As defined in Equation 4.2.7.1.1, the lattice energy is positive, because energy is always required to separate the ions. For the reverse process of Equation 4.2.7.1.1:

$$a\,\mathrm{M}^{b+}\,(\mathrm{g}) + b\,\mathrm{X}^{a-}\,(\mathrm{g})\ \rightarrow \mathrm{M}_a\mathrm{L}_b\,(\mathrm{s})$$

the energy released is called **energy of crystallization** (E_{cryst}). Therefore,

$$U_{lattice} = -E_{cryst}$$

Values of lattice energies for various solids have been given in literature, especially for some common solids. Some are given here.

Table 4.2.7.1.1: Comparison of Lattice Energies (U in 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

The following trends are obvious at a glance of the data in Table 4.2.7.1.1:

- 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.

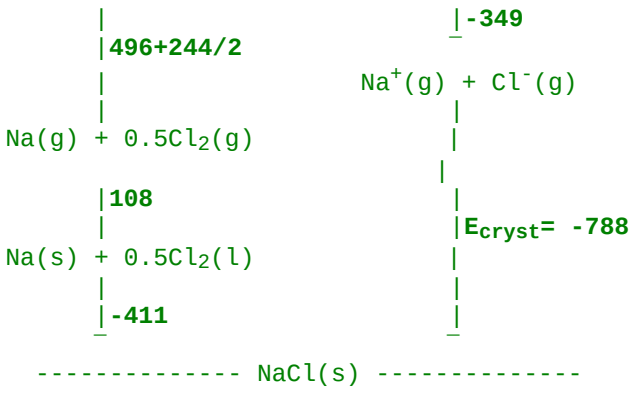
How is lattice energy estimated using Born-Haber cycle?

Estimating lattice energy using the Born-Haber cycle has been discussed in Ionic Solids. For a quick review, the following is an example that illustrate the estimate of the energy of crystallization of NaCl.

Hsub of Na = 108 kJ/mol (Heat of sublimation)
D of Cl2 = 244 (Bond dissociation energy)
IP of Na(g) = 496 (Ionization potential or energy)
EA of Cl(g) = -349 (Electron affinity of Cl)
Hf of NaCl = -411 (Enthalpy of formation)

The Born-Haber cycle to evaluate $E_{lattice}$ is shown below:

```
----------Na+ + Cl(g)--------
                            |
```



E_{cryst} = -411-(108+496+244/2)-(-349) kJ/mol
= -788 kJ/mol.

Discussion
The value calculated for *U* depends on the data used. Data from various sources differ slightly, and so is the result. The lattice energies for NaCl most often quoted in other texts is about 765 kJ/mol.

Compare with the method shown below

Na(s) + 0.5 Cl_2(l) ® NaCl(s)	- 411	H_f
Na(g) ® Na(s)	- 108	-H_{sub}
Na^+(g) + e ® Na(g)	- 496	-*IP*
Cl(g) ® 0.5 Cl_2(g)	- 0.5 * 244	-0.5*D
Cl^-(g) ® Cl(g) + 2 e	349	-*EA*
Add all the above equations leading to		
Na^+(g) + Cl^-(g) ® NaCl(s)	-788 kJ/mol = E_{cryst}	

Lattice Energy is Related to Crystal Structure

There are many other factors to be considered such as covalent character and electron-electron interactions in ionic solids. But for simplicity, let us consider the ionic solids as a collection of positive and negative ions. In this simple view, appropriate number of cations and anions come together to form a solid. The positive ions experience both attraction and repulson from ions of opposite charge and ions of the same charge.

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 6 Cl^- ions at a distance 1*r*, 12 Na^+ ions at a distance 2*r*, 8 Cl^- at 3*r*, 6 Na^+ at 4*r*, 24 Na^+ at 5*r*, and so on. Thus, the energy due to one ion is

$$E = \frac{Z^2 e^2}{4\pi\epsilon_o r} M \tag{4.2.7.1.2}$$

The Madelung constant, M, is a poorly converging series of interaction energies:

$$M = \frac{6}{1} - \frac{12}{2} + \frac{8}{3} - \frac{6}{4} + \frac{24}{5} \ldots \tag{4.2.7.1.3}$$

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).

The above discussion is valid only for the sodium chloride (also called rock salt) structure type. This is a geometrical factor, depending on the arrangement of ions in the solid. The Madelung constant depends on the structure type, and its values for several structural types are given in Table 6.13.1.

A is the number of anions coordinated to cation and *C* is the numbers of cations coordinated to anion.

Table 4.2.7.1.2*: 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.				

Madelung constants for a few more types of crystal structures are available from the Handbook Menu. There are other factors to consider for the evaluation of energy of crystallization, and the treatment by *M. Born* led to the formula for the evaluation of crystallization energy E_{cryst}, for a mole of **crystalline solid**.

$$E_{cryst} = \frac{NZ^2e^2}{4\pi\epsilon_o r}\left(1 - \frac{1}{n}\right) \tag{4.2.7.1.4}$$

where *N* is the Avogadro's number (6.022x10^{-23}), and *n* is a number related to the electronic configurations of the ions involved. The *n* values and the electronic configurations (e.c.) of the corresponding inert gases are given below:

n =	5	7	9	10	12
e.c.	He	Ne	Ar	Kr	Xe

The following values of *n* have been suggested for some common solids:

n =	5.9	8.0	8.7	9.1	9.5
e.c.	LiF	LiCl	LiBr	NaCl	NaBr

Example 4.2.7.1.1

Estimate the energy of crystallization for NaCl.

Solution

Using the values giving in the discussion above, the estimation is given by Equation 4.2.7.1.4:

$$E_c ryst = \frac{(6.022 \times 10^{23}/mol(1.6022 \times 10^{-19})^2(1.747558)}{4\pi\,(8.854 \times 10^{-12}C^2/m)(282 \times 10^{-12}\ m} \left(1 - \frac{1}{9.1}\right)$$
$$= -766kJ/mol$$

Discussion

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-Haber cycle to evaluate other chemical properties, for example the electron affinity, which is really difficult to determine directly by experiment.

Exercise 4.2.7.1.1

Which one of the following has the largest lattice energy? LiF, NaF, CaF_2, AlF_3

Answer available at the end of this section.

Exercise 4.2.7.1.2

Which one of the following has the largest lattice energy? LiCl, NaCl, $CaCl_2$, Al_2O_3

Answer available at the end of this section.

Exercise 4.2.7.1.3

Lime, CaO, is know to have the same structure as NaCl and the edge length of the unit cell for CaO is 481 pm. Thus, Ca-O distance is 241 pm. Evaluate the energy of crystallization, E_{cryst} for CaO.

Answer available at the end of this section.

Exercise 4.2.7.1.4

Assume the interionic distance for $NaCl_2$ to be the same as those of NaCl (r = 282 pm), and assume the structure to be of the fluorite type (M = 2.512). Evaluate the energy of crystallization, E_{cryst} .

Answer available at the end of this section.

Contributors and Attributions

- Chung (Peter) Chieh (Professor Emeritus, Chemistry @ University of Waterloo)

Answers

Exercise 4.2.7.1.1

Skill: Explain the trend of lattice energy.

Exercise 4.2.7.1.2

Corrundum Al_2O_3 has some covalent character in the solid as well as the higher charge of the ions.

Exercise 4.2.7.1.3

Energy of crystallization is -3527 kJ/mol

Skill: Evaluate the lattice energy and know what values are needed.

Exercise 4.2.7.1.4

-515 kJ/mol

Discussion: This number has not been checked. If you get a different value, please let me know.

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4.2.7.2: 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.

Introduction

This module will introduce the idea of lattice energy, as well as one process that allows us to calculate it: the Born-Haber Cycle. In order to use the Born-Haber Cycle, there are several concepts that we must understand first.

Lattice Energy

Lattice Energy is a type of potential energy that may be defined in two ways. In one definition, 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. The other definition says that lattice energy is the reverse process, meaning it 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.

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.

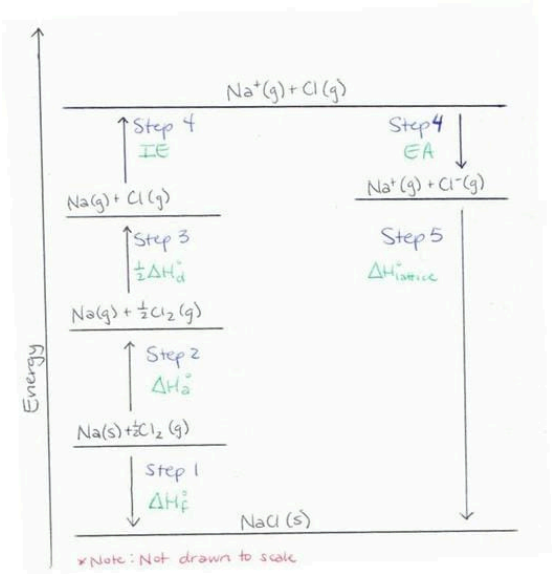
Born-Haber Cycle

There are several important concept to understand before the Born-Haber Cycle can be applied 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.
- Sublimation 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 energy of atomization.
- **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.

Using the Born-Haber Cycle

The values used in the Born-Haber Cycle are all predetermined changes in enthalpy for the processes described in the section above. Hess' Law allows us to add or subtract these values, which allows us to determine the lattice energy.



Step 1

Determine the energy of the metal and nonmetal in their elemental forms. (Elements in their natural state have an energy level of zero.) Subtract from this the heat of formation of the ionic solid that would be formed from combining these elements in the appropriate ration. This is the energy of the ionic solid, and will be used at the end of the process to determine the lattice energy.

Step 2

The Born-Haber Cycle requires that the elements involved in the reaction are in their gaseous forms. Add the changes in enthalpy to turn one of the elements into its gaseous state, and then do the same for the other element.

Step 3

Metals exist in nature as single atoms and thus no dissociation energy needs to be added for this element. However, many nonmetals will exist as polyatomic species. For example, Cl exists as Cl_2 in its elemental state. The energy required to change Cl_2 into 2Cl atoms must be added to the value obtained in Step 2.

Step 4

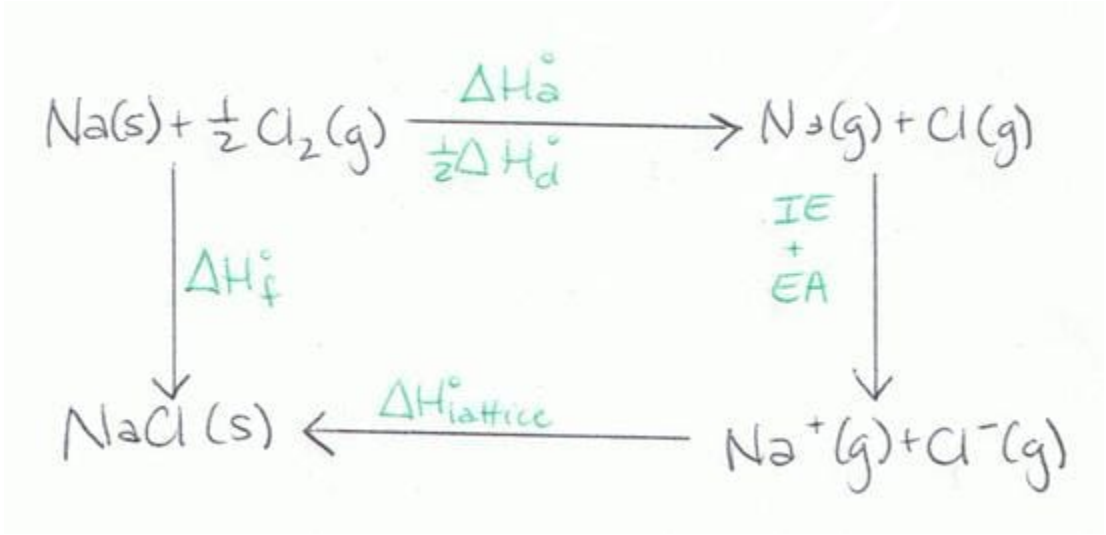
Both the metal and nonmetal now need to be changed into their ionic forms, as they would exist in the ionic solid. To do this, the ionization energy of the metal will be added to the value from Step 3. Next, the electron affinity of the nonmetal will be subtracted from the previous value. It is subtracted because it is a release of energy associated with the addition of an electron.

*This is a common error due to confusion caused by the definition of electron affinity, so be careful when doing this calculation.

Step 5

Now the metal and nonmetal will be combined to form the ionic solid. This will cause a release of energy, which is called the lattice energy. The value for the lattice energy is the difference between the value from Step 1 and the value from Step 4.

The diagram below is another representation of the Born-Haber Cycle.



Equation

The Born-Haber Cycle can be reduced to a single equation:

Heat of formation= Heat of atomization+ Dissociation energy+ (sum of Ionization energies)+ (sum of Electron affinities)+ Lattice energy

*Note: In this general equation, the electron affinity is added. However, when plugging in a value, determine whether energy is released (exothermic reaction) or absorbed (endothermic reaction) for each electron affinity. If energy is released, put a negative sign in front of the value; if energy is absorbed, the value should be positive.

Rearrangement to solve for lattice energy gives the equation:

Lattice energy= Heat of formation- Heat of atomization- Dissociation energy- (sum of Ionization energies)- (sum of Electron Affinities)

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Problems

1. Define lattice energy, ionization energy, and electron affinity.
2. What is Hess' Law?
3. Find the lattice energy of KF(s).
   Note: Values can be found in standard tables.
4. Find the lattice energy of $MgCl_2$(s).
5. Which one of the following has the greatest lattice energy?
   a. A) MgO

b. B) NaC
c. C) LiCl
d. D) $MgCl_2$

6. Which one of the following has the greatest Lattice Energy?
   a. NaCl
   b. $CaCl_2$
   c. $AlCl_3$
   d. KCl

Solutions

1. Lattice energy: The difference in energy between the expected experimental value for the energy of the ionic solid and the actual value observed. More specifically, this is the energy gap between the energy of the separate gaseous ions and the energy of the ionic solid.
   Ionization energy: The energy change associated with the removal of an electron from a neutral atom or ion.
   Electron affinity: The release of energy associated with the addition of an electron to a neutral atom or ion.
2. Hess' Law states that the overall energy of a reaction may be determined by breaking down the process into several steps, then adding together the changes in energy of each step.
3. Lattice Energy= [-436.68-89-(0.5*158)-418.8-(-328)] kJ/mol= **-695.48 kJ/mol**
4. Lattice Energy= [-641.8-146-243-(737.7+1450.6)-(2*-349)] kJ/mol= **-2521.1 kJ/mol**
5. MgO. It has ions with the largest charge.
6. $AlCl_3$. According to the periodic trends, as the radius of the ion increases, lattice energy decreases.

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2. Combs, Leon. "Lattice Energy". Dr. Leon L. Combs. 1999. erkki.kennesaw.edu/genchem8/ge00002.htm
3. Picture of NaCl diagram intro.chem.okstate.edu/1314f0...BornHaber2.GIF
4. Housecroft, Catherine E. and Alan G. Sharpe. Inorganic Chemistry. 3rd ed. England: Pearson Education Limited, 2008.174-175.

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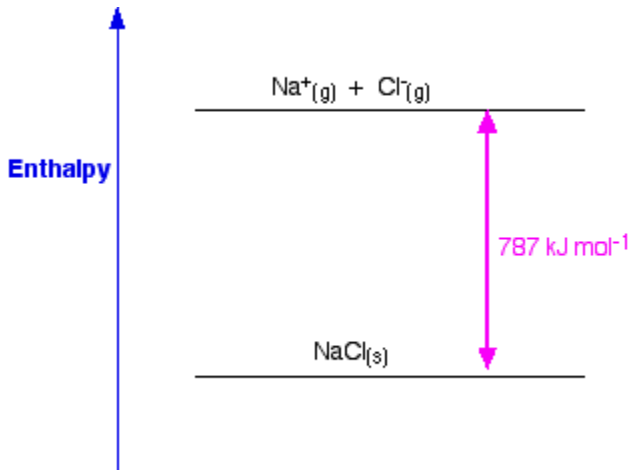
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4.2.7.3: Lattice Enthalpies and Born Haber Cycles

Lattice enthalpy is a measure of the strength of the forces between the ions in an ionic solid. The greater the **lattice enthalpy**, the stronger the forces. This page introduces lattice enthalpies (lattice energies) and Born-Haber cycles.

Defining Lattice Enthalpy

There are two different ways of defining lattice enthalpy which directly contradict each other, and you will find both in common use. In fact, there is a simple way of sorting this out, but many sources do not use it. Lattice enthalpy is a measure of the strength of the forces between the ions in an ionic solid. The greater the lattice enthalpy, the stronger the forces. 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. You can show this on a simple enthalpy diagram.



For sodium chloride, the solid is more stable than the gaseous ions by 787 kJ mol^{-1}, and that is a measure of the strength of the attractions between the ions in the solid. Remember that energy (in this case heat energy) is released when bonds are made, and is required to break bonds.

So lattice enthalpy could be described in either of two ways.

- It could be described as the enthalpy change when 1 mole of sodium chloride (or whatever) was formed from its scattered gaseous ions. In other words, you are looking at a downward arrow on the diagram.
- Or, it could be described as the enthalpy change when 1 mole of sodium chloride (or whatever) is broken up to form its scattered gaseous ions. In other words, you are looking at an upward arrow on the diagram.

Both refer to the same enthalpy diagram, but one looks at it from the point of view of making the lattice, and the other from the point of view of breaking it up. Unfortunately, both of these are often described as "lattice enthalpy".

Definitions

- 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**.

This is an absurdly confusing situation which is easily resolved by never using the term "lattice enthalpy" without qualifying it.

- You should talk about "lattice dissociation enthalpy" if you want to talk about the amount of energy needed to split up a lattice

into its scattered gaseous ions. For NaCl, the lattice dissociation enthalpy is +787 kJ mol^{-1}.
- You should talk about "lattice formation enthalpy" if you want to talk about the amount of energy released when a lattice is formed from its scattered gaseous ions. For NaCl, the lattice formation enthalpy is -787 kJ mol^{-1}.

That immediately removes any possibility of confusion.

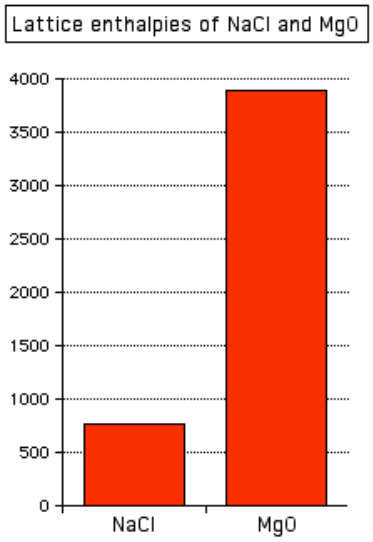
Factors affecting Lattice Enthalpy

The two main factors affecting lattice enthalpy are

- The charges on the ions and
- The ionic radii (which affects the distance between the ions).

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.

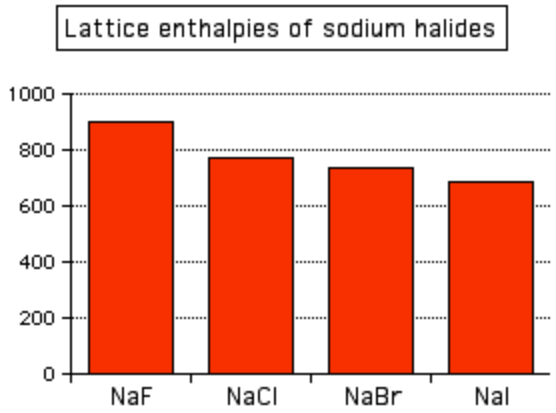


You can see that the lattice enthalpy of magnesium oxide is much greater than that of sodium chloride. That's because in magnesium oxide, 2+ ions are attracting 2- ions; in sodium chloride, the attraction is only between 1+ and 1- ions.

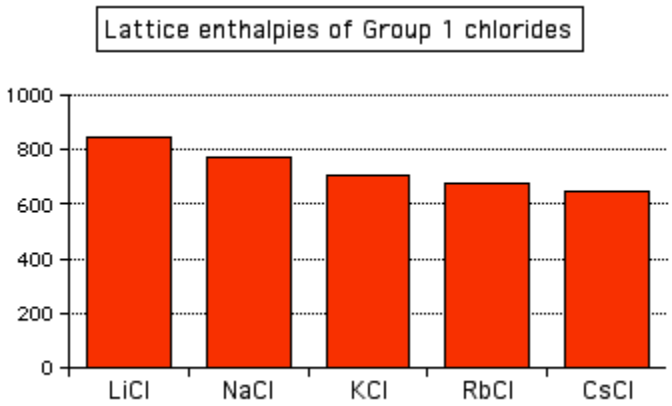
The Radius of the Ions

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:



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.



Calculating Lattice Enthalpy

It is impossible to measure the enthalpy change starting from a solid crystal and converting it into its scattered gaseous ions. It is even more difficult to imagine how you could do the reverse - start with scattered gaseous ions and measure the enthalpy change when these convert to a solid crystal. Instead, lattice enthalpies always have to be calculated, and there are two entirely different ways in which this can be done.

1. You can can use a Hess's Law cycle (in this case called a Born-Haber cycle) involving enthalpy changes which can be measured. Lattice enthalpies calculated in this way are described as experimental values.
2. Or you can do physics-style calculations working out how much energy would be released, for example, when ions considered as point charges come together to make a lattice. These are described as theoretical values. In fact, in this case, what you are actually calculating are properly described as lattice energies.

Born-Haber Cycles

Standard Atomization Enthalpies

Before we start talking about Born-Haber cycles, we need to define the **atomization enthalpy**, ΔH_a^o. The standard atomization enthalpy 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:

$$\frac{1}{2}Cl_2(g) \rightarrow Cl(g) \quad \Delta H_a^o = +122\,kJ\,mol^{-1}$$

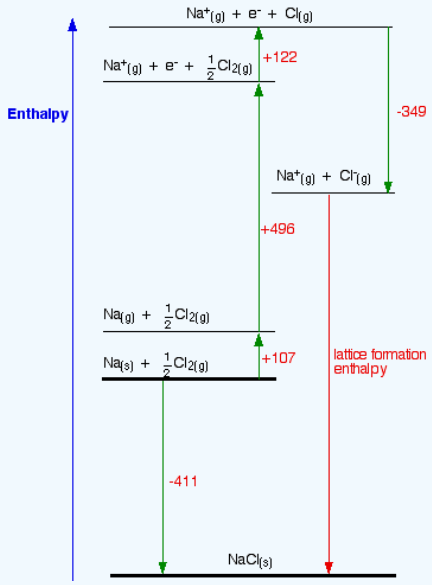
$$\frac{1}{2}Br_2(l) \rightarrow Br(g) \quad \Delta H_a^o = +122\,kJ\,mol^{-1}$$

$$Na(s) \rightarrow Na(g) \quad \Delta H_a^o = +107\,kJ\,mol^{-1}$$

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.

Example 4.2.7.3.1: Born-Haber Cycle for $NaCl$

Consider a Born-Haber cycle for sodium chloride, and then talk it through carefully afterwards. You will see that I have arbitrarily decided to draw this for lattice formation enthalpy. If you wanted to draw it for lattice dissociation enthalpy, the red arrow would be reversed - pointing upwards.



Focus to start with on the higher of the two thicker horizontal lines. We are starting here with the elements sodium and chlorine in their standard states. Notice that we only need half a mole of chlorine gas in order to end up with 1 mole of NaCl. The arrow pointing down from this to the lower thick line represents the enthalpy change of formation of sodium chloride.

The Born-Haber cycle now imagines this formation of sodium chloride as happening in a whole set of small changes, most of which we know the enthalpy changes for - except, of course, for the lattice enthalpy that we want to calculate.

- The +107 is the atomization enthalpy of sodium. We have to produce gaseous atoms so that we can use the next stage in the cycle.
- The +496 is the first ionization energy of sodium. Remember that first ionization energies go from gaseous atoms to gaseous singly charged positive ions.
- The +122 is the atomization enthalpy of chlorine. Again, we have to produce gaseous atoms so that we can use the next stage in the cycle.
- The -349 is the first electron affinity of chlorine. Remember that first electron affinities go from gaseous atoms to gaseous singly charged negative ions.
- And finally, we have the positive and negative gaseous ions that we can convert into the solid sodium chloride using the lattice formation enthalpy.

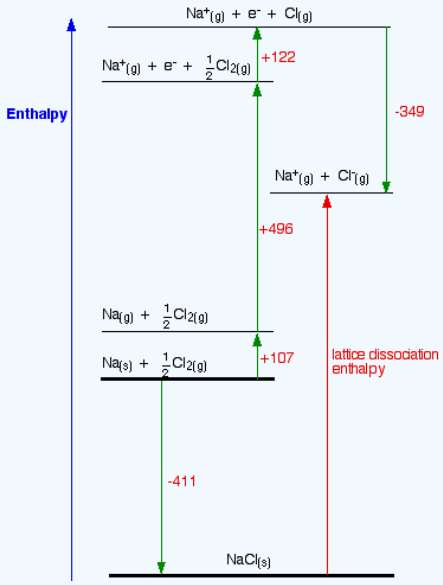
Now we can use Hess' Law and find two different routes around the diagram which we can equate. As drawn, the two routes are obvious. The diagram is set up to provide two different routes between the thick lines. So, from the cycle we get the calculations directly underneath it . . .

$$-411 = +107 + 496 + 122 - 349 + LE$$

$$LE = -411 - 107 - 496 - 122 + 349$$

$$LE = -787 \text{ kJ mol}^{-1}$$

How would this be different if you had drawn a lattice dissociation enthalpy in your diagram? Your diagram would now look like this:



The only difference in the diagram is the direction the lattice enthalpy arrow is pointing. It does, of course, mean that you have to find two new routes. You cannot use the original one, because that would go against the flow of the lattice enthalpy arrow. This time both routes would start from the elements in their standard states, and finish at the gaseous ions.

$$-411 + LE = +107 + 496 + 122 - 349$$

$$LE = +107 + 496 + 122 - 349 + 411$$

$$LE = +787 \text{ kJ mol}^{-1}$$

Once again, the cycle sorts out the sign of the lattice enthalpy.

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.

Example 4.2.7.3.2: Born-Haber Cycle for $MgCl_2$

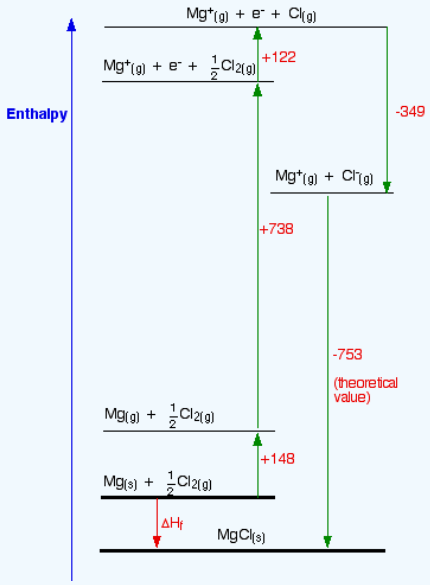
The question arises as to why, from an energetics point of view, magnesium chloride is $MgCl_2$ rather than MgCl or $MgCl_3$ (or any other formula you might like to choose). It turns out that $MgCl_2$ is the formula of the compound which has the most negative enthalpy change of formation - in other words, 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 and contrast the enthalpy change of formation for the imaginary compounds MgCl and $MgCl_3$. That means that we will have to use theoretical values of their lattice enthalpies. We ca not use experimental ones, because these compounds obviously do not exist! I'm taking theoretical values for lattice enthalpies for these compounds that I found on the web. I can't confirm these, but all the other values used by that source were accurate. The exact values do not matter too much anyway, because the results are so dramatically clear-cut.

1. The Born-Haber cycle for MgCl

We will start with the compound MgCl, because that cycle is just like the NaCl one we have already looked at.

$$Mg\,(s) + \tfrac{1}{2}\,Cl_2\,(g) \rightarrow MgCl\,(s)$$



Find two routes around this without going against the flow of any arrows. That's easy:

$$\Delta H_f = +148 + 738 + 122 - 349 - 753$$

$$\Delta H_f = -94 \text{ kJ mol}^{-1}$$

So the compound MgCl is definitely energetically **more stable** than its elements. I have drawn this cycle very roughly to scale, but that is going to become more and more difficult as we look at the other two possible formulae. So I am going to rewrite it as a table. 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

2. 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

$$Mg\,(s) + \tfrac{3}{2}\,Cl_2\,(g) \rightarrow MgCl_3\,(s)$$

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.

Contributors and Attributions

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4.2.7.4: The Born-Lande' equation

The Born-Landé equation is a concept originally formulated in 1918 by the scientists Born and Landé and is used to calculate the lattice energy (measure of the strength of bonds) of a compound. This expression takes into account both the Born interactions as well as the Coulomb attractions.

Introduction

Due to its high simplicity and ease, the Born-Landé equation is commonly used by chemists when solving for lattice energy. This equation proposed by Max Born and Alfred Landé states that lattice energy can be derived from ionic lattice based on electrostatic potential and the potential energy due to repulsion. 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:

$$\Delta U = -\frac{N_A M \left|Z^+\right| \left|Z^-\right| e^2}{4\pi\epsilon_o r} \tag{4.2.7.4.1}$$

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:

$$\Delta U = \frac{N_A B}{r^n} \tag{4.2.7.4.2}$$

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 to form:

$$\Delta U(0K) = \frac{N_A M \left|Z^+\right| \left|Z^-\right| e^2}{4\pi\epsilon_o r_o}\left(1 - \frac{1}{n}\right) \tag{4.2.7.4.3}$$

with

- r_0 is the closest ion distance

Calculate Lattice Energy

Lattice energy, based on the equation from above, is dependent on multiple factors. We see that the charge of ions is proportional to the increase in lattice energy. In addition, as ions come into closer contact, lattice energy also increases.

Example 4.2.7.4.1

Which compound has the greatest lattice energy?

- AlF_3
- NACl
- LiF
- $CaCl_2$

Solution

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.

Example 4.2.7.4.2

What is the lattice energy of NaCl? (Hint: you must look up the values for the constants for this compound)

Solution

-756 kJ/mol (again, this value is found in a table of constants)

Example 4.2.7.4.3

Calculate the lattice energy of NaCl.

Solution

$$Lattice\ Energy\ of\ NaCl = -\frac{\frac{6.022\,x\,10^{23}}{mole}\left(1.6022^{-19}\right)\times 1.747}{4\pi \times 8.85\,x\,10^{-12}\frac{c^2}{m}\times 282\,x\,10^{-12}m}\left(1-\frac{1}{9}\right) \approx -756\ \frac{kJ}{mol}$$

References

1. Johnson, D. A. *Metals and Chemical Change*. Cambridge: Royal Society of Chemistry, 2002.
2. Cotton, F. Albert, and F. Albert Cotton. *Advanced Inorganic Chemistry*. New York: Wiley, 1999.

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4.2.P: Problems

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4.3: METALS AND ALLOYS- STRUCTURE, BONDING, ELECTRONIC AND MAGNETIC PROPERTIES

Learning Objectives

- Identify and assign unit cells, coordination numbers, asymmetric units, numbers of atoms contained within a unit cell, and the fraction of space filled in a given structure.
- Relate molecular orbital theory to the delocalization of valence electrons in metals.
- Understand the concepts of electron wavelength and density of states.
- Understand the consequences of the nearly free electron model for the band structure of metals and their conductivity.
- Explain why some metals are magnetic and others are diamagnetic, and how these phenomena relate to bonding and orbital overlap.
- Use the Curie-Weiss law to explain the temperature dependence of magnetic ordering.
- Acquire a physical picture of different kinds of magnetic ordering and the magnetic hysteresis loops of ferro- and ferrimagnets.

It should come as no surprise that the properties of extended solids are also connected to their structures, and so to understand what they do we should begin with their crystal structures. Most of the metals in the periodic table have relatively simple structures and so this is a good place to begin.

4.3.1: Prelude to Metals and Alloys

4.3.2: Unit Cells and Crystal Structures

4.3.3: Bravais Lattices

4.3.4: Crystal Structures of Metals

4.3.5: Bonding in Metals

4.3.6: Conduction in Metals

4.3.7: Atomic Orbitals and Magnetism

4.3.8: Ferro-, Ferri- and Antiferromagnetism

4.3.9: Hard and Soft Magnets

4.3.10: Discussion Questions

4.3.11: Problems

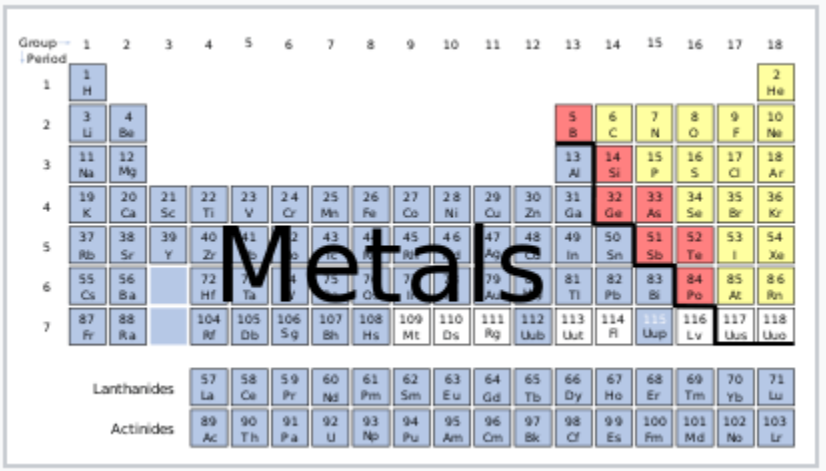
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4.3.1: Prelude to Metals and Alloys

In the chemistry of molecular compounds, we are accustomed to the idea that properties depend strongly on structure. For example we can rationalize the polarity of the water molecule based on its shape. We also know that two molecules with the same composition (e.g., ethanol and dimethyl ether) have very different properties based on the bonding arrangements of atoms. It should come as no surprise that the properties of extended solids are also connected to their structures, and so to understand what they do we should begin with their crystal structures. Most of the metals in the periodic table have relatively simple structures and so this is a good place to begin. We will see in Chapter 8 that the structures of more complex compounds are also in many cases related to the simple structures of metals and alloys.



Over 2/3 of the elements in the periodic table exist in their pure form as metals. All elemental metals (except the three - Cs, Ga, Hg - that are liquid) are crystalline solids at room temperature, and most have one of three simple crystal structures.

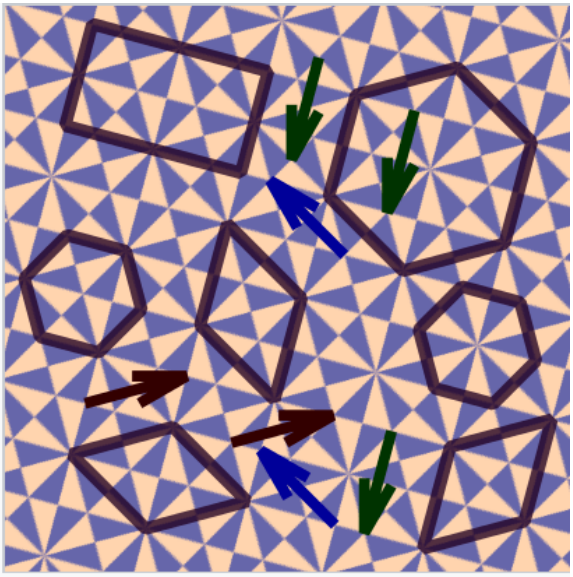
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4.3.2: Unit Cells and Crystal Structures

Crystals can be thought of as repeating patterns, much like wallpaper or bathroom tiles, but in three dimensions. The fundamental repeating unit of the crystal is called the **unit cell**. It is a three dimensional shape that can be repeated over and over by unit translations to fill space (and leave minimal gaps) in the structure. Some possible unit cells are shown in the tiling pattern at the right, along with arrows that indicate **unit translation vectors**. In three dimensions, the hexagonal or rhombic unit cells of this pattern would be replaced by three dimensional boxes that would stack together to fill all space. As shown in the figure, the origin of the unit cell is arbitrary. The same set of boxes will fill all space no matter where we define the origin of the lattice. We will see that pure metals typically have very simple crystal structures with cubic or hexagonal unit cells. However the crystal structures of alloys can be quite complicated.

When considering the crystal structures of metals and alloys, it is not sufficient to think of each atom and its neighboring ligands as an isolated system. Instead, think of the entire metallic crystal as a network of atoms connected by a sea of shared valence electrons. The **electrons are delocalized** because there are **not enough of them** to fill each "bond" between atoms with an electron pair. For example, in the crystal structures of s-block and p-block metals, each atom has either 8 or 12 nearest neighbors, but the maximum number of s + p electrons is 8. Thus, there are not enough to put two electrons between each pair of atoms. Transition metals can also use their d-orbitals in bonding, but again there are never enough electrons to completely fill all the "bonds."



Possible unit cells in a periodic tile pattern. The arrows connect translationally equivalent points (lattice points) in the pattern.

The atoms in a metal lattice arrange themselves in a certain pattern which can be represented as a 3D box structure known as the **unit cell** which repeats across the entire metal.

Simple Cubic	Body Centered Cubic	Face Centered Cubic	Hexagonal Close Packed
Simple cubic.svg	Lattice body centered cubic.svg	Lattice face centered cubic.svg	Hexagonal close packed.png
1 atom/cell	2 atoms/cell	4 atoms/cell	2 atoms/cell

Metal atoms can be approximated as spheres, and therefore are not 100 % efficient in packing, the same way a stack of cannonballs has some empty spaces between the balls. Different unit cells have different packing efficiencies. The number of atoms that is included in the unit cell only includes the fractions of atoms *inside* of the box. Atoms on the corners of the unit cell count as ⅛ of an atom, atoms on a face count as ½, an atom in the center counts as a full atom. Using this, let's calculate the

number of atoms in a simple cubic unit cell, a face centered cubic (fcc) unit cell, and a body centered cubic (bcc) unit cell.

Simple Cubic:

8 corner atoms × ⅛ = 1 atom/cell. The packing in this structure is not efficient (52%) and so this structure type is very rare for metals.

Body Centered Cubic, bcc:

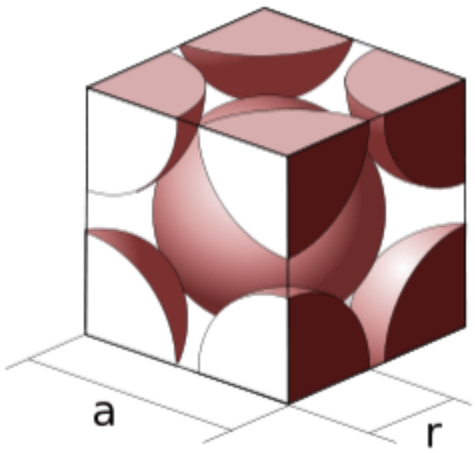
(8 corner atoms × ⅛) + (1 center atom × 1)= 2 atoms/cell. The packing is more efficient (68%) and the structure is a common one for alkali metals and early transition metals. Alloys such as brass (CuZn) also adopt these structures.

Face Centered Cubic, fcc (also called Cubic Close Packed, ccp):

(8 corner atoms × ⅛)+ (6 face atoms × ½)= 4 atoms/cell. This structure, along with its hexagonal relative (hcp), has the most efficient packing (74%). Many metals adopt either the fcc or hcp structure.

Hexagonal Close Packed, hcp:

Like the fcc structure, the packing density of hcp is 74%.

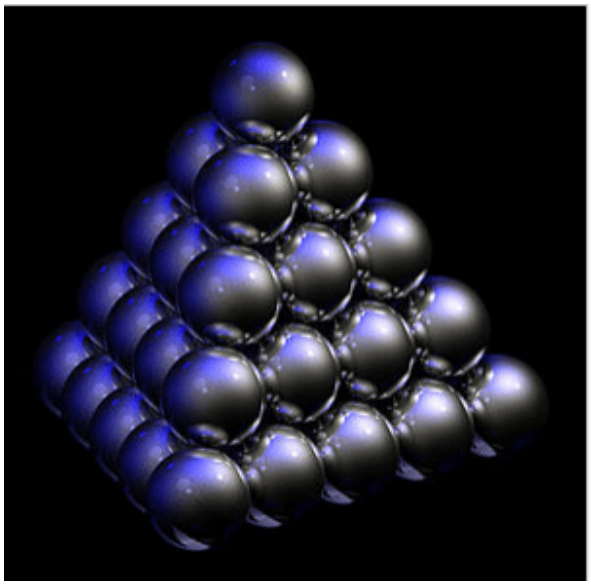


The unit cell of a bcc metal contains two atoms.

Calculating the packing fraction. The packing fractions of the crystal structures shown above can be calculated by dividing the volume of the atoms in the cell by the volume of the cell itself. The volume of the atoms in the cell is equal to the number of atoms/cell times the volume of a sphere, $(4/3)\pi r^3$. The volume of the cubic cells is found by cubing the side length. As an example, let's calculate the packing efficiency of a simple cubic unit cell. As we saw earlier in the section, a simple cubic unit cell contains one atom. The side length of the simple cubic unit cell is 2r, since the centers of each atom occupy the corners of the unit cell.

$$\text{Packing efficiency} = \frac{(1\ atom) \times (\frac{4}{3})\pi r^3}{(2r)^3} = 0.523 \tag{4.3.2.1}$$

The same method can be applied to bcc and fcc structures.



Face-centered cubic stack of cannonballs.

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4.3.3: Bravais Lattices

Crystal lattices can be classified by their **translational** and **rotational symmetry**. In three-dimensional crytals, these symmetry operations yield 14 distinct lattice types which are called **Bravais lattices**. In these lattice diagrams (shown below) the dots represent lattice points, which are places where the whole structure repeats by translation. For example, in the body-centered cubic (**bcc**) structure of sodium metal, which is discussed below, we put one atom at the corner lattice points and another in the center of the unit cell. In the NaCl structure, which is discussed in Chapter 8, we place one NaCl formula unit on each lattice point in the face-centered cubic (**fcc**) lattice. That is, one atom (Na or Cl) would be placed on the lattice point and the other one would be placed halfway between. Similarly, in the cubic diamond structure, we place one C_2 unit around each lattice point in the fcc lattice.

The fourteen Bravais lattices fall into seven **crystal systems** that are defined by their rotational symmetry. In the lowest symmetry system (**triclinic**), there is no rotational symmetry. This results in a unit cell in which none of the edges are constrained to have equal lengths, and none of the angles are 90°. In the **monoclinic** system, there is one two-fold rotation axis (by convention, the b-axis), which constrains two of the angles to be 90°. In the **orthorhombic** system, there are three mutually perpendicular two-fold axes along the three unit cell directions. **Orthorhombic** unit cells have three unequal unit cell edges that are mutually perpendicular. **Tetragonal** unit cells have a four-fold rotation axis which constrains all the angles to be 90° and makes the a and b axes equivalent. The **rhombohedral** system has a three-fold axis, which constrains all the unit cell edges and angles to be equal, and the **hexagonal** system has a six-fold axis, which constrains the a and b lattice dimensions to be equal and the angle between them to be 120°. The **cubic** system has a three-fold axis along the body diagonal of the cube, as well as two-fold axes along the three perpendicular unit cell directions. In the cubic system, all unit cell edges are equal and the angles between them are 90°.

The translational symmetry of the Bravais lattices (the lattice **centerings**) are classified as follows:

- Primitive (P): lattice points on the cell corners only (sometimes called simple)
- Body-Centered (I): lattice points on the cell corners with one additional point at the center of the cell
- Face-Centered (F): lattice points on the cell corners with one additional point at the center of each of the faces of the cell
- Base-Centered (A, B, or C): lattice points on the cell corners with one additional point at the center of each face of one pair of parallel faces of the cell (sometimes called end-centered)

Not all combinations of the crystal systems and lattice centerings are unique. There are in total 7 × 6 = 42 combinations, but it can be shown that several of these are in fact equivalent to each other. For example, the monoclinic I lattice can be described by a monoclinic C lattice by different choice of crystal axes. Similarly, all A- or B-centred lattices can be described either by a C- or P-centering. This reduces the number of combinations to 14 conventional Bravais lattices, shown in the table below.

When the fourteen Bravais lattices are combined with the **32 crystallographic point groups**, we obtain the **230 space groups**. These space groups describe all the combinations of symmetry operations that can exist in unit cells in three dimensions. For two-dimensional lattices there are only 17 possible plane groups, which are also known as wallpaper groups.

Crystal family	**Lattice system**	**Schönflies**	**14 Bravais Lattices**			
			Primitive	**Base-centered**	**Body-centered**	**Face-centered**
Triclinic		C_i	Triclinic			
Monoclinic		C_{2h}	Monoclinic, simple	Monoclinic, centered		
Orthorhombic		D_{2h}	Orthorhombic, simple	Orthorhombic, base-centered	Orthorhombic, body-centered	Orthorhombic, face-centered
Tetragonal		D_{4h}	Tetragonal, simple		Tetragonal, body-centered	
Hexagonal	rhombohedral	D_{3d}	Rhombohedral			
	hexagonal	D_{6h}	Hexagonal			
Cubic		O_h	Cubic, simple		Cubic, body-centered	Cubic, face-centered

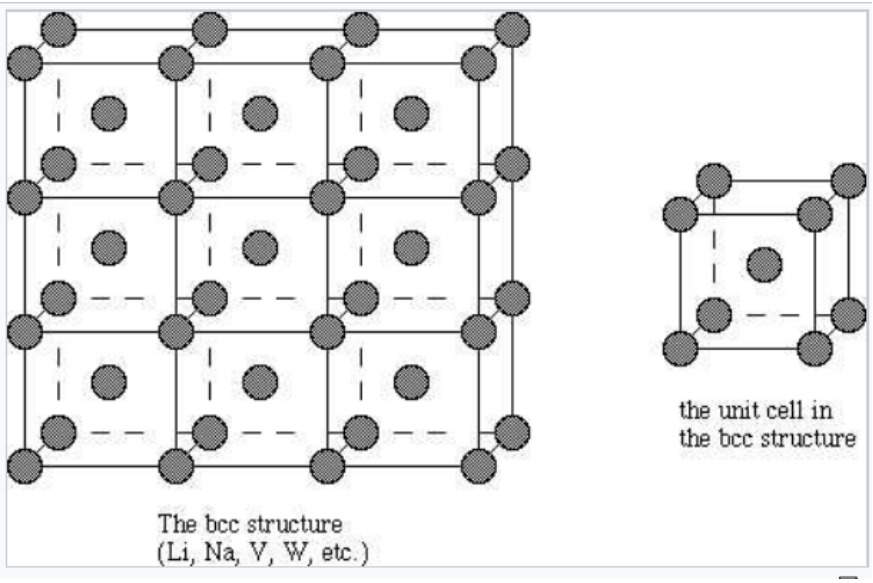
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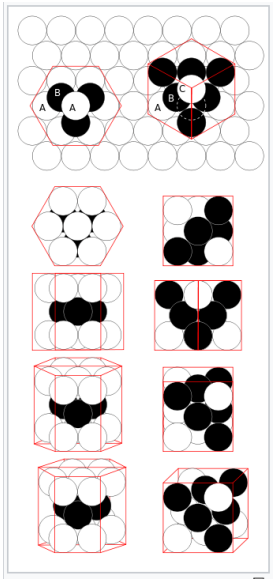
4.3.4: Crystal Structures of Metals

The Crystalline Nature of Metals

All metallic elements (except Cs, Ga, and Hg) are crystalline solids at room temperature. Like ionic solids, metals and alloys have a very strong tendency to crystallize, whether they are made by thermal processing or by other techniques such as solution reduction or electroplating. Metals crystallize readily and it is difficult to form a glassy metal even with very rapid cooling. Molten metals have low viscosity, and the identical (essentially spherical) atoms can pack into a crystal very easily. Glassy metals can be made, however, by rapidly cooling alloys, particularly if the constituent atoms have different sizes. The different atoms cannot pack in a simple unit cell, sometimes making crystallization slow enough to form a glass.



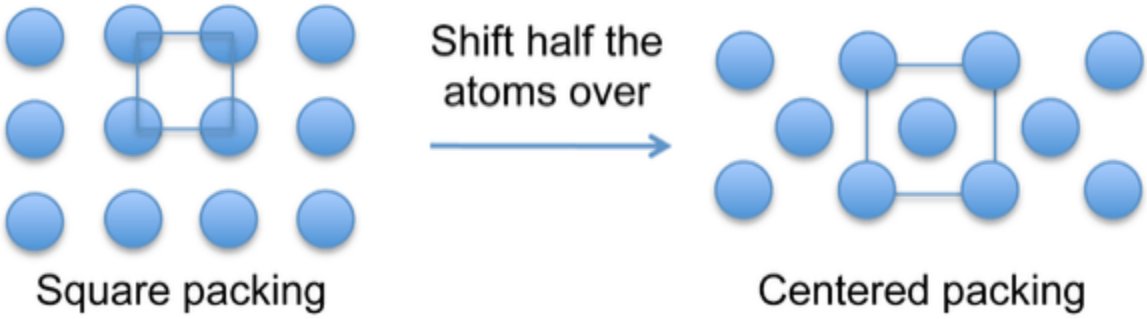
Body-centered cubic



hcp (left) and fcc (right) close-packing of spheres

Crystal structures

Most metals and alloys crystallize in one of three very common structures: body-centered cubic (bcc), hexagonal close packed (hcp), or cubic close packed (ccp, also called face centered cubic, fcc). In all three structures the coordination number of the metal atoms (i.e., the number of equidistant nearest neighbors) is rather high: 8 for bcc, and 12 for hcp and ccp. We can contrast this with the low coordination numbers (i.e., low valences - like 2 for O, 3 for N, or 4 for C) found in nonmetals. In the bcc structure, the nearest neighbors are at the corners of a cube surrounding the metal atom in the center. In the hcp and ccp structures, the atoms pack like stacked cannonballs or billiard balls, in layers with a six-coordinate arrangement. Each atom also has six more nearest neighbors from layers above and below. The stacking sequence is ABCABC... in the ccp lattice and ABAB... in hcp. In both cases, it can be shown that the spheres fill 74% of the volume of the lattice. This is the highest volume fraction that can be filled with a lattice of equal spheres.



Atoms in metallic crystals have a tendency to pack in dense arrangments that fill space efficiently. The simple square packing (above) upon which the simple cubic structure is based is inefficient and thus rare among metallic crystal structures. Body- or face-centered structures fill space more efficiently and more common.

Periodic trends in structure and metallic behavior

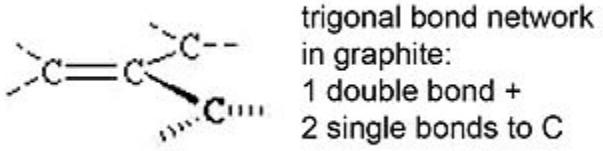
Remember where we find the metallic elements in the periodic table - everywhere except the upper right corner. This means that

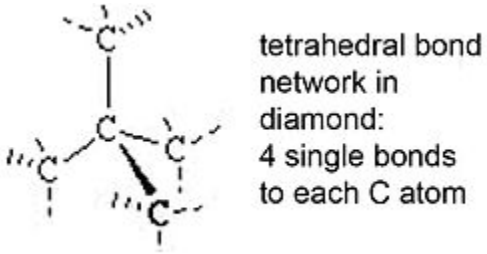
as we go down a group in the p-block (let's say, group IVA, the carbon group, or group VA, the nitrogen group), the properties of the elements gradually change from nonmetals to metalloids to metals. The carbon group nicely illustrates the transition. Starting at the top, the element carbon has two stable allotropes - graphite and diamond. In each one, the valence of carbon atoms is exactly satisfied by making four electron pair bonds to neighboring atoms. In graphite, each carbon has three nearest neighbors, and so there are two single bonds and one double bond. In diamond, there are four nearest neighbors situated at the vertices of a tetrahedron, and so there is a single bond to each one.

The two elements right under carbon (silicon and germanium) in the periodic table also have the diamond structure (recall that these elements cannot make double bonds to themselves easily, so there is no graphite allotrope for Si or Ge). While diamond is a good insulator, both silicon and germanium are semiconductors (i.e., metalloids). Mechanically, they are hard like diamond. Like carbon, each atom of Si and Ge satisfies its valence of four by making single bonds to four nearest neighbors.

The next element under germanium is tin (Sn). Tin has two allotropes, one with the diamond structure, and one with a slightly distorted bcc structure. The latter has metallic properties (metallic luster, malleability), and conductivity about 10^9 times higher than Si. Finally, lead (Pb), the element under Sn, has the ccp structure, and also is metallic. Note the trends in coordination number and conducting properties:

Element	Structure	Coord. no.	Conductivity
C	graphite, diamond	3, 4	semimetal, insulator
Si	diamond	4	semiconductor
Ge	diamond	4	semiconductor
Sn	diamond, distorted bcc	4, 8	semiconductor, metal
Pb	ccp	12	metal





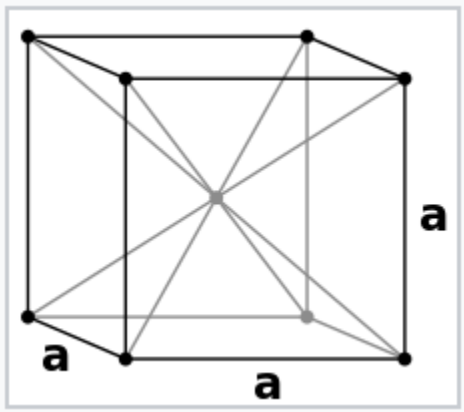
The elements C, Si, and Ge obey the octet rule, and we can easily identify the electron pair bonds in their structures. Sn and Pb, on the other hand, adopt structures with high coordination numbers. They *do not have enough valence electrons* to make electron pair bonds to each neighbor (this is a common feature of metals). What happens in this case is that the valence electrons become "smeared out" or delocalized over all the atoms in the crystal. It is best to think of the bonding in metals as a crystalline arrangement of positively charged cores with a "sea" of shared valence electrons gluing the structure together. Because the electrons are not localized in any particular bond between atoms, they can move in an electric field, which is why metals conduct electricity well. Another way to describe the bonding in metals is nondirectional. That is, an atom's nearest neighbors surround it in every direction, rather than in a few particular directions (like at the corners of a tetrahedron, as we found for diamond). Nonmetals (insulators and semiconductors), on the other hand, have directional bonding. Because the bonding is non-directional and coordination numbers are high, it is relatively easy to deform the coordination sphere (i.e., break or stretch bonds) than it is in the case of a nonmetal. This is why elements like Pb are much more malleable than C, Si, or Ge.

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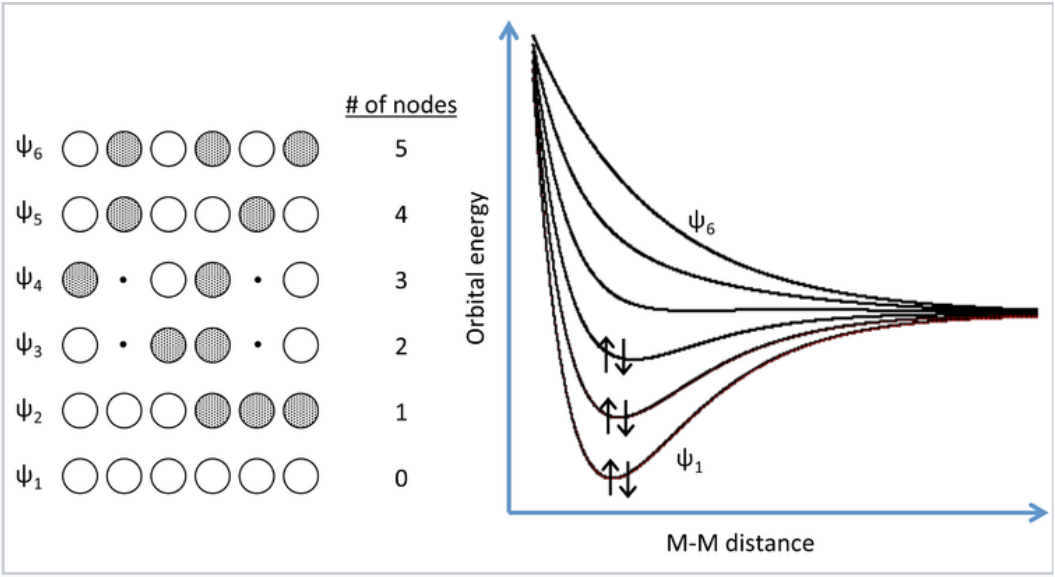
4.3.5: Bonding in Metals

The electron pair description of chemical bonds, which was the basis of the octet rule for p-block compounds, breaks down for metals. This is illustrated well by Na metal, the structure of which is shown at the left. Na has too few valence electrons to make electron pair bonds between each pair of atoms. We could think of the Na unit cell as having eight no-bond resonance structures in which only one Na-Na bond per cell contains a pair of electrons.



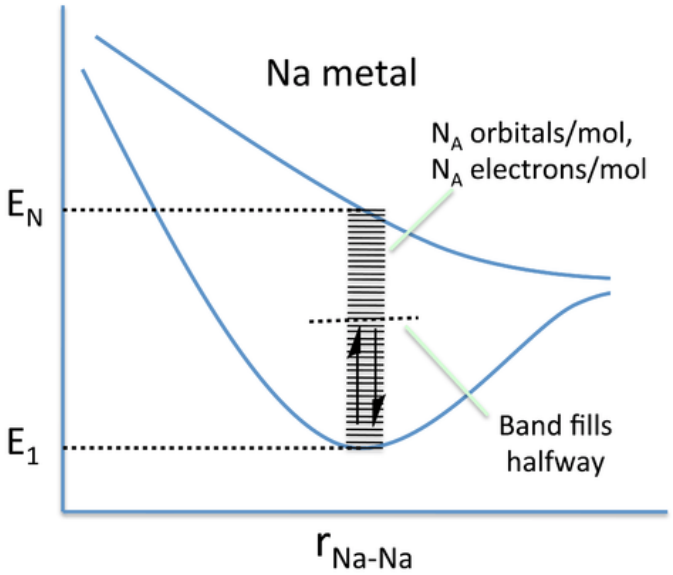
Sodium metal crystallizes in the body-centered cubic structure, in which each atom has eight nearest neighbors. Since the electronic configuration of Na is $[Ar]3s^1$, there are only two valence electrons per unit cell that are shared among eight Na-Na bonds. This means that the Na-Na bond order is 1/8 in Na metal.

A more realistic way to describe the bonding in metals is through **band theory**. The evolution of energy bands in solids from simple MO theory (Chapter 2) is illustrated at the right for a chain of six Na atoms, each of which has one 3s valence orbital and contributes one valence electron. In general, **n** atomic orbitals (in this case the six Na 3s orbitals) will generate **n** molecular orbitals with **n-1** possible nodes. In Chapter 2, we showed that the energy versus internuclear distance graph for a two hydrogen atom system has a low energy level and a high energy level corresponding to the bonding and antibonding molecular orbitals, respectively. These two energy levels were well separated from each other, and the two electrons in H_2 energetically prefer the lower energy level. If more atoms are introduced to the system, there will be a number of additional levels between the lowest and highest energy levels.



MO picture for a linear chain of six Na atoms. Three of the six MOs can accommodate all six valence electrons. Adding more atoms to the chain makes more molecular orbitals of intermediate energy, which eventually merge into a continuous band of orbitals. For Na, the 3s band is always half-filled because each MO can accommodate two electrons.

In band theory, the atom chain is extrapolated to a very large number - on the order of 10^{22} atoms in a crystal - so that the different combinations of bonding and anti-bonding orbitals create "bands" of possible energy states for the metal. In the language of physics, this approach of building the bands from discrete atomic orbitals is called the "tight-binding" approximation. The number of atoms is so large that the energies can be thought of as a continuum rather than a series of distinct levels. A metal will only partially fill this band, as there are fewer valence electrons than there are energy states to fill. In the case of Na metal, this results in a half-filled 3s band.



Nearly free electron model

In metals, the valence electrons are delocalized over many atoms. The total energy of each electron is given by the sum of its kinetic and potential energy:

$$E = KE + PE$$

$$E \approx p^2/2m + V$$

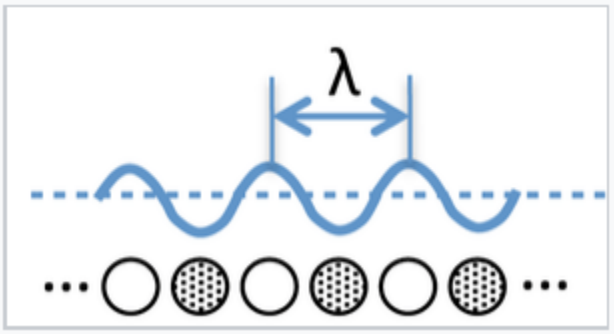
where **p** is the momentum of the electron (a vector quantity), m is its mass, and V is an average potential that the electron feels from the positive cores of the atoms. This potential holds the valence electrons in the crystal but, in the free electron model, is essentially uniform across the crystal.

Electron wavelength and wavenumber

What are the consequences of this model for band theory? For a hypothetical infinite chain (i.e., a 1D crystal) of Na atoms, the molecular orbitals at the bottom of the 3s band are fully bonding and the *wavelength* of electrons (2x the distance between nodes) in these orbitals is very long. At the top of the band, the highest orbital is fully antibonding and the wavelength is 2 times the distance between atoms (2a), since there is one node per atom. Remember that the **wavelength of an electron (λ)** is inversely proportional to its momentum p, according to the de Broglie relation **λ = h/p**.

For a (nearly) free electron, the kinetic energy can be expressed in terms of its wavelength, using KE = $p^2/2m$ and the de Broglie relation:

$$KE = \frac{p^2}{2m} = \frac{h^2}{2m\lambda^2} \tag{4.3.5.1}$$



We can think of the wavelength of an electron in a molecular orbital as twice the distance between nodes. If there are N atoms in a linear chain, the wavelength of the nth orbital is given by λ = 2Na/n, where a is the distance between atoms.

At this point, it is convenient to define the **wavenumber** of the electron as **k**, which has units of inverse length and is inversely proportional to λ. **k** is also directly proportional to the momentum **p**. Like **p**, **k** is a vector quantity. In a 1D crystal, **k** can be either positive or negative, corresponding to an electron moving to the left or right along the chain.

$$k = \frac{2\pi}{\lambda} = \frac{2\pi p}{h} \text{ where h is Planck's constant} \tag{4.3.5.2}$$

The most important property of **k** is that it is *directly proportional to the number of nodes* **n** in a molecular orbital within the band. For a 1D crystal of sodium atoms that contains **N** unit cells, each separated by a distance a, a molecular orbital with n nodes has a wavelength λ = 2Na/n and the wavenumber k = πn/Na. We can see from this definition that k = 0 at the bottom of the band (where λ is infinite) and k = π/a at the top of the band where the MO contains **N** nodes and λ = 2a.

Energies of orbitals in a metallic crystal

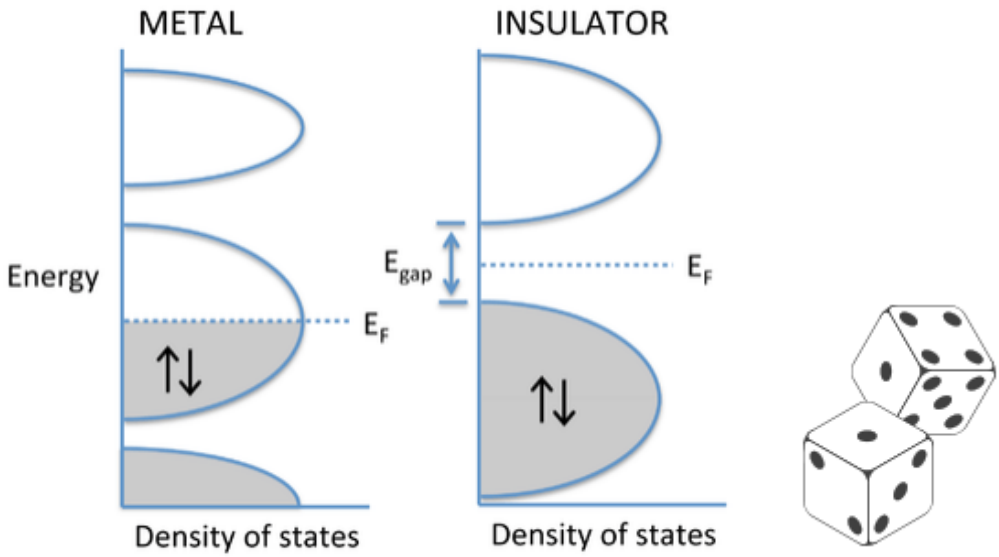
Electrons with long wavelengths do not "feel" the individual atoms in the lattice and so they behave as if they are *nearly free* (but confined to the crystal). Near the bottom of the band, the electron energy increases *parabolically* with the number of nodes (KE $\propto$ $\mathbf{n}^2$), since the momentum **p** is directly proportional to **n**. Because **p** is also directly proportional to **k**, we can write:

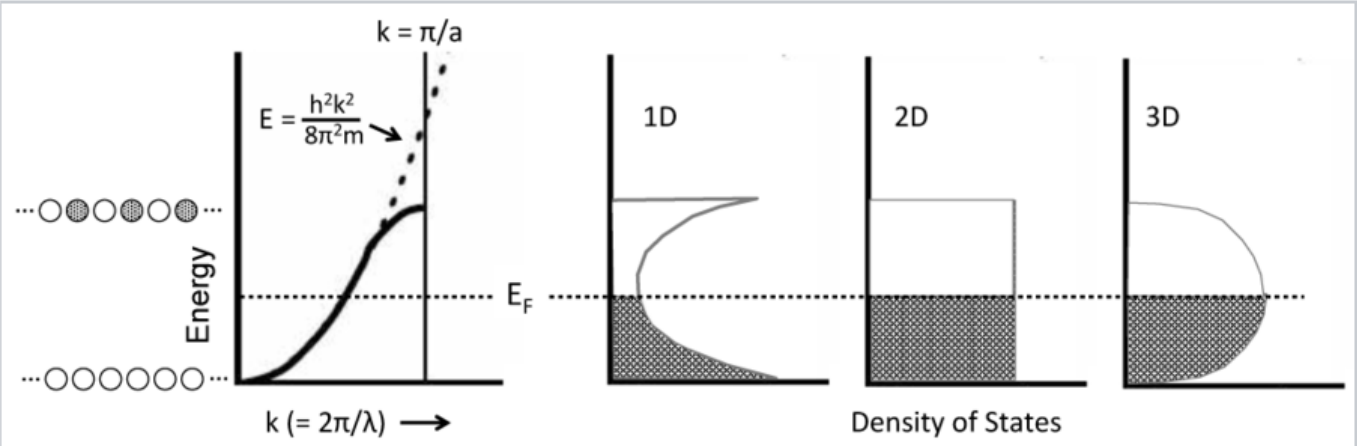
$$KE = \frac{p^2}{2m} = \frac{h^2k^2}{8\pi^2 m} \tag{4.3.5.3}$$

This parabolic relationship is followed as long as the electron wavelength is long compared to the distance between atoms. Near the top of the band, the wavelength becomes shorter and the electrons start to feel the positively charged atomic cores. In particular, the electrons prefer to have the maxima in their wavefunctions line up with the atomic cores, which is the most electrostatically favorable situation. The electron-atom attraction lowers the energy and causes the E vs. k curve to deviate from the parabolic behavior of a "free" electron as shown in the figure below.

Density of States (DOS)

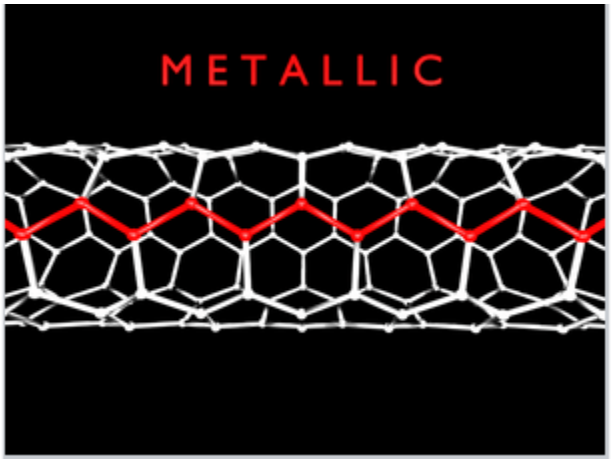
The density of states is defined as the number of orbitals per unit of energy within a band. Because of the parabolic relation between E and k, the density of states for a 1D metallic crystal is highest near the bottom and top of the energy band where the slope of the E vs. k curve is closest to zero. The shape of the DOS curve is different in crystals of higher dimensionality as shown in the figure in the left, because statistically there are more ways to make an orbital with N/2 nodes than there are with zero or N nodes. The situtation is analogous to the numbers you can make by rolling dice. With one die, the numbers 1-6 have equal probability. However, with two dice there is only one way to make a two (snake eyes) or a twelve (boxcars), but many ways to make a seven (a winner!).





Electrons in metals follow a parabolic dispersion curve, where the energy increases with the square of the wavenumber, k. Near the top of the band, the dispersion curve deviates from the parabolic dotted line. Because there is one MO for each value of k, the number of orbitals per unit energy (the density of states, DOS) is highest at the bottom and top of the band for a 1D chain of atoms. The density of states is constant with energy for a 2D crystal, and has a maximum in the middle of the band for a 3D crystal. At low temperature, all the MOs below the Fermi level E_F are occupied, and all the MOs above it are empty.

While most of the time we will talk about 3D crystals that have their maximum DOS near the middle of the energy band, there are examples of quasi-1D systems, such as carbon nanotubes. Metallic carbon nanotubes have strong optical absorption bands that correspond to transitions between the two regions of high DOS (the van Hove singularities) near the bottom and top of the bands.



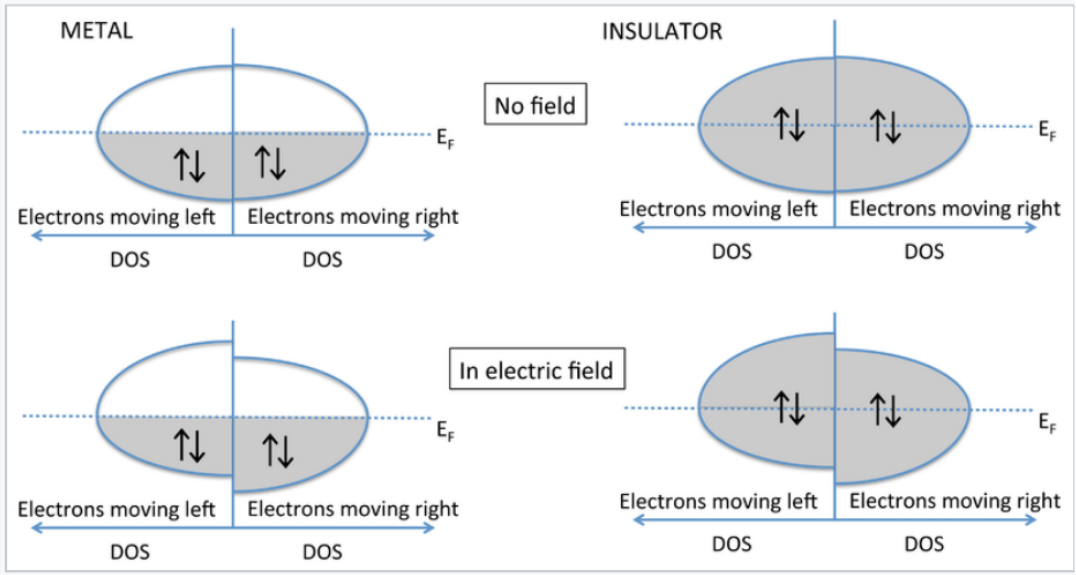
Single-walled carbon nanotubes with "armchair" chirality are metallic and have characteristic sharp absorption bands in the infrared. Prof. Millie Dresselhaus (below) did foundational research on the electronic properties of carbon nanotubes and other low-dimensional conductors.



Metals, semiconductors, and insulators

The degree to which bands fill determines whether a crystalline solid is a metal, semiconductor, or insulator. If the highest occupied molecular orbitals lie within a band - i.e., if the Fermi level E_F cuts through a band of orbitals - then the electrons are free to change their speed and direction in an electric field and the solid is metallic. However, if the solid contains just enough electrons to completely fill a band, and the next highest set of molecular orbitals is empty, then it is a semiconductor or insulator. In this case, there is an energy gap between the filled and empty bands, which are called the valence and conduction bands, respectively. Although the distinction is somewhat arbitrary, materials with a large gap (> 3 eV) are called insulators, and those with smaller gaps are called semiconductors. We will learn more about the properties of semiconductors in Chapter 10.

Why don't insulators conduct electricity? The energy vs. DOS diagram below shows what happens when an electric field is applied to a metal or an insulator. In this case we have changed the diagram to show explicitly the energies of electrons moving left and right. These energies are the same in the absence of an electric field. Once we apply a field (e.g., by putting a voltage across a metal wire), the electrons moving in the direction of the field have lower energy than those moving in the opposite direction. In the case of the metal, the populations of electrons moving with and against the electric field are different, and there is a net flow of current. Note that this can happen only when the Fermi level cuts through a partially filled band. With a semiconductor or insulator, the valence band is filled and the conduction band is empty. Applying an electric field changes the energies of electrons traveling with and against the field, but because the band is filled, the same number are going in both directions and there is no net current flow.



E vs. DOS diagrams comparing the behavior of metals and insulators in an applied electric field.

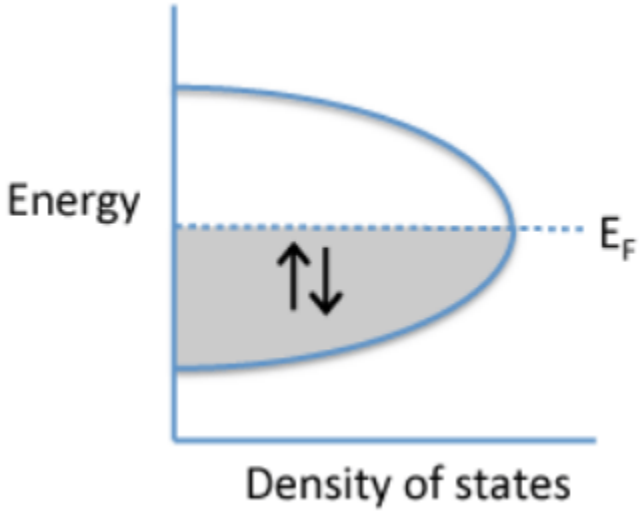
Note that in this picture, all the molecular orbitals extend over the entire crystal. The valence electrons are *delocalized,* even in the case of a semiconductor or insulator. However, there can be no net movement of electrons unless the band is partially filled.

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4.3.6: Conduction in Metals

In metals, the valence electrons are in molecular orbitals that extend over the entire crystal lattice. As we will learn in Chapter 7, metals are almost always crystalline and the individual crystal grains are typically micron size. This means that the spatial extent of the orbitals is *very large* compared to the size of the atoms or the unit cell. The diagram at the left shows a generic plot of electron energy vs. density of states for a metal such as Na, Cu, or Ag. In these cases, there are N orbitals for N electrons, and each orbital can accommodate two electrons. Therefore the Fermi level, which corresponds to the energy of the highest occupied MO at zero temperature, is somewhere in the middle of the band of orbitals. The energy level spacing between orbitals is very small compared to the thermal energy kT, so we can think of the orbitals as forming a continuous band.



Classically, if the electrons in this band were free to be thermally excited, we would expect them to have a specific heat of 3R per mole of electrons. However, experimentally we observe that C_p is only about 0.02 R per mole. This suggests that *only about 1%* of the electrons in the metal can be thermally excited at room temperature. However, essentially *all* of the valence electrons are free to move in the crystal and contribute to electrical conduction. To understand this apparent paradox, we need to recall that the electrons exist in *quantized energy levels*.

Because of quantization, electrons in metals have a Fermi-Dirac distribution of energies. In this distribution, most of the electrons are spin-paired, although the individual electrons in these pairs can be quite far apart since the orbitals extend over the entire crystal. A relatively small number of electrons at the top of the Fermi sea are unpaired by thermal excitation. This is the origin of the Pauli paramagnetism of metals.

How fast are electrons traveling in a typical metal? Because of the bell shape of the E vs. DOS curve, most of the electrons have E ≈ E_F. At the midpoint energy (E_F) of the band, the MO's have one node for every two atoms. We can calculate the de Broglie wavelength as twice the distance between nodes and thus:

> **λ = 4a** at the midpoint of the band.

where **a** is the interatomic spacing. Since a typical value of **a** is about 2 Å, we obtain the **de Broglie wavelength λ ≈ 8 Å**.

Using the de Broglie relation p = h/λ, we can write:

$$\mathbf{p} = \frac{\mathbf{h}}{\lambda} = \mathbf{m_e v_F} \tag{4.3.6.1}$$

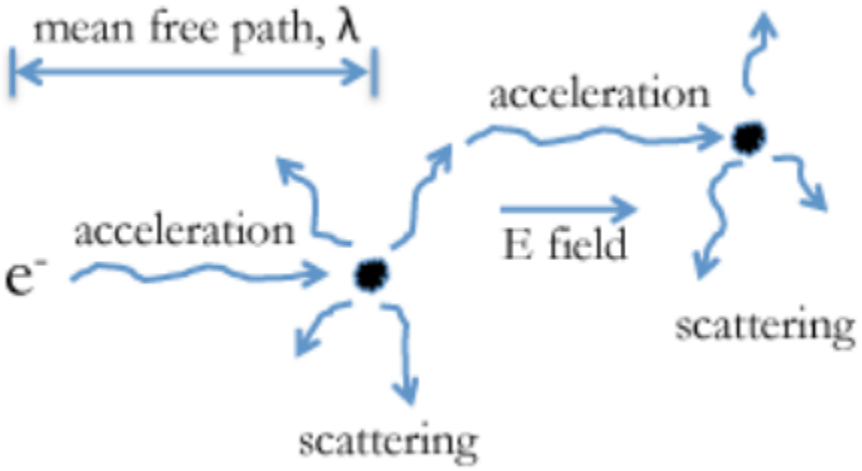
where $\mathbf{m_e}$ is the mass of the electron and $\mathbf{v_F}$ is the velocity of electrons with energy E_F.

Solving for $V_F = \frac{h}{m_e \lambda}$ we obtain $\mathbf{v_F} = \frac{(6.62\times10^{-34} Js)}{(9.1\times10^{-31} kg)(8\times10^{-10} m)} = \mathbf{1.0 \times 10^6 m/s}$

Experimental values of v_F are 1.07 x 10^6 and 1.39 x 10^6 m/s for Na and Ag, respectively, so our approximations are pretty good.

How fast are electrons moving in metals? Really, really fast!! **1,000,000 meters per second!** This is about 1/300 the speed of light, and about 3000 times the speed of sound in air (3 x 10^2 m/s).

However, the **drift velocity** of electrons in metals - the speed at which electrons move in applied electric field - is quite slow, on the order of 0.0001 m/s, or .01 cm/s. You can easily outrun an electron drifting in a metal, even if you have been drinking all night and have been personally reduced to a very slow crawl.



In order to understand the great disparity between the Fermi velocity and the drift velocity of electrons in metals, we need to consider a picture for the scattering of electrons, and their acceleration in an electric field, as shown at the left. If we apply a voltage across a metal (e.g., a metal wire), the electrons are subjected to an electric field **E**, which is the voltage divided by the length of the wire. This electric field exerts a force on the electron, causing it to accelerate. However, the electron is frequently scattered, mostly by phonons (lattice vibrations). Each time the electron is scattered its acceleration starts all over again. The time between scattering events is **τ** and the distance the electrons travel between scattering events is the **mean free path**, **λ**. (Note that this is NOT the same λ as the de Broglie wavelength, they just unfortunately have the same symbol!)

We can write the force on the electron as:

$$\mathbf{F} = \mathbf{eE} = \mathbf{m_e a} = \frac{\mathbf{m_e v_{drift}}}{\tau} \tag{4.3.6.2}$$

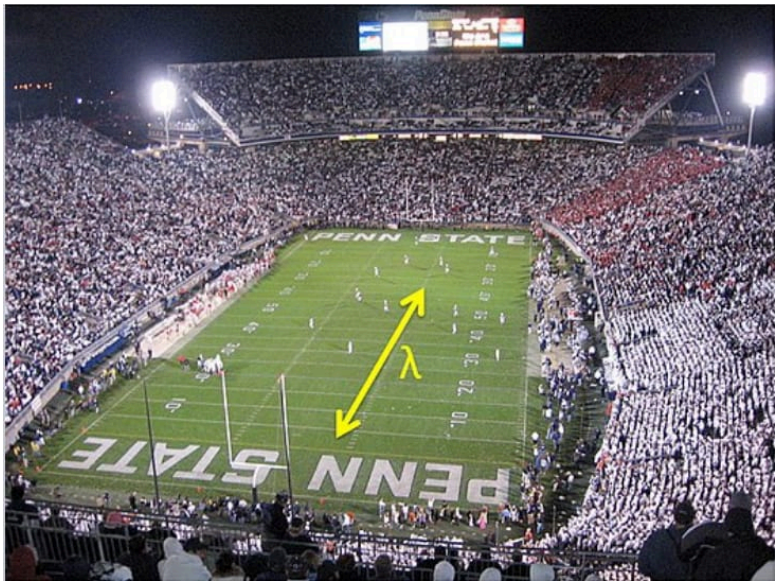
In this equation, **a** is the acceleration in the electric field, $\mathbf{m_e}$ is the mass, and v_{drift} is the **drift velocity** of the electron.

Experimentally, the mean free path is typically obtained by measuring the scattering time. For an electron in Cu metal at 300 K, the scattering time τ is about 2 x 10^{-14} s. From this we can calculate the mean free path as:

$$\lambda = \mathbf{v_{avg}}\tau \approx \mathbf{v_F}\tau = (1 \times 10^6 m/s)(2 \times 10^{-14}) = \mathbf{40nm} \tag{4.3.6.3}$$

The mean free path (40 nm = 400 Å) is quite long compared to the interatomic spacing (2 Å). To put it in perspective, if the interatomic spacing were scaled to the length of a football (0.3 m), the mean free path would be over half the length of the football field (60 m). Thus an electron travels a fairly long way between scattering events and scarcely notices the atomic structure of the metal in which it is traveling.

To summarize, electrons are traveling in metals at the Fermi velocity v_F, which is very, very fast (10^6 m/s), but the flux of electrons is the same in all directions. That is, they are *going nowhere fast*. In an electric field, a very small but directional *drift velocity* is superimposed on this fast random motion of valence electrons.



For ordinary metals, the mean free path of a valence electron (λ) is quite long relative to the interatomic spacing, represented in this analogy as the length of a football.

We can calculate the drift velocity of electrons as the acceleration in the electric field times the scattering time:

From F = ma, we obtain the acceleration (a) as:

$$\mathbf{a} = \frac{\mathbf{F}}{\mathbf{m_e}} = \frac{\mathbf{eE}}{\mathbf{m_e}} \tag{4.3.6.4}$$

And thus,

$$\mathbf{v_{drift}} = \mathbf{a}\tau = \frac{\mathbf{eE}\tau}{\mathbf{m_e}} \tag{4.3.6.5}$$

If we divide both sides of this equation by the magnitude of the electric field (**E**), we obtain the **mobility (μ)**:

$$\mu = \frac{\mathbf{v_{drift}}}{\mathbf{E}} = \frac{\mathbf{e}\tau}{\mathbf{m_e}} \tag{4.3.6.6}$$

μ has units of velocity/field = cm/s / V/cm = cm^2/Vs

An important consequence of the calculation of v_{drift} is **Ohm's Law**, V = iR. From the equations above, we can see that the drift velocity increases linearly with the applied electric field. The drift velocity (cm/s) is proportional to the current (i, coul/s), and the electric field (E, V/cm) is proportional to the voltage (V):

$$\mathbf{Current\ (i)} = \mathbf{nev_{drift}} \times \mathbf{area} \tag{4.3.6.7}$$

$$\mathbf{Voltage\ (V)} = \mathbf{E} \times \mathbf{length} \tag{4.3.6.8}$$

Here **n** is the density of valence electrons (#/cm^3) and **e** is the charge of the electron (coul). Combining these equations with our equation for v_{drift} we obtain:

$$V = i(\frac{m_e}{ne^2\tau})\frac{(}{length}area) = iR \tag{4.3.6.9}$$

Thus, V = iR, where R is the combination of the two terms in parentheses. The first of these is the **resistivity**, ρ, and the second is a geometrical factor.

The **conductivity (σ)** of a metal, which is the inverse of ρ, is proportional to μ, which in turn is proportional to τ (and λ):

$$\sigma = \mathrm{ne}\mu = \frac{\mathrm{ne}^2\tau}{\mathrm{m_e}} \tag{4.3.6.10}$$

We can use this equation to work out the conductivity of a specific metal (Cu), for which n = 8.5 x 10^{22} cm^{-3} and τ = 2 x 10^{-14} s. Putting in the numbers for m_e and e, we obtain σ = 7 x 10^5 Ω^{-1} cm^{-1} for Cu, in good agreement with the measured value (6 x 10^5 $\Omega^{-1}cm^{-1}$).

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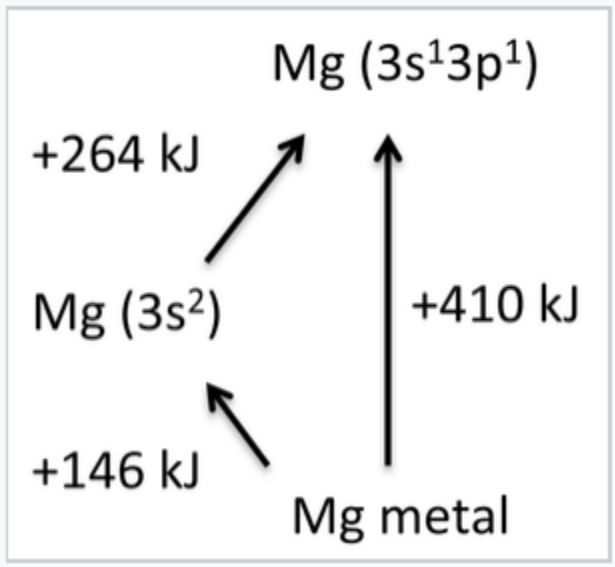
4.3.7: Atomic Orbitals and Magnetism

The MO picture we developed in Section 6.4 helps us rationalize the electrical conductivity of Na ($3s^1$), but what about Mg, which (as an atom in the gas phase) has a $3s^2$ electronic configuration? The two valence electrons are spin-paired in atomic Mg, as they are in the helium atom ($1s^2$). When the 3s orbitals of Mg combine to form a band, we would expect the band to be completely filled, since Mg has two electrons per orbital. By this reasoning, solid Mg should be an insulator. But Mg has all the properties of a metal: high electrical and thermal conductivity, metallic luster, malleability, etc. In this case the 3s and 3p bands are sufficiently broad (because of strong orbital overlap between Mg atoms) that they form a continuous band. This band, which contains a total of four orbitals (one 3s and three 3p) per atom, is only partially filled by the two valence electrons.



Mg crystals

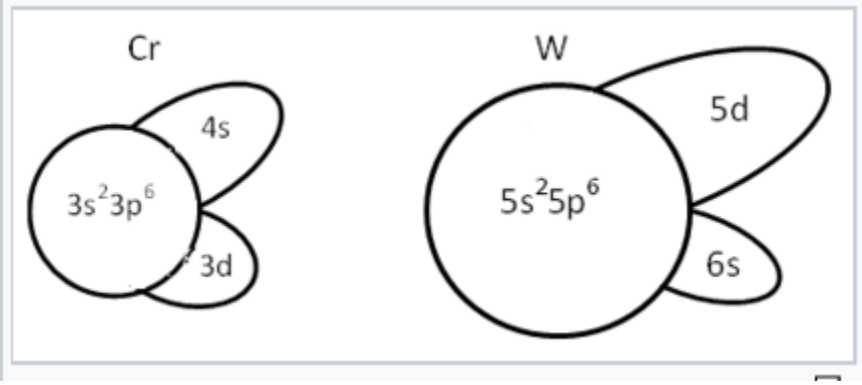
Another way to think about this is to consider the **hybridization** of the 3s and 3p electrons in Mg. Hybridization requires promotion from the $3s^2 3p^0$ ground state of an Mg atom to a $3s^1 3p^1$ excited state. The **promotion energy** (+264 kJ/mol) is more than offset by the **bonding energy** (-410 kJ/mol), the energy released when gaseous atoms in the excited state condense to form the metallic solid. The heat of vaporization, or the cohesive energy of a metal, is the difference between the bonding energy and the promotion energy. Experimentally, we can measure the vaporization energy (+146 kJ/mol) and the promotion energy and use them to calculate the bonding energy. From this we learn that each s or p electron is worth about 200 kJ/mol in bonding energy. The concepts of promotion energy and bonding energy are very useful in rationalizing periodic trends in the bond strengths and magnetic properties of metals, which are described below.



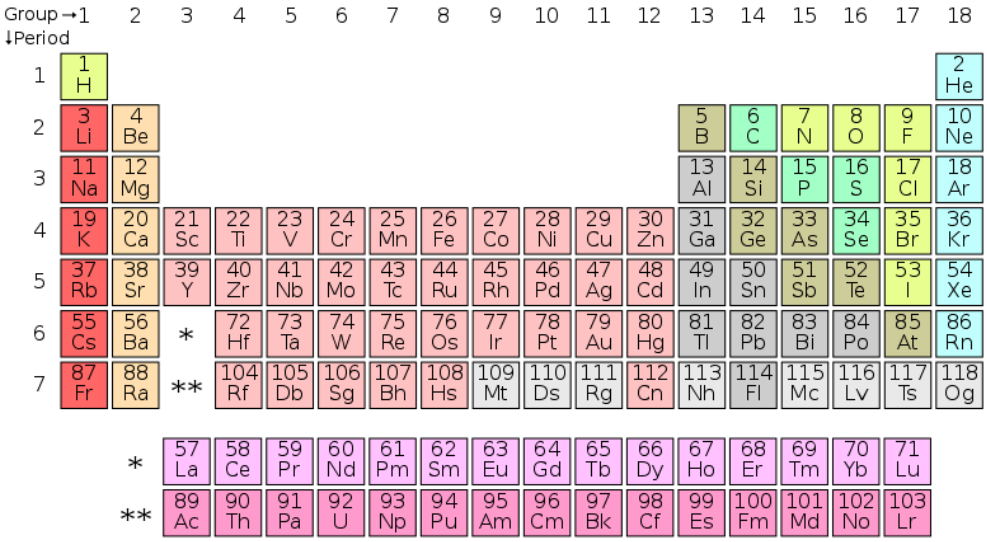
The cohesive energy of Mg metal is the difference between the bonding and promotion energies. The ground state of a gas phase Mg atom is $[Ar]3s^2$, but it can be promoted to the $[Ar]3s^13p^1$ state, which is 264 kJ/mol above the ground state. Mg uses two electrons per atom to make bonds, and the sublimation energy of the metal is 146 kJ/mol.

Periodic trends in d-electron bonding

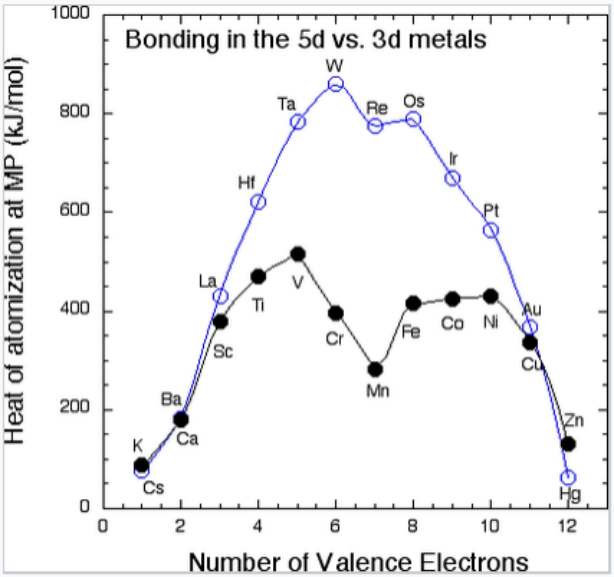
While electrons in s and p orbitals tend to form strong bonds, d-electron bonds can be strong or weak. There are two important periodic trends that are related to orbital size and orbital overlap. As we move *across the periodic table* (Sc - Ti - V - Cr - Fe), the *d orbitals contract* because of increasing nuclear charge. Moving *down the periodic table* (V - Nb - Ta), the *d orbitals expand* because of the increase in principal quantum number. These trends explain the distinct behavior of the 3d elements relative to those in the 4d and 5d series. In the 3d series, the contraction of orbitals affects the ability of the d electrons to contribute to bonding. Past V in the first row of the transition metals, the 3d electrons become much less effective in bonding because they overlap weakly with their neighbors. Weak overlap of 3d orbitals gives narrow d-bands and results in the emergence of magnetic properties as discussed below.



Schematic representation of the sizes of different orbitals of Cr and W. In the first transition series, shielding of the 3d orbitals is poor. Therefore the 4s and 4p orbitals are more effective in bonding than the 3d. In the third transition series, the situation is reversed. The increased nuclear charge is felt most strongly by the 6s, which takes on the character of an inert electron pair. The 5d orbitals are well shielded by the complete n=4 shell so they have good orbital overlap with neighboring atoms.

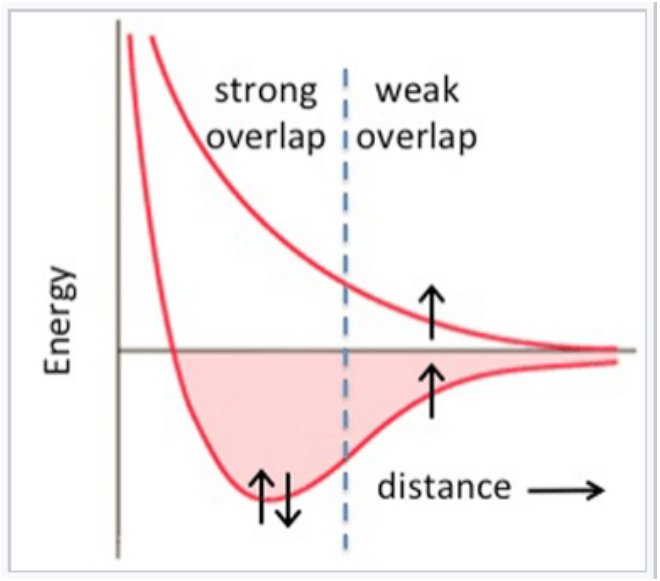


In the **4d and 5d series**, a plot of cohesive energy vs. number of valence electrons (below left) has a "volcano" shape that is peaked at the elements Mo and W ($5s^1 4d^5$ and $6s^1 5d^5$, respectively). The number of bonding electrons, and therefore the bonding energy, increases steadily going from Rb to Mo in the 4d series, and from Cs to W in the 5d series. Mo and W have the most bonding energy because they can use all six of their valence electrons in bonding without promotion. Elements past Mo and W have more d electrons, but some of them are spin paired and so some promotion energy is needed to prepare these electrons for bonding. For example, Pt metal must be promoted from the $6s^1 5d^9$ atomic ground state to $6s^1 5d^7 6p^2$ in order to make six bonds per atom, and the energy cost of promoting electrons from the 5d to the 6p orbitals is reflected in the net bonding energy. Because of their strong bonding energy, elements in the middle of the 4d and 5d series have very high melting points. We do not see magnetism in the 4d or 5d metals or their alloys because orbital overlap is strong and the bonding energy exceeds the electron pairing energy.



The heat of vaporization (the cohesive energy) of metals in the 3d and 5d series, measured at the melting point of the metal.

The **3d elements** (Sc through Zn) are distinctly different from the 4d and 5d elements in their bonding (and consequently in their magnetic properties). In the 3d series, we see the expected increase in cohesive energy going from Ca ($4s^2$) to Sc ($4s^23d^1$) to Ti ($4s^23d^2$) to V ($4s^23d^3$), but then something very odd happens. The 3d series has a "crater" in the cohesive energy plot where there was a peak in the 5d series. The cohesive energy actually *decreases* going from V to Mn, even though the number of valence electrons is increasing. We can explain this effect by remembering that the 3d orbitals are progressively contracting as more protons are added to the nucleus. For elements beyond V, the orbital overlap is so poor that the 3d electrons are no longer effective in bonding, and the valence electrons begin to unpair. At this point the elements become **magnetic**. Depending on the way the spins order, metals and alloys in this part of the periodic table can be ferromagnetic (spins on neighboring atoms aligned parallel, as in the case of Fe or Ni) or antiferromagnetic (spins on neighboring atoms antiparallel, as in the case of Mn). We have seen the trade-off between orbital overlap and magnetism before (in Chapter 5) in the context of paramagnetic transition metal complexes. It is worth recalling that this behavior is predicted in the energy vs. distance diagram of the hydrogen atom (from Chapter 2). At short interatomic distances (or with strong overlap between atomic orbitals), the spins of the electrons pair and a bond is formed. Unpairing the electrons becomes favorable at larger interatomic distances where the overlap between orbitals is poor.



With strong overlap between orbitals of neighboring atoms, the bonding energy exceeds the pairing energy and electrons spin-pair. With weaker overlap, bonding is weak and spins unpair, resulting in magnetic behavior.

Interestingly, many alloys of the **4f elements** (the lanthanides) are also magnetic because the 4f orbitals, like the 3d orbitals, are poorly shielded from the nuclear charge and are ineffective in bonding. Strong permanent magnets often contain alloys of Nd, Sm, or Y, usually with magnetic 3d elements such as Fe and Co.

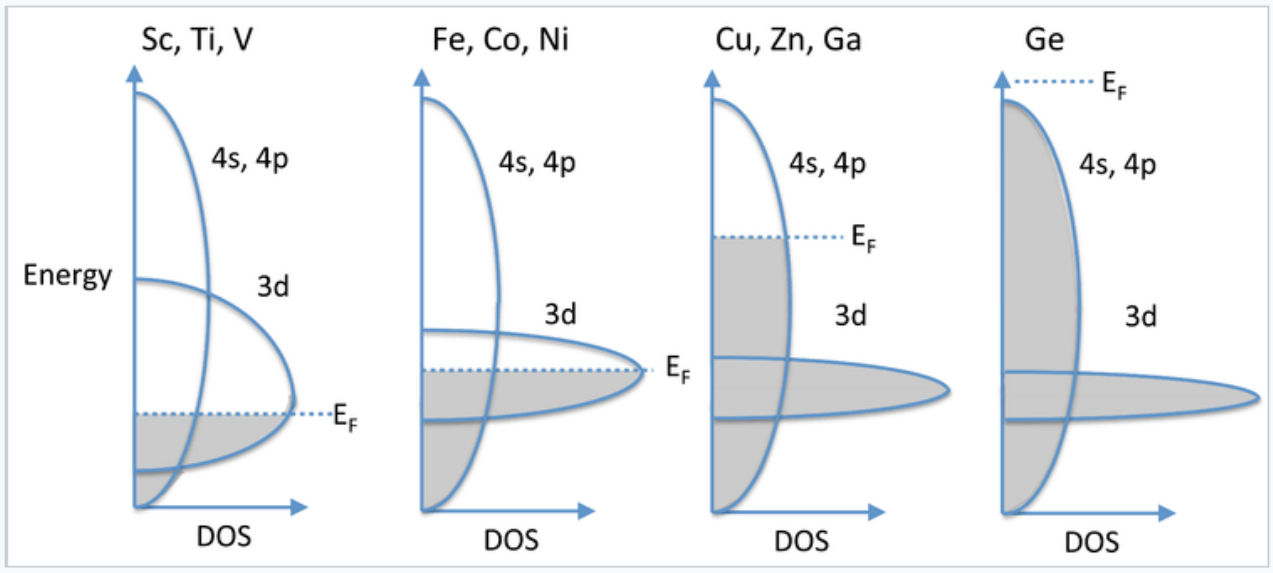
Because the 4f orbitals are contracted and not very effective in bonding, other physical properties of the lanthanides can also be affected. For example, it has been proposed that oxides of the 4f elements have weak surface interactions with polar molecules such as water because of f-orbital contraction. Experimentally, CeO_2, Er_2O_3, and Ho_2O_3 are observed to be hydrophobic, whereas main group and early transition metal oxides (e.g., Al_2O_3, SiO_2, TiO_2) are quite hydrophilic.[1]

Late transition metal alloys

Although the bonding in the 5d series follows a "normal" volcano plot, the situation is a bit more complex for alloys of Re, Os, Ir, Pt, and Au. There is strong overlap between the 5d orbitals, but because these elements contain more than five d-electrons per atom, they cannot make as many bonds as 4d or 5d elements with half-filled d-shells such as Mo or W. This progressive filling of the d-band explains the steady decrease in bonding energy going from Os to Au. Pt and Au are both soft metals with relatively low heats of vaporization. However, these metals (especially Ir, Pt, and Au) can combine with early transition metals to form stable alloys with very negative heats of formation and high melting points. For example, ZrC and Pt react to form a number of stable alloys (ZrPt, Zr_9Pt_{11}, Zr_3Pt_4, $ZrPt_3$)[2] plus carbon. This reactivity is unusual because we normally think of Pt as a "noble" (i.e., unreactive) metal, and because ZrC is a very stable, refractory metal carbide. The favorable combination of early and late transition metals has been interpreted as arising from a d-electron "acid-base" interaction.[3] For example, in $HfPt_3$, Hf is the "acid" with an electron configuration of $6s^25d^2$, while Pt is the "base" with the electron configuration of $6s^15d^9$. They combine to create a stable "salt" product with a filled 5d electron configuration without promoting any electrons to higher orbitals. The implication is that Pt donates d-electrons to the "d-acid," Zr or Hf. However, electronic structure calculations on model compounds show that much of the bonding energy in ZrPt and $ZrPt_3$ arises from electron transfer from Zr to Pt (not the other way around) and the polarity of the resulting metal-metal bonds.[4] Regardless of the source of their stability, some early-late transition metal alloys are of particular interest for use in catalysis. For example, the alloy $ScPt_3$ is a good catalyst for oxygen reduction in fuel cells. Even though Sc is an active metal that is easily oxidized, it is stabilized in the aqueous acid environment of the fuel cell by its strong interaction with Pt.[5]

Filling of the 3d and 4s,4p bands

In the 3d series, we see magnetic behavior for elements and alloys between Cr and Ni. Past Ni, the elements (Cu, Zn, Ga,...) are no longer magnetic and they are very good electrical conductors, implying that their valence electrons are highly delocalized. We can understand this behavior by considering the overlap of 4s, 4p, and 3d orbitals, all of which are close in energy. The 4s and 4p have strong overlap and form a broad, continuous band. On the other hand, the 3d electrons are contracted and form a relatively narrow band. Progressing from the early 3d elements (Sc, Ti, V), we begin to fill the 3d orbitals, which are not yet so contracted that they cannot contribute to bonding. Thus, the valence electrons in Sc, Ti, and V are all spin-paired, except for a small number near the Fermi level that give rise to a weak Pauli paramagnetism. Moving across the 3d series to the magnetic elements (Fe, Co, Ni), the d-orbitals are now so contracted that their electrons unpair and we see cooperative ordering of spins (ferromagnetism and antiferromagnetism). Referring to the band diagram at the right, the 3d band is only partially filled and the Fermi level cuts through it. For Cu, Zn, and Ga, the 3d orbitals are even more contracted and the 3d band is thus more narrow, but now it is completely filled and the Fermi level is in the 4s,4p band. The strong orbital overlap in these bands results in spin pairing and a high degree of electron delocalization. Consequently, metals in this part of the periodic table (Cu, Ag) are diamagnetic and are among the best electrical conductors at room temperature. Finally, at Ge, the 4s,4p band is completely filled and the solid is a semiconductor.



Progressive filling of the 3d and 4s,4p bands going across the periodic table from Sc to Ge.

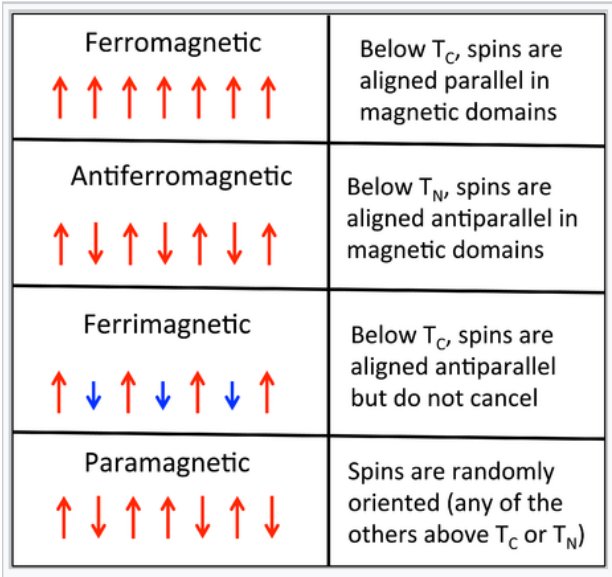
Materials are classified as diamagnetic if they contain no unpaired electrons. Diamagnetic substances are very weakly repelled from an inhomogeneous magnetic field. As we learned in Chapter 5, molecules or ions that have unpaired spins are paramagnetic and are attracted to a magnet, i.e., they move towards the high field region of an inhomogeneous field. This attractive force results from the alignment of spins with the field, but in the case of paramagnetism each molecule acts independently. In metals, alloys, oxides, and other solid state compounds, the unpaired spins interact strongly with each other and can order spontaneously, resulting in the cooperative magnetic phenomena described below.

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4.3.8: Ferro-, Ferri- and Antiferromagnetism

The magnetism of metals and other materials are determined by the orbital and spin motions of the unpaired electrons and the way in which unpaired electrons align with each other. All magnetic substances are **paramagnetic** at sufficiently high temperature, where the thermal energy (kT) exceeds the interaction energy between spins on neighboring atoms. Below a certain critical temperature, spins can adopt different kinds of ordered arrangements.



A pictorial description of the ordering of spins in ferromagnetism, antiferromagnetism, ferrimagnetism, and paramagnetism

Let's begin by considering an individual atom in the bcc structure of iron metal. Fe is in group VIIIb of the periodic table, so it has eight valence electrons. The atom is promoted to the $4s^1 3d^7$ state in order to make bonds. A localized picture of the d-electrons for an individual iron atom might look like this:



Since each unpaired electron has a spin moment of 1/2, the total spin angular momentum, **S**, for this atom is:

$S = 3\frac{1}{2} = \frac{3}{2}$ (in units of h/2π)

We can think of each Fe atom in the solid as a little bar magnet with a spin-only moment **S** of 3/2. The spin moments of neigboring atoms can align in parallel (↑ ↑), antiparallel (↑ ↓), or random fashion. In bcc Fe, the tendency is to align parallel because of the positive sign of the exchange interaction. This results in **ferromagnetic** ordering, in which all the spins within a magnetic domain (typically hundreds of unit cells in width) have the same orientation, as shown in the figure at the right. Conversely, a negative exchange interaction between neighboring atoms in bcc Cr results in **antiferromagnetic** ordering. A third arrangement, **ferrimagnetic** ordering, results from an antiparallel alignment of spins on neighboring atoms when the magnetic moments of the neighbors are unequal. In this case, the spin moments do not cancel and there is a net magnetization. The ordering mechanism is like that of an antiferromagnetic solid, but the magnetic properties resemble those of a ferromagnet. Ferrimagnetic ordering is most common in metal oxides, as we will learn in Chapter 7.

Magnetization and susceptibility

The **magnetic susceptibility**, **χ**, of a solid depends on the ordering of spins. Paramagnetic, ferromagnetic, antiferromagnetic, and ferrimagnetic solids all have χ > 0, but the magnitude of their susceptibility varies with the kind of ordering and with temperature. We will see these kinds of magnetic ordering primarily among the **3d** and **4f** elements and their alloys and compounds. For example, Fe, Co, Ni, $Nd_2Fe_{14}B$, $SmCo_5$, and YCo_5 are all ferromagnets, Cr and MnO are antiferromagnets, and Fe_3O_4 and $CoFe_2O_4$ are ferrimagnets. Diamagnetic compounds have a weak *negative* susceptibility (χ < 0).

Definitions

- H = applied magnetic field (units: Henry (H))
- B = induced magnetic field in a material (units: Tesla (T))
- M = magnetization, which represents the magnetic moments within a material in the presence of an external field H.

Magnetic susceptibility χ = M/H

Usually, χ is given in *molar* units in the *cgs system*:

χ_M = molar susceptibility (units: cm^3/mol)

Typical values of χ_M:

Compound	**Type of Magnetism**	**χ at 300K (cm^3/mol)**
SiO_2	Diamagnetic	-3×10^{-4}
Pt metal	Pauli paramagnetic	$+2 \times 10^{-4}$
$Gd_2(SO_4)_3 \cdot 8H_2O$	Paramagnetic	$+5 \times 10^{-2}$
Ni-Fe alloy	Ferromagnetic	$+10^4 - 10^6$

To correlate χ with the number of unpaired electrons in a compound, we first correct for the small diamagnetic contribution of the core electrons:

$$\chi^{corr} = \chi^{obs} - \chi^{diamagnetic\ cores} \tag{4.3.8.1}$$

Susceptibility of paramagnets

For a paramagnetic substance,

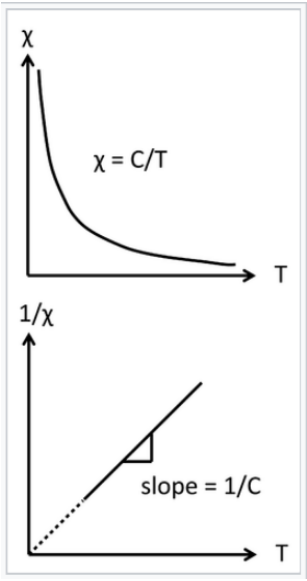
$$\chi_M^{corr} = \frac{C}{T} \tag{4.3.8.2}$$

The inverse relationship between the magnetic susceptibility and T, the absolute temperature, is called **Curie's Law**, and the proportionality constant C is the **Curie constant**:

$$C = \frac{N_A}{3k_B}\mu_{eff}^2 \tag{4.3.8.3}$$

Note that C is not a "constant" in the usual sense, because it depends on μ_{eff}, the **effective magnetic moment** of the molecule or ion, which in turn depends on its number of unpaired electrons:

$$\mu_{eff} = \sqrt{n(n+2)}\mu_B \tag{4.3.8.4}$$



Curie law behavior of a paramagnet. A plot of 1/χ vs. absolute temperature is a straight line, with a slope of 1/C and an intercept of zero.

Here μ_B is the Bohr magneton, a physical constant defined as $\mu_B = eh/4\pi m_e = 9.274 \times 10^{-21}$ erg/gauss (in cgs units).

In cgs units, we can combine physical constants,

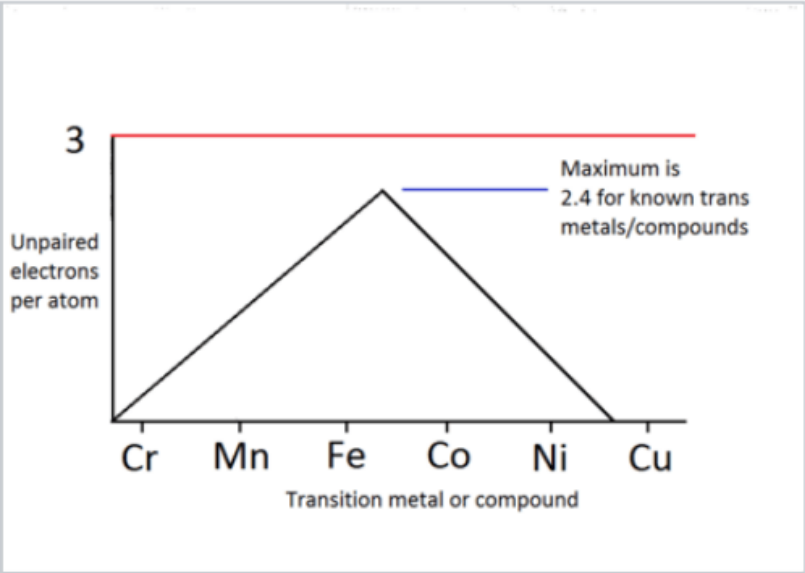
$$\frac{N_A}{3k_B}\mu_B^2 = .125 \tag{4.3.8.5}$$

Combining these equations, we obtain

$$\chi_M^{corr} = \frac{.125}{T}(\frac{\mu_{eff}}{\mu_B})^2 \tag{4.3.8.6}$$

These equations relate the molar susceptibility, a bulk quantity that can be measured with a magnetometer, to μ_{eff}, a quantity that can be calculated from the number of unpaired electrons, n. Two important points to note about this formula are:

- The magnetic susceptibility is inversely proportional to the absolute temperature, with a proportionality constant C (Curie's Law)
- So far we are talking only about paramagnetic substances, where there is no interaction between neighboring atoms.



Number of unpaired electrons per atom, determined from Curie constants of transition metals and their 1:1 alloys.

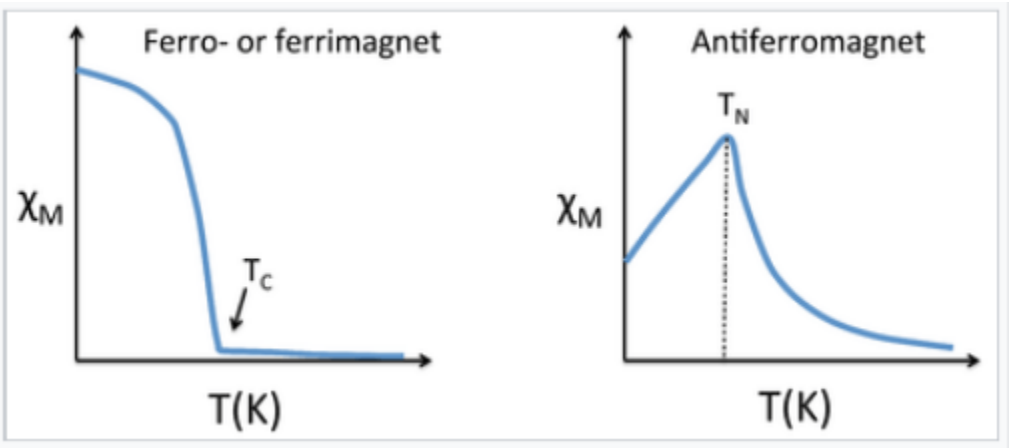
Returning to the isolated Fe atom with its three unpaired electrons, we can measure the Curie constant for iron metal (above the temperature of its transition to a paramagnetic solid) and compare it to the calculation of μ_{eff}. Since n = 3, we calculate:

$$\mu_{eff} = \sqrt{(3)(5)}\mu_B = 3.87\mu_B \tag{4.3.8.7}$$

The plot at the right shows the number of unpaired electrons per atom, calculated from measured Curie constants, for the magnetic elements and 1:1 alloys in the 3d series. The plot peaks at a value of 2.4 spins per atom, slightly lower than we calculated for an isolated iron atom. This reflects that fact that there is some pairing of d-electrons, i.e., that they do contribute somewhat to bonding in this part of the periodic table.

Susceptibility of ferro-, ferri-, and antiferromagnets

Below a certain critical temperature, the spins of a solid paramagnetic substance order and the susceptibility deviates from simple Curie-law behavior. Because the ordering depends on the short-range exchange interaction, this critical temperature varies widely. Metals and alloys in the 3d series tend to have high critical temperatures because the atoms are directly bonded to each other and the interaction is strong. For example, Fe and Co have critical temperatures (also called the Curie temperature, T_c, for ferromagnetic substances) of 1043 and 1400 K, respectively. The Curie temperature is determined by the strength of the magnetic exchange interaction and by the number of unpaired electrons per atom. The number of unpaired electrons peaks between Fe and Co as the d-band is filled, and the exchange interaction is stronger for Co than for Fe. In contrast to ferromagnetic metals and alloys, paramagnetic salts of transition metal ions typically have critical temperatures below 1K because the magnetic ions are not directly bonded to each other and thus their spins are very weakly coupled in the solid state. For example, in gadolinium sulfate, the paramagnetic Gd^{3+} ions are isolated from each other by SO_4^{2-} ions.

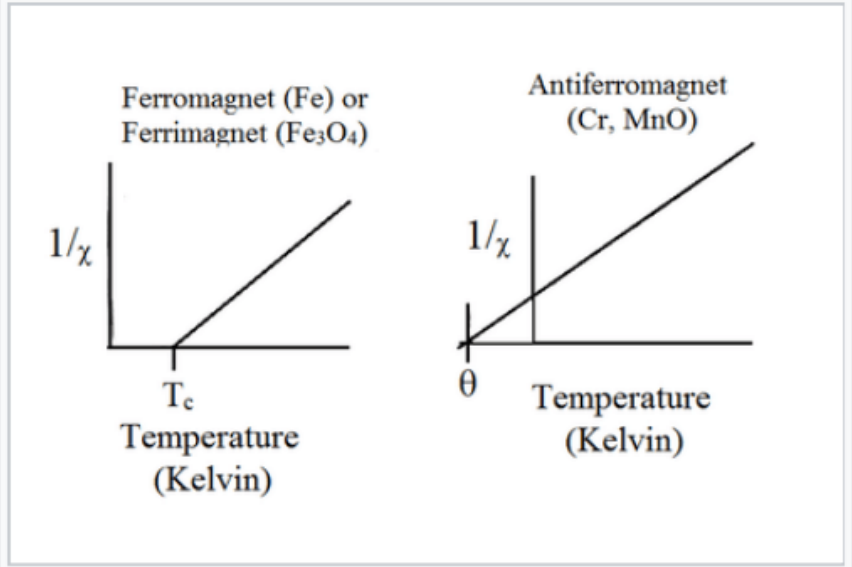


Magnetic susceptibility vs temperature (Kelvin) for ferrimagnetic, ferromagnetic, and antiferromagnetic materials

Above the critical temperature T_C, **ferromagnetic** compounds become paramagnetic and obey the **Curie-Weiss law:**

$$\chi = \frac{C}{T - T_c} \tag{4.3.8.8}$$

This is similar to the Curie law, except that the plot of 1/χ vs. T is shifted to a positive intercept T_C on the temperature axis. This reflects the fact that ferromagnetic materials (in their paramagnetic state) have a greater tendency for their spins to align in a magnetic field than an ordinary paramagnet in which the spins do not interact with each other. Ferrimagnets follow the same kind of ordering behavior. Typical plots of χ vs. T and 1/χ vs. T for ferro-/ferrimagnets are shown above and below.



Plots of 1/χ vs. T for ferromagnets, ferrimagnets, and antiferromagnets.

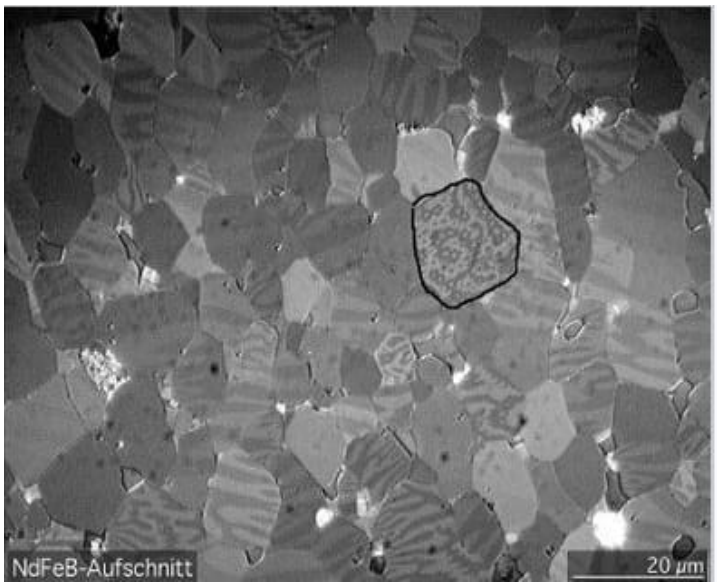
Antiferromagnetic solids are also paramagnetic above a critical temperature, which is called the Néel temperature, T_N. For antiferromagnets, χ reaches a maximum at T_N and is smaller at higher temperature (where the paramagnetic spins are further disordered by thermal energy) and at lower temperature (where the spins pair up). Typically, antiferromagnets retain some positive susceptibility even at very low temperature because of canting of their paired spins. However the maximum value of χ is much

lower for an antiferromagnet than it is for a ferro- or ferrimagnet. The Curie-Weiss law is also modified for an antiferromagnet, reflecting the tendency of spins (in the paramagnetic state above T_N) to resist parallel ordering. A plot of $1/\chi$ vs. T intercepts the temperature axis at a negative temperature, $-\theta$, and the Curie-Weiss law becomes:

$$\chi = \frac{C}{T + \theta} \tag{4.3.8.9}$$

Ordering of spins below T_C

Below T_C, the spins align spontaneously in ferro- and ferrimagnets. Complex magnetization behavior is observed that depends on the history of the sample. For example, if a ferromagnetic material is cooled in the absence of an applied magnetic field, it forms a mosaic structure of magnetic domains that each have internally aligned spins. However, neighboring domains tend to align the opposite way in order to minimize the total energy of the system. This is illustrated in the figure at the left for a Nd-Fe-B magnet. The sample consists of 5-10 μm wide crystal grains that can be easily distinguished by the sharp boundaries in the image. Within each grain are a series of lighter and darker stripes (imaged by using the optical Kerr effect) that are ferromagnetic domains with opposite orientations. Averaged over the whole sample, these domains have random orientation so the net magnetization is zero.



Microcrystalline grains within a piece of $Nd_2Fe_{14}B$ (the alloy used in neodymium magnets) with magnetic domains made visible with a Kerr microscope. The domains are the light and dark stripes visible within each grain.

When a sample like this one is magnetized (i.e., exposed to a strong magnetic field), the domain walls move and the favorably aligned domains grow at the expense of those with the opposite orientation. This transformation can be seen in real time in the Kerr microscope. The domain walls are typically hundreds of atoms wide, so movement of a domain wall involves a cooperative tilting of spin orientation (analogous to "the wave" in a sports stadium) and is a relatively low energy process.

The movement of domain walls in a grain of silicon steel is driven in this movie by increasing the external magnetic field in the "downward" direction, and is imaged using a Kerr microscope. White areas are domains with their magnetization directed up, dark areas - which eventually comprise the entire grain - are domains with their magnetization directed down.

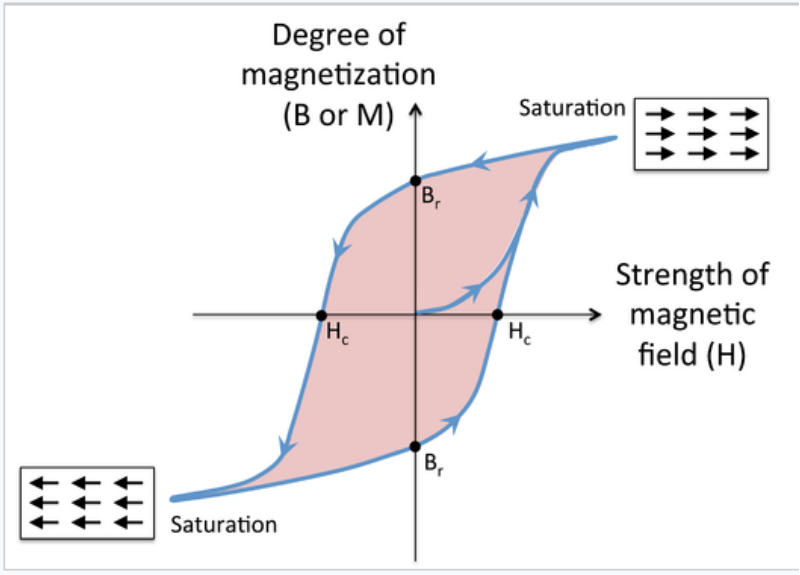
The process of magnetization moves the solid away from its lowest energy state (random domain orientation), so magnetization involves input of energy. When the external magnetic field is removed, the domain walls relax somewhat, but the solid (especially

in the case of a "hard" magnet) can retain much of its magnetization. If you have ever magnetized a nail or a paper clip by using a permanent magnet, what you were doing was moving the walls of the magnetic domains inside the ferromagnet. The object thereafter retains the "memory" of its magnetization. However, annealing a permanent magnet destroys the magnetization by returning the system to its lowest energy state in which all the magnetic domains cancel each other.



Rotation of orientation and increase in size of magnetic domains in response to an externally applied magnetic field.

Magnetic hysteresis. Cycling a ferro- or ferrimagnetic material in a magnetic field results in hysteresis in the magnetization of the material, as shown in the figure at the left. At the beginning, the magnetization is zero, but it begins to rise rapidly as the magnetic field is applied. At high field, the magnetic domains are aligned and the magnetization is said to be saturated. When the field is removed, a certain **remanent magnetization** (indicated as the point $\mathbf{B_r}$ on the graph) is retained, i.e., the material is magnetized. Applying a field in the opposite direction begins to orient the magnetic domains in the other direction, and at a field $\mathbf{H_c}$ (the **coercive field**), the magnetization of the sample is reduced to zero. Eventually the material reaches saturation in the opposite direction, and when the field is removed again, it has remanent magnetization Br, but in the opposite direction. As the field continues to reverse, the magnet follows the hysteresis loop as indicated by the arrows. The area of colored region inside the loop is proportional to the magnetic work done in each cycle. When the field cycles rapidly (for example, in the core of a transformer, or in read-write cycles of a magnetic disk) this work is turned into heat.



Magnetization of a ferro- or ferrimagnet vs. applied magnetic field H. Starting at the origin, the upward curve is the initial magnetization curve. The downward curve after saturation, along with the lower return curve, form the main loop. The intercepts Hc and Br are the coercivity and remanent magnetization.

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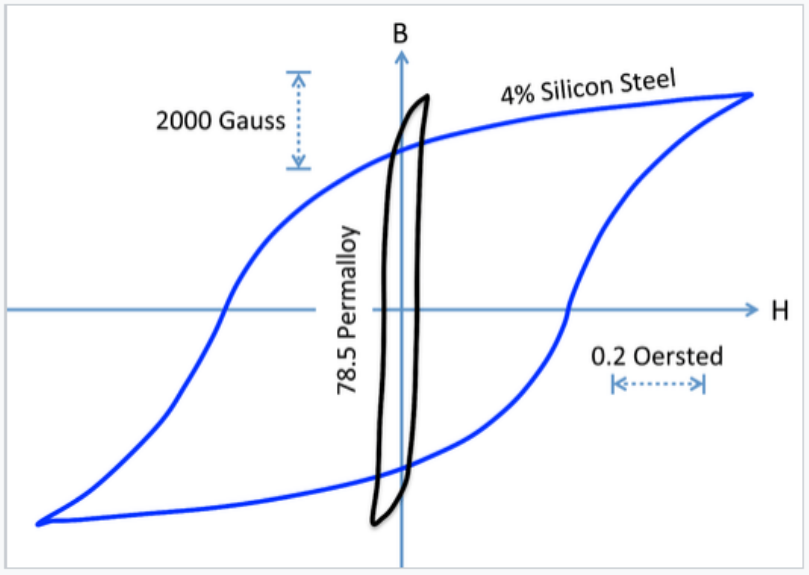
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4.3.9: Hard and Soft Magnets

Whether a ferro- or ferrimagnetic material is a **hard** or a **soft magnet** depends on the strength of the magnetic field needed to align the magnetic domains. This property is characterized by $\mathbf{H_c}$, the coercivity. Hard magnets have a high coercivity (H_c), and thus retain their magnetization in the absence of an applied field, whereas soft magnets have low values.

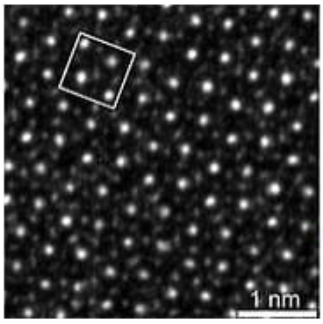
The figure at the right compares hysteresis loops for hard and soft magnets. Recall that the energy dissipated in magnetizing and demagnetizing the material is proportional to the area of the hysteresis loop. We can see that soft magnets, while they can achieve a high value of B_{sat}, dissipate relatively little energy in the loop. This makes **soft magnets** preferable for use in **transformer cores**, where the field is switched rapidly. **Permalloy**, an alloy consisting of about 20% Fe and 80% Ni, is a soft magnet that has very high magnetic permeability μ (i.e., a large maximum slope of the B vs. H curve) and a very narrow hysteresis loop.

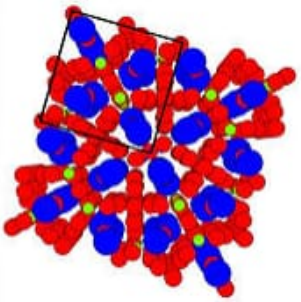
Some materials, such as iron metal, can exist as either hard or soft magnets. Whether bcc iron is a hard or soft magnet depends on the crystal grain size. When crystal grains in iron are sub-micron size, and comparable to the size of the magnetic domains, then the magnetic domains are pinned by crystal grain boundaries. When the magnetic domains are pinned a stronger coercive magnetic field needs to be applied to cause them to re-align. When iron is annealed, the crystal grains grow and the magnetic domains become more free to align with applied magnetic fields. This decreases the coercive field and the material becomes a soft magnet.



Hysteresis loops comparing a hard magnet (iron-silicon steel) to a soft magnet (permalloy) on the same scale. H_c for permallloy is 0.05 Oe, about 10 times lower than that of the hard magnet. The remanent magnetizations of the two materials are comparable.

Hard magnets such as CrO_2, γ-Fe_2O_3, and cobalt ferrite ($CoFe_2O_4$) are used in magnetic recording media, where the high coercivity allows them to retain the magnetization state (read as a logical 0 or 1) of a magnetic bit over long periods of time. Hard magnets are also used in disk drives, refrigerator magnets, electric motors and other applications. Drive motors for hybrid and electric vehicles such as the Toyota Prius use the hard magnet $Nd_2Fe_{14}B$ (also used to make strong refrigerator magnets) and require 1 kilogram (2.2 pounds) of neodymium.[6]. A high-resolution transmission electron microscope image of $Nd_2Fe_{14}B$ is shown below and compared to the crystal structure with the unit cell marked.




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4.3.10: Discussion Questions

- Discuss the relationship between the trends in bonding energy of the transition metals and their magnetic properties.
- Draw the hcp unit cell in sections and show how you would calculate (a) the number of atoms in the unit cell and (b) the fraction of space filled by equal spheres.

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4.3.11: Problems

1. C-centered Bravais lattices exist in the monoclinic and orthorhombic systems but not in the tetragonal system. That is because the C-centered tetragonal lattice is equivalent to one of the other Bravais lattices. Which one is it? Show with a drawing how that lattice is related to the C-centered tetragonal lattice. How many atoms are in the unit cell of that lattice?

2. Which of the following sequences of close packed layers fills space most efficiently? Explain your answer.

(a) ABACCABA...

(b) ABABAB...

(c) AABBAABB...

(d) ABACABAC...

3. Calculate the fraction of space that is occupied by packing spheres in the (a) simple cubic, (b) body-centered cubic structure, (c) face-centered cubic (cubic close packed) structures. Assume that nearest neighbor spheres are in contact with each other.

4. The hexagonal close packed (hcp) structure is shown below. If the radius of the spheres is R, what is the vertical distance between layers in units of R? What fraction of space is filled by the spheres in the hcp lattice?

HCP crystal structure.svg

5. Consider a one-dimensional chain of sodium atoms that contains N atoms, where N is a large number. The distance between atoms in the chain is the lattice constant **a**. In the highest occupied molecular orbital of the chain, what is the distance between nodes (in units of **a**)?

6. Starting from the left side of the periodic table, the melting and boiling points of the elements first increase, and then decrease. For example, the order of boiling points is Rb < Sr < Y < Zr < Nb < Mo > Tc ≈ Ru > Rh > Pd > Ag. Briefly explain the reason for this trend.

7. Going across the periodic table from left to right starting from potassium, the bonding energies and heats of vaporization increase in the order K < Ca < Sc < Ti < V, but then decrease going from V to Mn (V > Cr > Mn). The heats of vaporization of V, Cr, and Mn are much less than those of Nb, Mo, and Tc, respectively. Explain these trends.

8. Some alloys of early and late transition metals (e.g., $ZrPt_3$) have much higher enthalpies of vaporization (per metal atom) than either pure metal. Why are such alloys unusually stable, relative to the pure metals?

9. Graphite is a semimetal composed of sheets of fused benzene rings. There are no bonds between sheets, only van der Waals interactions. What is the C-C bond order in graphite? Show why the C-C distance (1.42 Å) is different from that of benzene (1.40 Å).

10. Fe, Co, and Ni are ferromagnetic, whereas Ru, Ir, and Pt are diamagnetic. Explain why magnetic metals are found only among the 3d and 4f elements. Why are Sc and Ti, which are also 3d elements, diamagnetic?

11. The Curie temperature of cobalt is 1127•C, which is higher than that of Fe (770•C) or Ni (358•C). Why does Co have the highest Curie temperature?

12. Iron metal comes in magnetically “soft” and “hard” forms. Briefly explain the structural differences between them and draw magnetic hysteresis curves for each, indicating on your curves the coercive field and the remanent magnetization.

13. Aluminum metal has the fcc structure, a lattice constant of 4.046 Å, three valence electrons per atom, and an electron scattering time (at room temperature) of 11.8 fs. Use these values to calculate the room temperature resistivity (in ohm-cm) of Al metal.

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4.4: IONIC AND COVALENT SOLIDS - STRUCTURES

Learning Objectives

- Describe many crystal structures in terms of close-packed frameworks with systematic filling of octahedral and tetrahedral holes.
- Represent crystal structures by drawing them in sections.
- Rationalize, using chemical principles, why certain crystal structures are stable for certain compounds but not for others, as well as why certain structural and bonding motifs are preferred for certain compounds relative to others.
- Predict which crystal structures are most favorable for a given composition based on ionicity and periodic trends.
- Explain structure-dependent properties such as ferroelectricity and magnetic ordering based on crystal structures.
- Understand intercalation reactions in layered and open framework solids.
- Predict the preferred formation of normal or inverse spinels using arguments from transition metal chemistry (e.g. crystal field stabilization energies).

Inorganic solids often have simple crystal structures, and some of these structures are adopted by large families of ionic or covalent compounds. Examples of the most common structures include NaCl, CsCl, NiAs, zincblende, wurtzite, fluorite, perovskite, rutile, and spinel. We will develop these structures systematically from the close packed and non-close packed lattices shown below. Some layered structures, such as $CdCl_2$ and CdI_2, can be thought of as relatives of simple ionic lattices with some atoms "missing."

4.4.1: Prelude to Ionic and Covalent Solids - Structures

4.4.2: Close-packing and Interstitial Sites

4.4.3: Structures Related to NaCl and NiAs

4.4.4: Tetrahedral Structures

4.4.5: Layered Structures and Intercalation Reactions

4.4.6: Bonding in TiS_2, MoS_2, and Pyrite Structures

4.4.7: Spinel, Perovskite, and Rutile Structures

4.4.8: Discussion Questions

4.4.9: Problems

4.4.10: References

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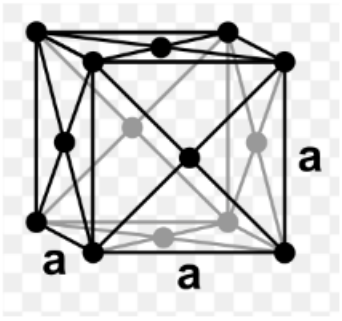
4.4.1: Prelude to Ionic and Covalent Solids - Structures

As we noted in our discussion of metal and alloy structures in Chapter 6, there is an intimate connection between the structures and the physical properties of materials. As we "graduate" from simple metal structures based on sphere packings to more complex structures, we find that this is still true. In this chapter we will try to systematize the structures of inorganic solids - metal oxides, halides, sulfides, and related compounds - and develop some rules for which structures to expect based on electronegativity differences, hard-soft acid-base rules, and other periodic trends. We will see that many of these structures are related to the sphere packings that we learned about in Chapter 6.

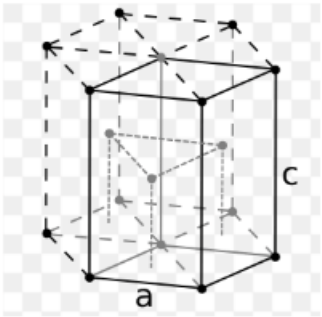


The morphology of twinned crystals of iron pyrite (FeS_2) is related to the underlying cubic symmetry of the unit cell. Like NaCl, the pyrite crystal structure can be thought of as a face-centered cubic array of anions (S_2^{2-}) with cations (Fe^{2+}) occupying all the octahedral holes.

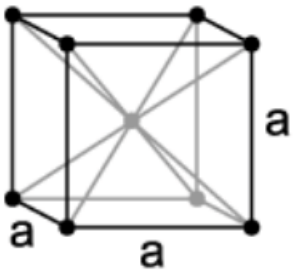
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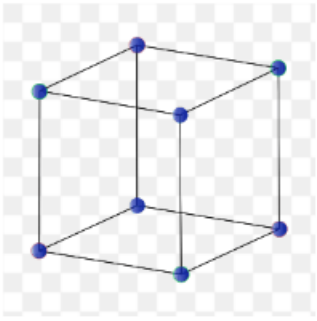
Face-centered cubic (fcc) or cubic close-packed (ccp)



Hexagonal close-packed (hcp)



Body-centered cubic



Simple cubic

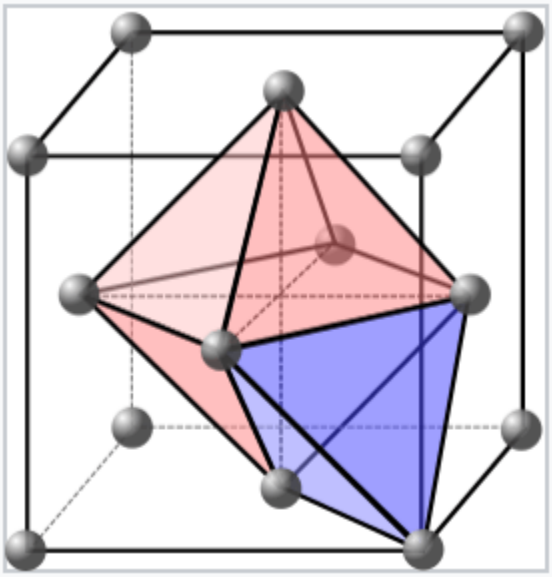
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4.4.2: Close-packing and Interstitial Sites

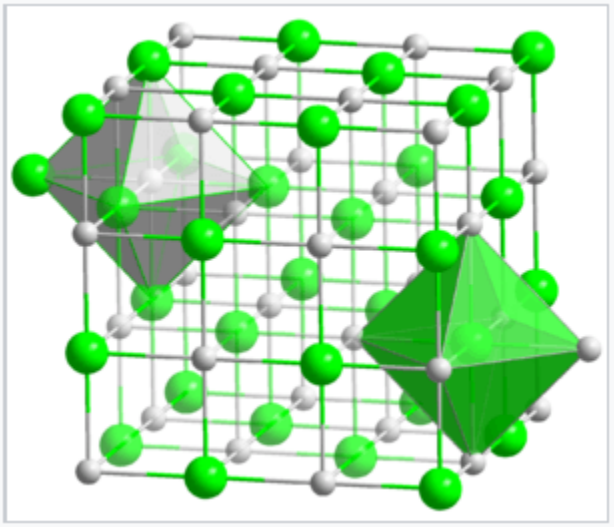
Many common inorganic crystals have structures that are related to cubic close packed (face-centered cubic) or hexagonal close packed sphere packings. These packing lattices contain two types of sites or "holes" that the interstitial atoms fill, and the coordination geometry of these sites is either **tetrahedral** or **octahedral**. An interstitial atom filling a tetrahedral hole is coordinated to four packing atoms, and an atom filling an octahedral hole is coordinated to six packing atoms. In both the hexagonal close packed and cubic close packed lattices, there is one octahedral hole and two tetrahedral holes per packing atom.

Question: Would anions or cations be better as packing atoms?
We might expect that anions, which are often larger than cations, would be better suited to the positions of packing atoms. While this is often true, there are many examples of structures in which cations are the packing atoms, and others in which the distinction is arbitrary. The NaCl structure is a good example of the latter.



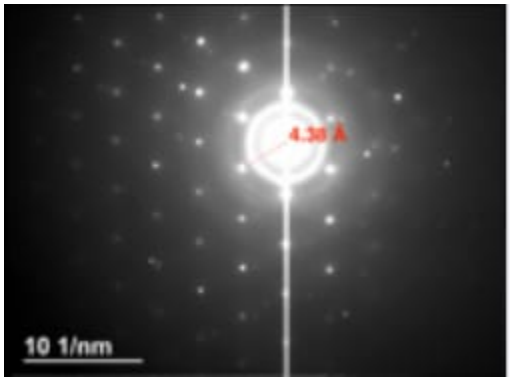
One octahedral and one tetrahedral site in a face-centered cubic unit cell. Each cell contains four packing atoms (gray), four octahedral sites (pink), and eight tetrahedral sites (blue).

In the NaCl structure, shown on the right, the green spheres are the Cl^- ions and the gray spheres are the Na^+ ions. The octahedral holes in a face-centered cubic lattice can be found at fractional coordinates (1/2 1/2 1/2), (1/2 0 0), (0 1/2 0), and (0 0 1/2). There are four of these holes per cell, and they are filled by the chloride ions. The packing atoms (Na^+) have coordinates (0 0 0), (0 1/2 1/2), (1/2 1/2 0), and (1/2 0 1/2). Note that each of the Na^+ positions is related to a Cl^- position by a translation of (1/2 0 0). Another way of stating this is that the structure consists of **two interpenetrating fcc lattices**, which are related to each other by a translation of half the unit cell along any of the three Cartesian axes. We could have equivalently placed the Cl ions at the fcc lattice points and the Na ions in the octahedral holes by simply translating the origin of the unit cell by (1/2 0 0). Thus the distinction between packing and interstitial atoms in this case is arbitrary.



Crystal structure of NaCl. Both the Na^+ and Cl^- ions are octahedrally coordinated.

NaCl is interesting in that it is a three-dimensional checkerboard, and thus there are no NaCl "molecules" that exist in the structure. When this structure was originally solved (in 1913 by using X-ray diffraction) by W. L. Bragg, his interpretation met resistance by chemists who thought that precise integer stoichiometries were a consequence of the valency of atoms in molecules. The German chemist P. Pfeiffer noted in 1915 that 'the ordinary notion of valency didn't seem to apply', and fourteen years later, the influential chemist H. E. Armstrong still found Bragg's proposed structure of sodium chloride 'more than repugnant to the common sense, not chemical cricket'! Nevertheless, Bragg and his father, W. H. Bragg, persevered and used the then-new technique of X-ray diffraction to determine the structures of a number of other compounds, including diamond, zincblende, calcium fluoride, and other alkali halides. These experiments gave chemists their first real look at the atomic structure of solids, and laid the groundwork for X-ray diffraction experiments that later elucidated the structures of DNA, proteins, and many other compounds. For their work on X-ray diffraction the Braggs received the Nobel prize in Physics in 1915.

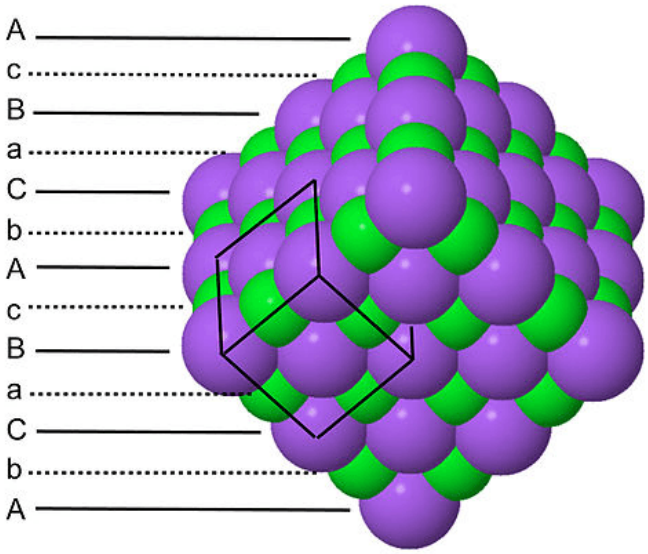


The lattice dimensions and positions of atoms in crystals such as NaCl are inferred from diffraction patterns.

Since each type of atom in the NaCl structure forms a face-centered cubic lattice, there are four Na and four Cl atoms per NaCl unit cell. It is because of this ratio that NaCl has a 1:1 stoichiometry. The shaded green and gray bipyramidal structures in the NaCl lattice show that the Na^+ ions are coordinated to six Cl^- ions, and vice versa. The NaCl structure can be alternatively drawn as a stacking of close-packed layer planes, AcBaCbAcBa... along the body diagonal of the unit cell. Here the uppercase letters represent the packing atoms, and the lower case letters are the interstitial atoms. This layered packing is illustrated below:

NaCl structure

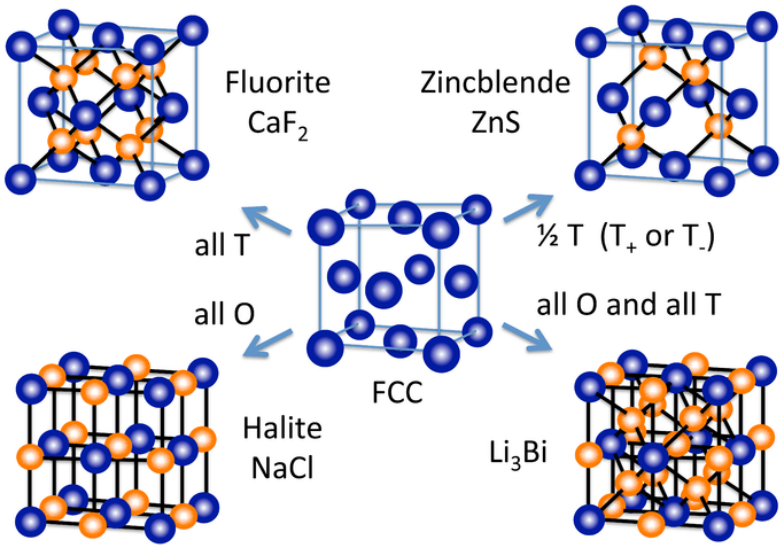
- ---------- A
- - - -c- - - -
- ---------- B
- - - -a- - - -
- ---------- C
- - - -b- - - -
- ---------- A
- - - -c- - - -
- ---------- B
- - - -a- - - -
- ---------- C
- - - -b- - - -
- ---------- A



Note that both the packing atoms and interstitials are stacked in the sequence A-B-C-A-B-C..., in keeping with the fact that each forms a cubic close-packed lattice.

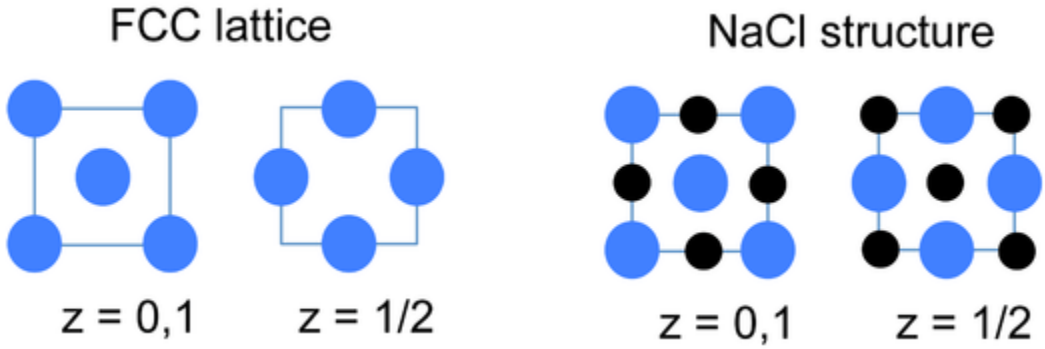
The NaCl structure is fairly common among ionic compounds:

- Alkali Halides (except CsCl, CsBr, and CsI)
- Transition Metal Monoxides (TiO, VO,..., NiO)
- Alkali Earth Oxides and Sulfides (MgO, CaO, BaS... except BeO and MgTe)
- Carbides and Nitrides (TiC, TiN, ZrC, NbC) -these are very stable refractory, interstitial alloys (metallic)



A number of other inorganic crystal structures are formed (at least conceptually) by filling octahedral and/or tetrahedral holes in close-packed lattices. The figure at the right shows some of the most common structures (fluorite, halite, zincblende) as well as a rather rare one (Li_3Bi) that derive from the fcc lattice. From the hcp lattice, we can make the NiAs and wurzite structures, which are the hexagonal relatives of NaCl and zincblende, respectively.

An alternative and very convenient way to represent inorganic crystal structures (especially complex structures such as Li_3Bi) is to draw the unit cell in slices along one of the unit cell axes. This kind of representation is shown at the left for the fcc lattice and the NaCl structure. Since all atoms in these structures have z-coordinates of either 0 or 1/2, only those sections need to be drawn in order to describe the contents of the unit cell. It is a useful exercise to draw some of the fcc compound structures (above) in sections.



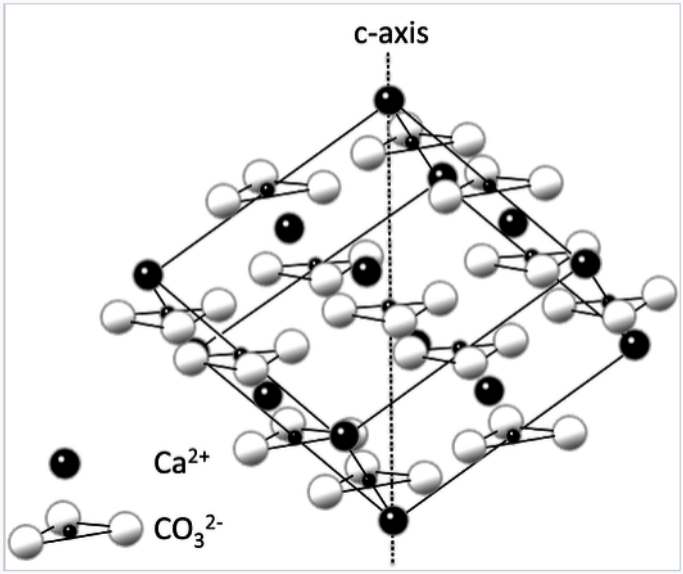
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4.4.3: Structures Related to NaCl and NiAs

There are a number of compounds that have structures similar to that of NaCl, but have a lower symmetry (usually imposed by the geometry of the anion) than NaCl itself. These compounds include:

- FeS_2 (pyrite, "fools gold"): S_2^{2-} (disulfide) and Fe^{2+}
- CaC_2 (a salt-like carbide): Ca^{2+} and linear C_2^{2-} anions
- $CaCO_3$ (calcite, limestone, marble): Ca^{2+} and triangular CO_3^{2-}.



The rhombohedral unit cell of the calcite crystal structure. The hexagonal c-axis is shown.

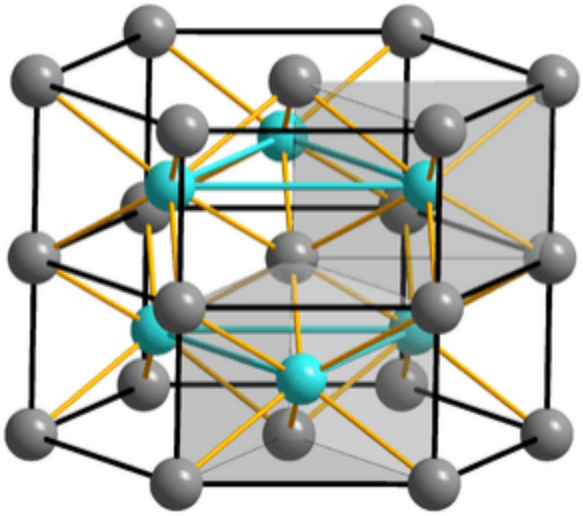
The **calcite** ($CaCO_3$) crystal structure is shown above. Triangular CO_3^{2-} ions fill octahedral holes between the Ca^{2+} ions (black spheres) in a distorted NaCl lattice. As in NaCl, each ion is coordinated by six of the other kind. From this image we can see why the $CaCO_3$ structure has a lower symmetry than that of NaCl. The fourfold rotation symmetry of the NaCl unit cell is lost when the spherical Cl^- ions are replaced by triangular CO_3^{2-} ions. Because of this symmetry lowering, transparent crystals calcite are birefringent, as illustrated below.



Calcite crystals are birefringent, meaning that their refractive indices are different along the two principal crystal directions. This gives rise to the phenomenon of double refraction.

NiAs structure

The NaCl structure can be described a face-centered cubic lattice with all of the octahedral holes filled. What if we start with a hexagonal-close packed lattice rather than a face-centered cubic lattice?



Nickel arsenide crystal structure. The Ni_6As trigonal prisms are shaded gray. One octahedron of six As atoms surrounding a Ni atom is shown in the center of the figure.

This is the structure adopted by **NiAs** and many other transition metal sulfides, phosphides, and arsenides. The cations are shown in gray while the anions are light blue in the figure at the right. The cations are in octahedral coordination, so each cation is coordinated to six anions. The anions are also coordinated to six cations, but they occupy trigonal prismatic sites. In terms of layer stacking, the NiAs structure is AcBcAcBc..., where the A and B sites (the hcp lattice) are occupied by the As atoms, and the c sites, which are eclipsed along the layer stacking axis, are occupied by Ni. Unlike the NaCl structure, where the anion and cation sites are interchangeable, NiAs has unique anion and cation sites. The layer stacking sequence for NiAs is shown below:

- ---------- A
- - - -c- - - -
- ---------- B
- - - -c- - - -
- ---------- A
- - - -c- - - -
- ---------- B
- - - -c- - - -

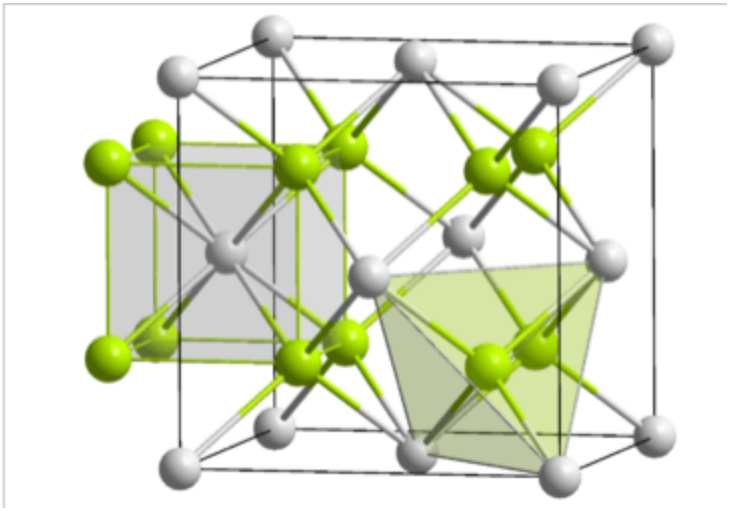
The NiAs structure cannot be adopted by ionic compounds because of the eclipsing cations, because the cation-cation repulsions would be internally destabilizing for an ionic compound. This structure is mainly adopted by covalent and polar covalent MX compounds, typically with "soft" X anions (S, Se, P, As,....) and low-valent transition metal cations. For example, some compounds with the NiAs structure are: MS, MSe, MTe (M=Ti, V, Fe, Co, Ni). Often these are nonstoichiometric or complex stoichiometries with ordered vacancies (Cr_7S_8, Fe_7S_8).

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4.4.4: Tetrahedral Structures

In ccp and hcp lattices, there are two tetrahedral holes per packing atom. A stoichiometry of either M_2X or MX_2 gives a structure that fills all tetrahedral sites, while an MX structure fills only half of the sites. An example of an MX_2 structure is **fluorite**, CaF_2, whose structure is shown in the figure at the left. The packing atom in fluorite is Ca^{2+} and the structure is composed of three interpenetrating fcc lattices. It should be noted that the Ca^{2+} ion (gray spheres) as a packing atom defies our "rule" that anions are larger than cations and therefore must be the packing atoms. The fluorite structure is common for ionic MX_2 (MgF_2, ZrO_2, etc.) and M_2X compounds (Li_2O). In contrast, the hcp relative of the fluorite structure is quite rare because of unfavorable close contacts between like-charged ions.



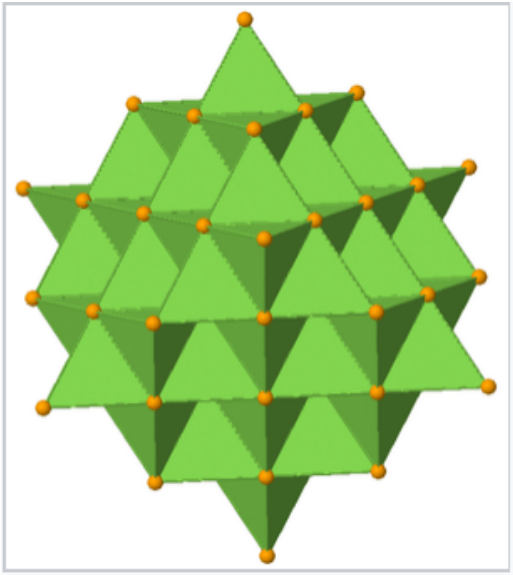
The fluorite (CaF_2) crystal structure showing the coordination environments of the Ca and F atoms

In terms of geometry, Ca^{2+} is in cubic coordination with eight F^- neighbors, and the fluoride ions are tetrahedrally coordinated by four Ca^{2+} ions. The 8:4 coordination geometry is consistent with the 1:2 Ca:F stoichiometry; in all crystal structures the ratio of the coordination numbers is the inverse of the stoichiometric ratio. The three interpenetrating fcc lattices have Ca at 0,0,0 , 1/2,1/2,0 , etc....F at 1/4,1/4,1/4 , 3/4,3/4,1/4 , etc... and F at 3/4,3/4,3/4 , 1/4,1/4/3/4 , etc.

Looking more closely at the tetrahedral sites in fluorite, we see that they fall into two distinct groups: T_+ and T_-. If a tetrahedron is oriented with a vertex pointing upwards along the stacking axis, the site is T_+. Likewise, a tetrahedron with a vertex oriented downward is T_-. The alternation of T_+ and T_- sites allows for efficient packing of ions in the structure. The layer stacking sequence in this structure (including fluoride ions in the T_+ and T_- sites) is:

- ---------- A
- - - -b- - - T_+
- - - -a- - - T_-
- ---------- B
- - - -c- - - T_+
- - - -b- - - T_-
- ---------- C
- - - -a- - - T_+
- - - -c- - - T_-
- ---------- A
- - - -b- - - T_+

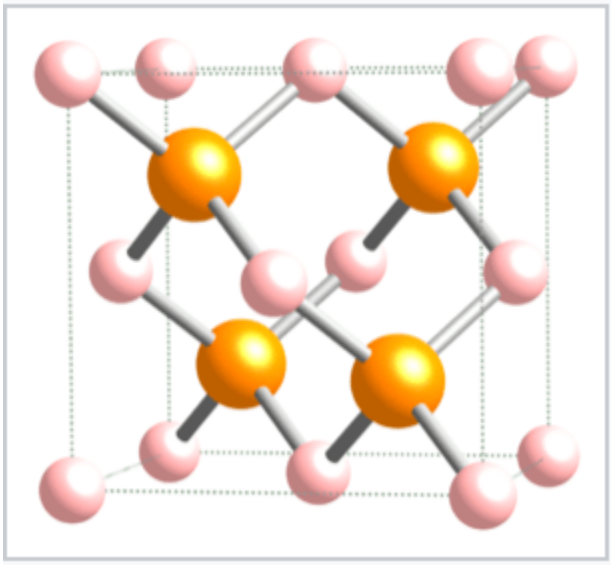
- - - -a- - - T_-



Polyhedral view of the fluorite crystal structure, showing T_+ and T_- Ca_4F tetrahedra. The Ca^{2+} ions are stacked ABCABC... along the body diagonal of the unit cell, which is the vertical direction in this image.

Tetrahedrally bonded compounds with a 1:1 stoichiometry (MX compounds) have only **half** of the tetrahedral sites (either the T_+ or T_- sites) filled. In this case, both the M and the X atoms are tetrahedrally coordinated. The **zincblende** and **wurtzite** structures are 1:1 tetrahedral structures based on fcc and hcp lattices, respectively. Both structures are favored by p-block compounds that follow the octet rule, and these compounds are usually semiconductors or insulators. The zincblende structure, shown below, can be thought of as two interpenetrating fcc lattices, one of anions and one of cations, offset from each other by a translation of 1/4 along the body diagonal of the unit cell. Examples of compounds with the zincblende structure include CuCl, CuI, ZnSe, HgS, BeS, CdTe, AlP, GaP, SnSb, CSi, and diamond. Additionally, the compound $CuInSe_2$ is zincblende in an ordered, doubled unit cell (the chalcopyrite structure). The solid solution compounds $CuIn_{1-x}Ga_xSe_2$ with this structure are among the most widely studied materials for use in efficient thin film photovoltaic cells. Using ZnS as a representative of zincblende, the coordination of both Zn and S atoms is tetrahedral. The layer sequence, which is AbBcCaAbBcC..., results in six-membered ZnS rings that have the same geometry as the "chair" version of cyclohexane. The chair conformation allows for a relatively long distance between opposite atoms in the ring and, as a result, it is more sterically favorable than the boat form. The sequence of close-packed layers in zincblende, filling only the T_+ sites and leaving the T_- sites empty, is shown below:

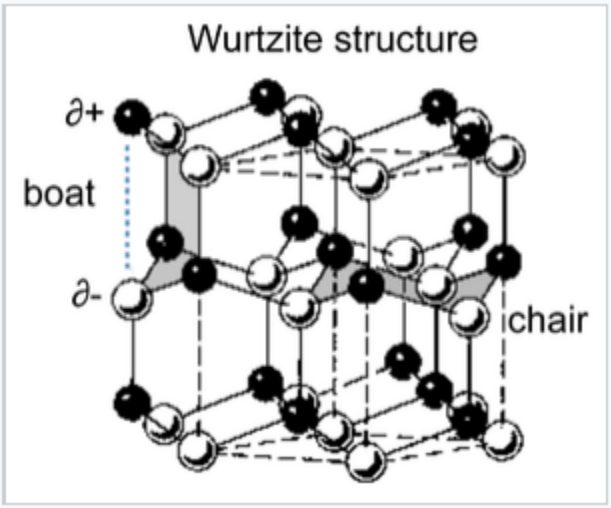
- ---------- A
- - - -b- - - T_+
- - - - - - T_-
- ---------- B
- - - -c- - - T_+
- - - - - - T_-
- ---------- C
- - - -a- - - T_+
- - - - - - T_-



The zincblende unit cell

The wurtzite structure is a close relative of zinc blende, based on filling half the tetrahedral holes in the hcp lattice. Like zincblende, wurtzite contains planes of fused six-membered rings in the chair conformation. Unlike zincblende, however, the rings joining these planes contain six-membered "boat" rings. The boat aligns the anions so that they are directly above the cations in the structure, a less favorable situation sterically but a more favorable one in terms of electrostatics. As a result, the wurtzite structure tends to favor more polar or ionic compounds (e.g., ZnO, $NH_4^+F^-$) than the zincblende structure. As with zincblende, both ions are in tetrahedral (4:4) coordination and there are typically eight valence electrons in the MX compound. Examples of compounds with this structure include: BeO, ZnO, MnS, CdSe, MgTe, AlN, and NH_4F. The layered structure of wurtzite is AbBaAbB and the layer sequence with T_+ sites filled is illustrated below:

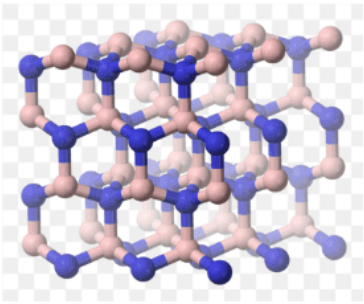
- ---------- A
- - - -b- - - T_+
- - - - - - - T_-
- ---------- B
- - - -a- - - T_+
- - - - - - - T_-
- ---------- A
- - - -b- - - T_+
- - - - - - - T_-
- ---------- B



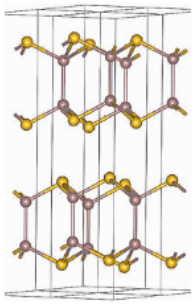
The chair and boat conformations of six-membered ZnS rings in the wurtzite structure.

An interesting consequence of the layer stacking in the wurtzite structure is that the crystals are polar. When cleaved along the c-axis (the stacking axis), crystals of ZnO, ZnS, and GaN have one negatively charged face and an opposite positively charged face. An applied electric field interacts with the crystal dipole, resulting in compression or elongation of the lattice along this direction. For this reason crystals of compounds in the wurtzite structure are typically piezoelectric.

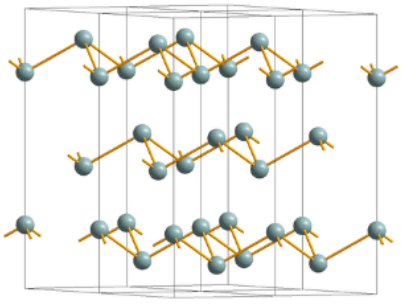
Some compounds are diamorphic and can have either the zincblende or wurtzite structure. Examples of these compounds that have intermediate polarities include CdS and ZnS. SiO_2 exists in polymorphs (crystobalite and tridymite) that resemble zincblende and wurtzite with O atoms midway between each of the Si atoms. The zincblende and wurtzite structures have efficient packing arrangements for tetrahedrally bonded networks and are commonly found in compounds that have tetrahedral bonding. Water, for example, has a tetrahedral hydrogen bonding network and is wurtzite-type. The undistorted wurtzite and zinc blende structures are typically found for AX compounds with eight valence electrons, which follow the octet rule. AX compounds with nine or ten electrons such as GaSe and GaAs crystallize in distorted variants of the wurtzite structure. In GaSe, the extra electrons form lone pairs and this creates layers in the structure, as can be seen in the figure below. To the right of GaSe, the structures of As, Sb, and SbAs show an ever further breakdown of the structure into layers as more valence electrons are added.



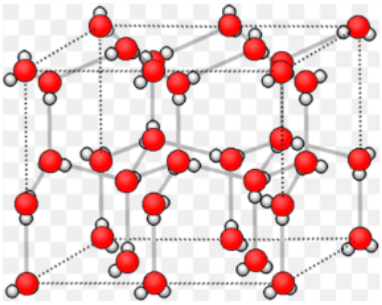
Wurtzite crystal structure



GaSe crystal structure



Crystal structure of Sb, SbAs, and gray As



Crystal structure of hexagonal ice

Hexagonal ice is the most stable polymorph of ice, which is obtained upon freezing at 1 atmosphere pressure. This polymorph (ice-I) has a hcp wurtzite-type structure. Looking at the structure shown at the right, we see that there are irregular arrangements of the O-H---O bonds. In the structure, hydrogen bonding enforces the tetrahedral coordination of each water molecule, resulting in a relatively open structure that is less dense than liquid water. For this reason, ice floats in water.

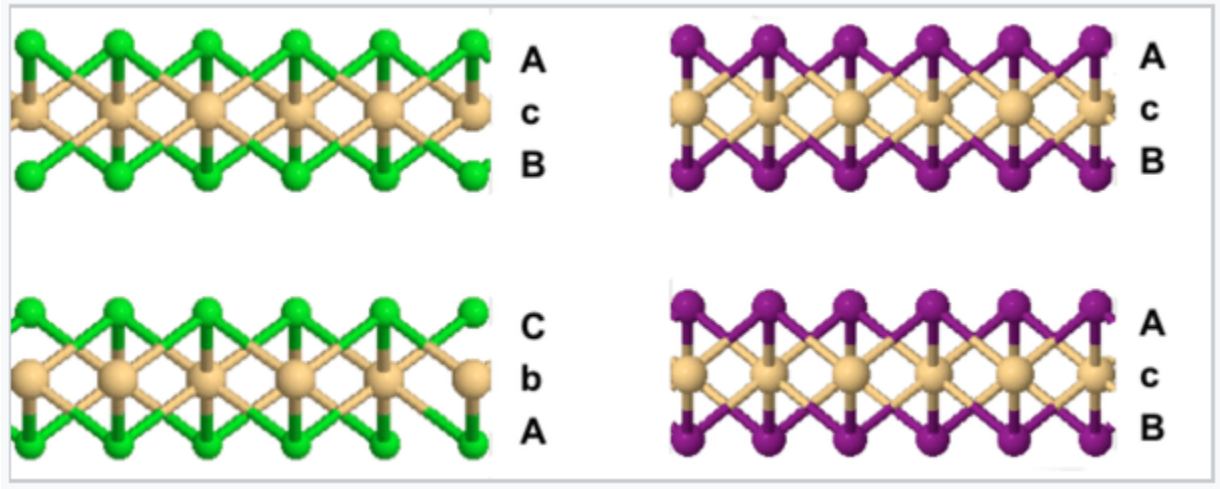
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4.4.5: Layered Structures and Intercalation Reactions

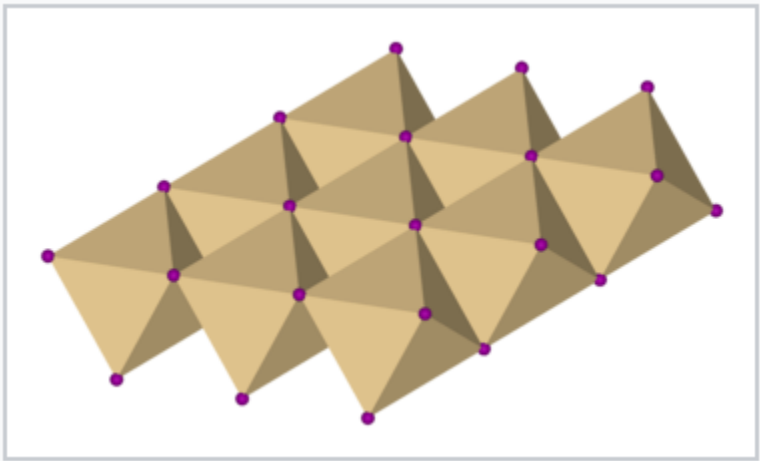
Layered structures are characterized by strong (and typically covalent) bonding between atoms in two dimensions and weaker bonding in the third. A broad range of compounds including metal halides, oxides, sulfides, selenides, borides, nitrides, carbides, and allotropes of some pure elements (B, C, P, As) exist in layered forms. Structurally, the simplest of these structures (for example binary metal halides and sulfides) can be described as having some fraction of the octahedral and/or tetrahedral sites are filled in the fcc and hcp lattices. For example, the $CdCl_2$ structure is formed by filling all the octahedral sites in alternate layers of the fcc lattice, and the CdI_2 structure is the relative of this structure in the hcp lattice.

In the **$CdCl_2$ structure**, the stacking sequence of anion layers is ABCABC...
In the **CdI_2 structure**, the anion stacking sequence is ABAB..., and all the cations are eclipsed along the stacking axis.



Comparison of the $CdCl_2$ (left) and CdI_2 (right) crystal structures

These are examples of **6-3 structures**, because the cations are coordinated by an octahedron of six anions, and the anions are coordinated by three cations to make a trigonal pyramid (like NH_3). Another way to describe these structures is to say that the MX_6 octahedra each share six edges in the MX_2 sheets.



Polyhedral drawing of one layer of the $CdCl_2$ or CdI_2 structure showing edge-sharing MX_6 octahedra

Because these structures place the packing atoms (the anions) in direct van der Waals contact, they are most stable for relatively **covalent** compounds. Otherwise, the electrostatic repulsion between contacting anions would destabilize the structure energetically. More ionic MX_2 compounds tend to adopt the fluorite (CaF_2) or rutile (TiO_2) structures, which are not layered.

Despite the fact that these two structure types are the same at the level of nearest and next-nearest neighbor ions, the CdI_2 structure is much more common than the $CdCl_2$ structure.

$CdCl_2$ structure:

MCl_2 (M = Mg, Mn, Fe, Co, Ni, Zn, Cd)

$NiBr_2$, NiI_2, $ZnBr_2$, ZnI_2

CdI_2 structure:

MCl_2 (M = Ti, V)

MBr_2 (M = Mg, Fe, Co, Cd)

MI_2 (M = Mg, Ca, Ti, V, Mn, Fe, Co, Cd, Ge, Pb, Th)

$M(OH)_2$ (M = Mg, Ca, Mn, Fe, Co, Ni, Cd)

MS_2 (M = Ti, Zr, Sn, Ta, Pt)

MSe_2 (M = Ti, Zr, Sn, V, Pt)

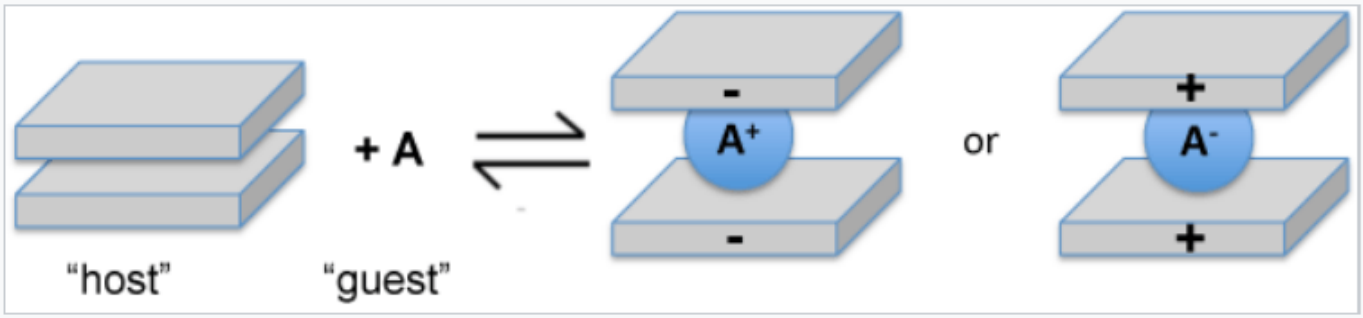
MTe_2 (M = Ti, Co, Ni, Rh, Pd, Pt)

Physically, layered compounds are **soft** and **slippery**, because the layer planes slide past each other easily. For example, graphite, MoS_2, and talc (a silicate) are layered compounds that are used widely as **lubricants** and lubricant additives.

An important reaction of layered compounds is **intercalation**. In intercalation reactions, guest molecules and ions enter the galleries that separate the sheets, usually with expansion of the lattice along the stacking axis. This reaction is typically reversible if it does not perturb the bonding within the sheets. Often the **driving force for intercalation is a redox reaction**, i.e., electron transfer between the host and guest. For example, lithium metal reacts with TiS_2, MoS_2, and graphite to produce $LiTiS_2$, Li_xMoS_2 ($x < 1$), and LiC_6. In these compounds, lithium is ionized to Li^+ and the sheets are negatively charged. Oxidizing agents such as

Br_2, $FeCl_3$, and AsF_5 also react with graphite. In the resulting intercalation compounds, the sheets are positively charged and the intercalated species are anionic.

Intercalation reactions are especially important for electrochemical energy storage in **secondary batteries**, such as **lithium ion** batteries, **nickel-metal hydride** batteries, and **nickel-cadmium** batteries. The reversible nature of the intercalation reaction allows the electrodes to be charged and discharged up to several thousand times without losing their mechanical integrity. In lithium ion batteries, the negative electrode material is typically graphite, which is intercalated by lithium to make LiC_6. Several different oxides and phosphates containing redox active transition metal ions (Mn, Fe, Co, Ni) are used as the positive electrode materials.



Oxidative or reductive intercalation involves the placement of anions or cations between sheets.

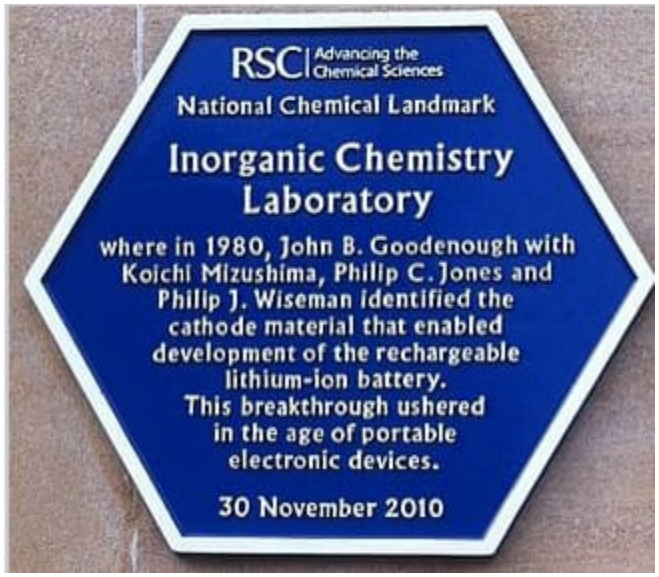
Lithium ion batteries based on CoO_2 were first described in 1980[1] by John B. Goodenough's research group at Oxford. In batteries based on CoO_2, which has the CdI_2 structure, the positive electrode half-reaction is:

$$\mathrm{LiCoO_2} \leftrightharpoons \mathrm{Li_{1-x}CoO_2} + x\,\mathrm{Li^+} + \mathrm{xe^-} \tag{4.4.5.1}$$

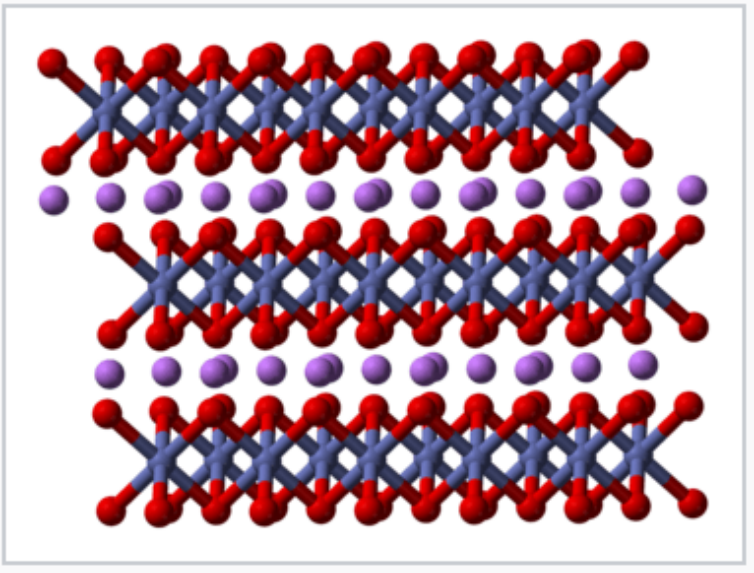
The negative electrode half reaction is:

$$x\,\mathrm{Li^+} + \mathrm{xe^-} + x\,\mathrm{C_6} \leftrightharpoons x\,\mathrm{LiC_6} \tag{4.4.5.2}$$

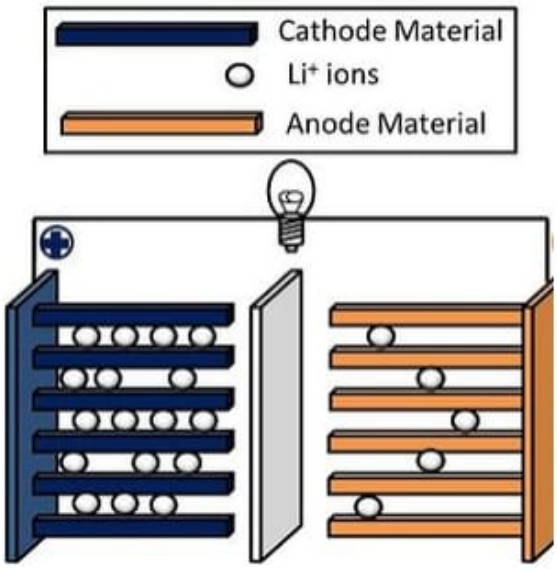
The battery is fully charged when the positive electrode is in the CoO_2 form and the negative electrode is in the LiC_6 form. Discharge involves the motion of Li^+ ions through the electrolyte, forming Li_xCoO_2 and graphite at the two electrodes.



Blue plaque erected by the Royal Society of Chemistry commemorating the development of cathode materials for the lithium-ion battery



Crystal structure of $LiCoO_2$[2]



The lithium ion battery is a "rocking chair" battery, so named because charging and discharging involve moving Li^+ ions from one side to the other. CoO_2 is one example of a positive electrode material that has been used in lithium ion batteries. It has a high energy density, but batteries based on CoO_2 have poor thermal stability. Safer materials include lithium iron phosphate ($LiFePO_4$), and $LiMO_2$ (M = a mixture of Co, Mn, and Ni). These batteries are used widely in laptop computers, portable electronics, cellular telephones, cordless tools, and electric and hybrid vehicles.

A similar intercalation reaction occurs in nickel-cadmium batteries and nickel-metal hydride batteries, except in this case the reaction involves the movement of protons in and out of the $Ni(OH)_2$ lattice, which has the CdI_2 structure:

$$\mathrm{NiO(OH) + H_2O + e^- \longrightarrow Ni(OH)_2 + OH^-} \tag{4.4.5.3}$$

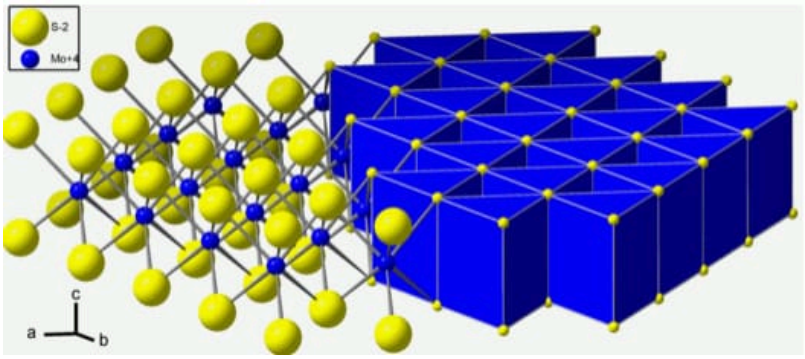
There are many layered compounds that cannot be intercalated by redox reactions, typically because some other stable product is formed. For example, the reaction of layered CdI_2 with Li produces LiI (NaCl structure) and Cd metal.

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4.4.6: Bonding in TiS_2, MoS_2, and Pyrite Structures

Many layered dichalcogenides, such as TiS_2 and ZrS_2, have the CdI_2 structure. In these compounds, as we have noted above, the metal ions are octahedrally coordinated by S. Interestingly, the structures of MoS_2 and WS_2, while they are also layered, are different. In these cases, the metal is surrounded by a **trigonal prism** of sulfur atoms. NbS_2, TaS_2, $MoSe_2$, $MoTe_2$, and WSe_2 also have the trigonal prismatic molybdenite structure, which is shown below alongside a platy crystal of MoS_2.

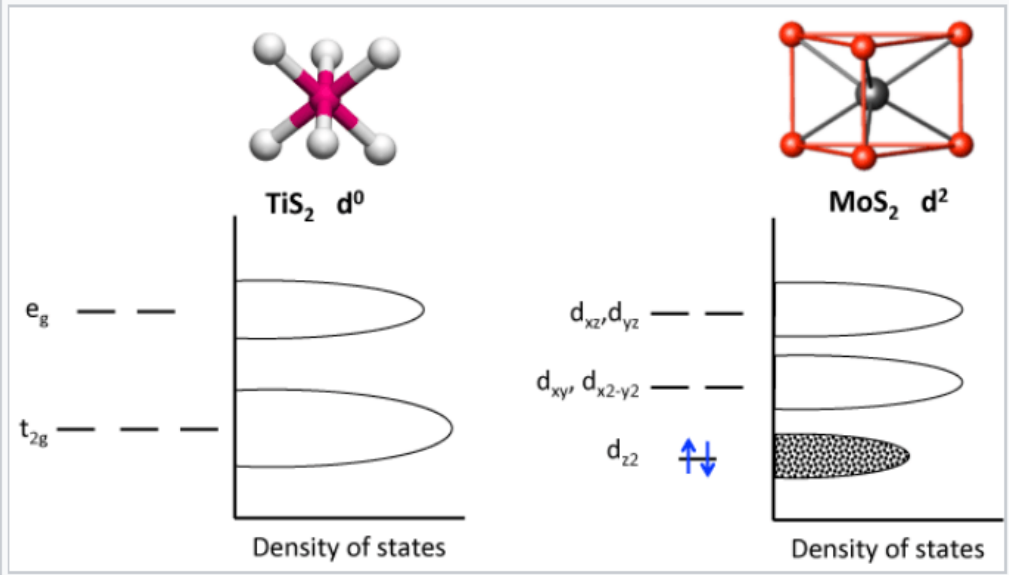




The coordination of the metal ions by a trigonal prism of chalcogenide ions is **sterically unfavorable** relative to octahedral coordination. There are close contacts between the chalcogenide ions, which are eclipsed in the stacking sequence **AbA/BaB/AbA/BaB**... (where "/" indicates the van der Waals gap between layers). What stabilizes this structure?

The molybdenite structure occurs most commonly in MX_2 compounds with a **d^1 or d^2 electron count**. The figure below compares the splitting of d-orbital energies in the octahedral and trigonal prismatic coordination environments:

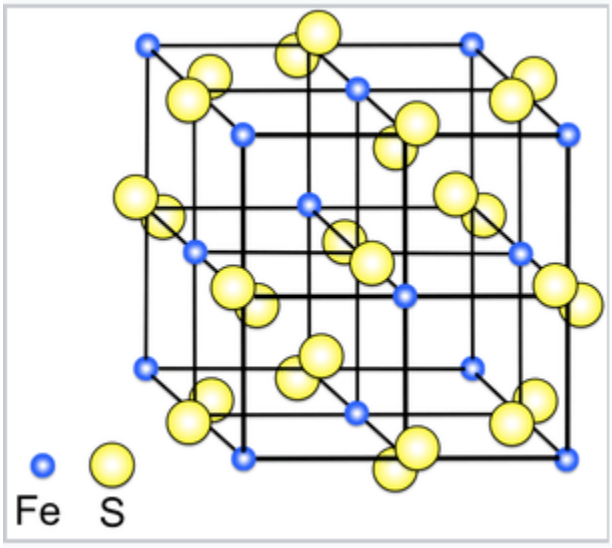
The trigonal prismatic structure is stabilized in MoS_2 by filling the lowest energy band, the d_{z2}. The d_{z2} orbital which points vertically through the triangular top and bottom faces of the trigonal prism, has the least interaction with the sulfide ligands and therefore the lowest energy. The d_{xz} and d_{yz} orbitals, which point at the ligands, have the highest energy. The d_{z2} orbital is lower in energy in this structure than the t_{2g} orbitals are in the octahedral structure of TiS_2.



d-orbital splittings and energy bands in TiS_2 and MoS_2. MoS_2 is a semiconductor with a 1.3 eV gap between its filled and empty bands.

Because it has an unfilled t_{2g} band, TiS_2 is relatively easy to reduce by intercalation with Li. For this reason, $LiTiS_2$ was one of the first intercalation compounds studied by Stanley Whittingham, who developed the concept of the non-aqueous lithium ion battery in the early 1970's.[3] Because it has a filled d_{z2} band, MoS_2 is harder to reduce, but it can be intercalated by reaction with the powerful reducing agent n-butyllithium to make Li_xMoS_2 ($x < 1$). Atoms in the van der Waals planes of these compounds are relatively unreactive, which gives MoS_2 its good oxidative stability and enables its application as a high temperature lubricant. Atoms at the edges of the crystals are however more reactive and in fact are catalytic. High surface area MoS_2, which has a high density of exposed edge planes, is used as a hydrodesulfurization catalyst and is also of increasing interest as an electrocatalyst for the reduction of water to hydrogen.

Layered metal dichalcogenides, including MoS_2, WS_2, and SnS_2, can form closed nanostructures that take the shape of multiwalled onions and multiwalled tubes. These materials were discovered by the group of Reshef Tenne in 1992, shortly after the discovery of carbon nanotubes. Since then nanotubes have been synthesized from many other materials, including vanadium and manganese oxides.



The pyrite (FeS_2) crystal structure. The structure is related to NaCl, with Fe^{2+} and S_2^{2-} ions occupying the cation and anion sites.

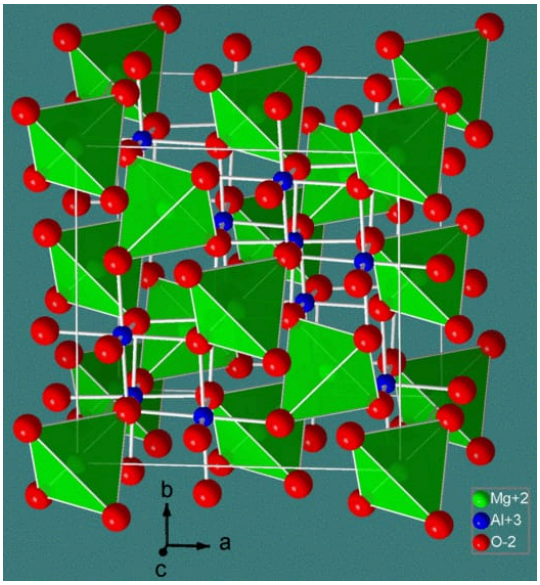
Although early (TiS_2) and late (PtS_2) transition metal disulfides have layered structures, a number of MS_2 compounds in the middle of the transition series, such as MnS_2, FeS_2 and RuS_2, have three-dimensionally bonded structures. For example, FeS_2 has the **pyrite structure**, which is related to the NaCl structure. The reason is that FeS_2 is not $Fe^{4+}(S^{2-})_2$, but is actually $Fe^{2+}(S_2^{2-})$, where S_2^{2-} is the disulfide anion (which contains a single bond like the peroxide anion O_2^{2-}). S^{2-} is too strong a reducing agent to exist in the same compound with Fe^{4+}, which is a strong oxidizing agent. Because FeS_2 is actually $Fe^{2+}(S_2^{2-})$, it is a 1:1 compound and adopts a 1:1 structure.

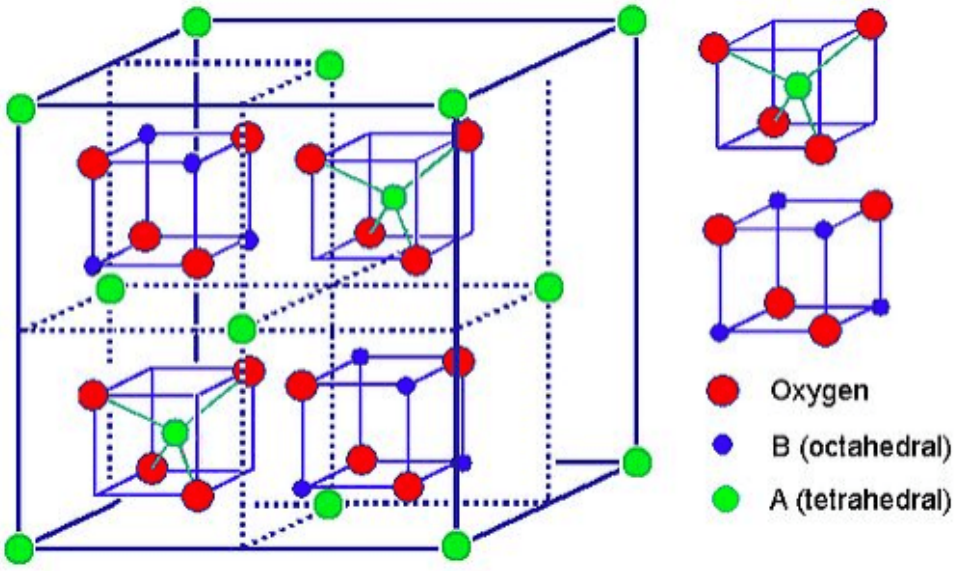
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4.4.7: Spinel, Perovskite, and Rutile Structures

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.





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)

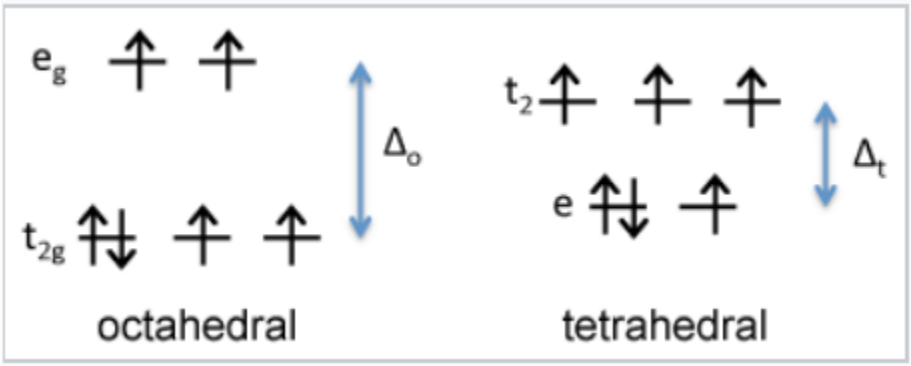
$A^{6+}B^{+}$, e.g., Na_2WO_4 (normal spinel)

Many magnetic oxides, such as Fe_3O_4 and $CoFe_2O_4$, are spinels.

Normal vs. inverse spinel structure

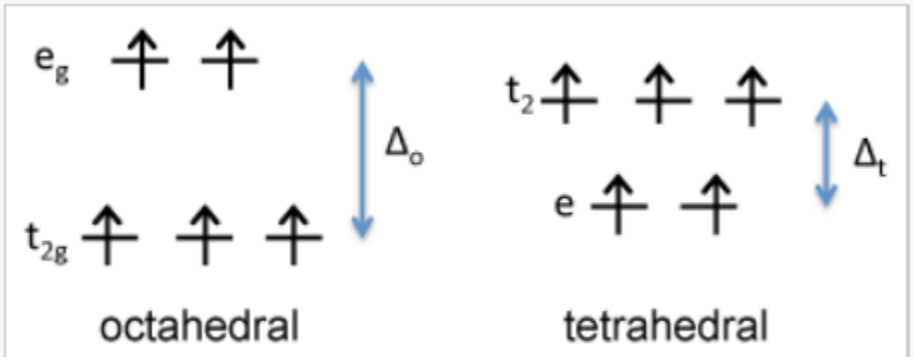
For transition metal oxide spinels, the choice of the normal vs. inverse spinel structure is driven primarily by the **crystal field stabilization energy** (CFSE) of ions in the tetrahedral and octahedral sites. For spinels that contain 3d elements such as Cr, Mn, Fe, Co, and Ni, the electron configuration 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.

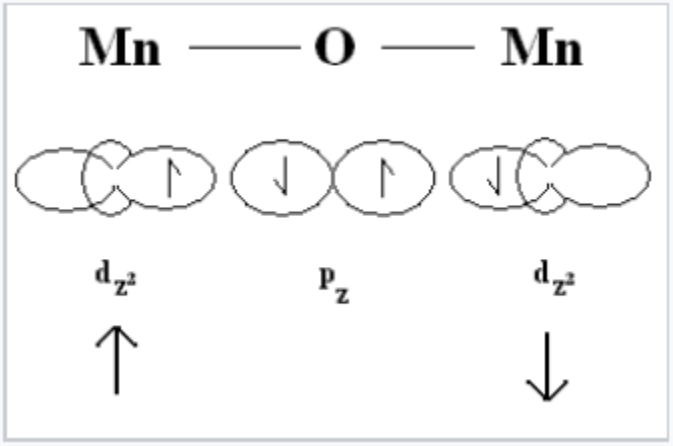
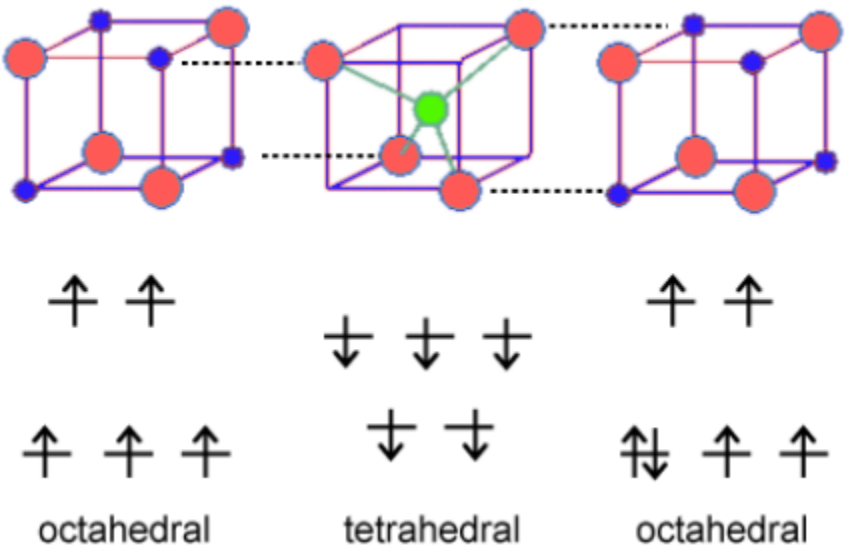


Illustration of antiferromagnetic superexchange between two transition metal cations through a shared oxygen atom.

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**.

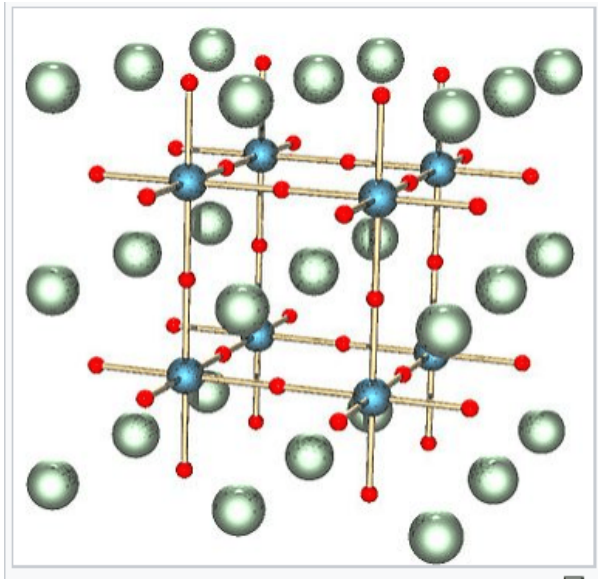


Because all the tetrahedral and octahedral sites in a spinel or inverse spinel crystal are coupled together identically, it works out that ions on the tetrahedral sites will all have one orientation (e.g., spin down) and ions on all the octahedral sites will have the opposite orientation (e.g., spin 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.

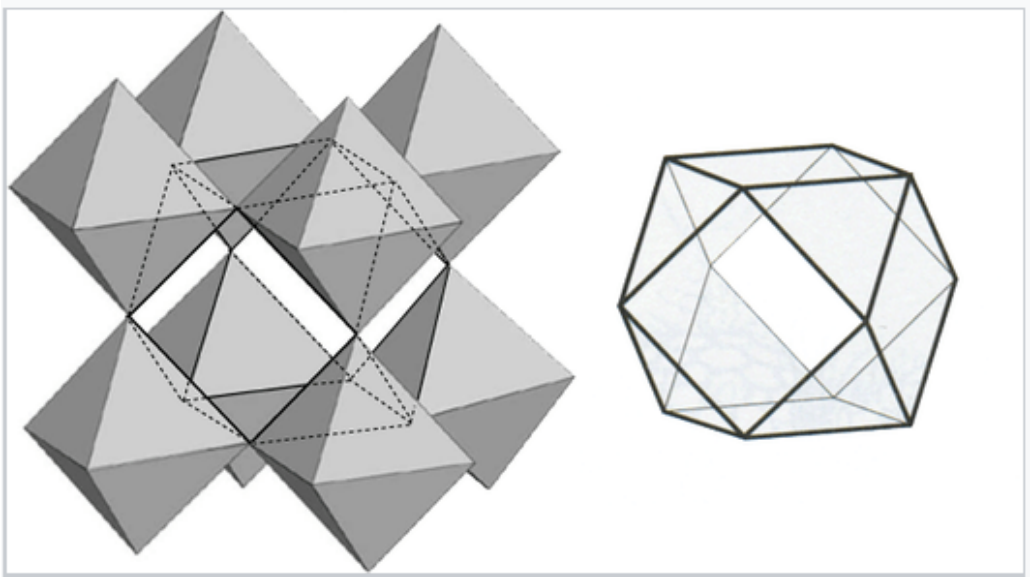
Perovskites are **ternary oxides** of general formula **ABO_3**. More generally, the perovskite formula is ABX_3, where the anion X can be **O, N, or halogen**. The A ions are typically large ions such as Sr^{2+}, Ba^{2+}, Rb^{+}, or a lanthanide 3+ ion, and the B ions are smaller transition metal ions 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

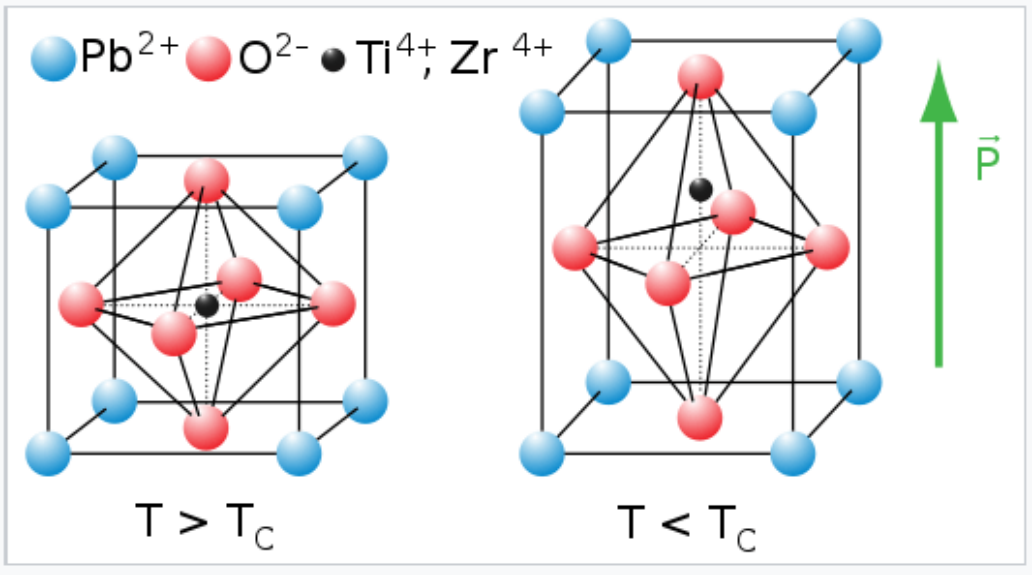
Because the A-site is empty in the ReO_3 structure, compounds with that structure can be reversibly **intercalated** by small ions such as **Li^+ or H^+**, which then occupy sites in the cuboctahedral cavity. For example, smart windows that darken in bright sunlight contain the **electrochromic** material 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:

$$x\,\mathrm{H}^+ + \mathrm{xe}^- + \mathrm{WO}_3 \;\leftrightharpoons\; \mathrm{H}_x\mathrm{WO}_3 \qquad (4.4.7.1)$$

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.



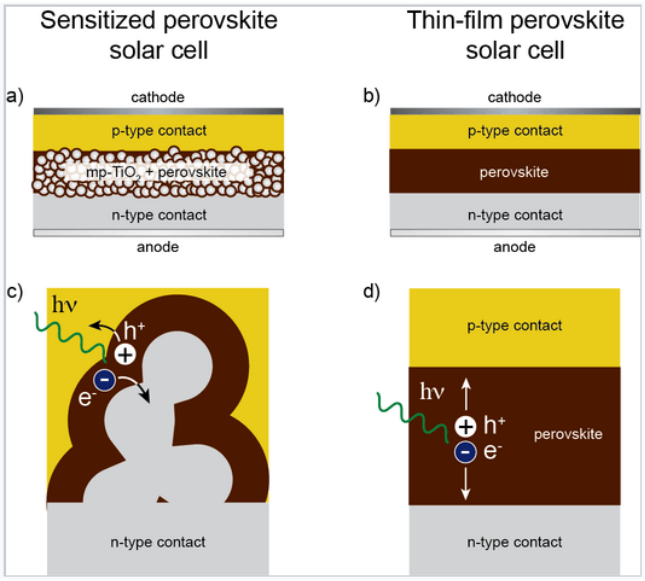
Tetragonal distortion of the perovskite unit cell in the ferroelectric oxide PZT, $PbTi_xZr_{1-x}$

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).

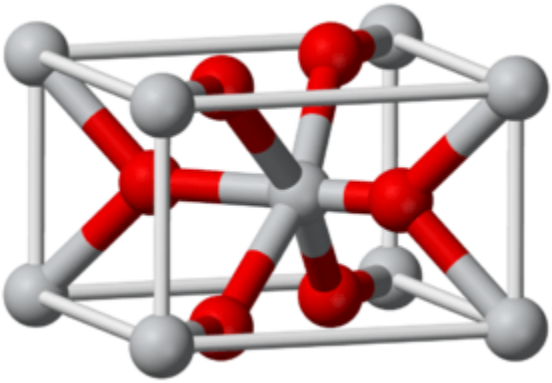
Tin and lead halide perovskites were first studied in the 1990s as materials for thin film electronics,[4] and more recently as light absorbers in dye-sensitized solar cells. Soon after the results on dye-sensitized perovskite cells were reported, it was discovered that halide perovskites could also 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.



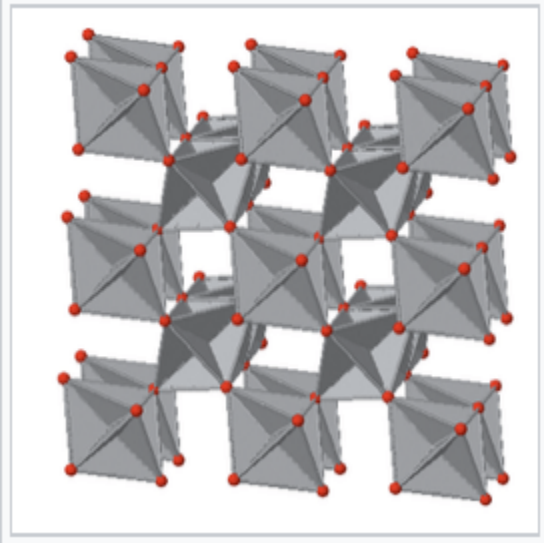
a) Solar cell architecture in which a lead halide perovskite absorber coats a layer of nanocrystalline anatase TiO_2. b) Thin-film solar cell, with a layer of lead halide perovskite sandwiched between two selective contacts. c) Charge generation and extraction in the sensitized architecture and d) in 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.

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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4.4.8: Discussion Questions

- Using the Liverpool 3D visualization website (http://www.chemtube3d.com/solidstate/_table.htm) determine the anion and cation coordination geometries in cadmium chloride and anatase. Describe the arrangement of octahedra (in terms of whether they share edges, faces, etc.) in these structures.
- Count the number of atoms in the Li_3Bi and ReO_3 unit cells, and determine the coordination environments of each of the ions.
- Silicon, germanium, and many other semiconductors adopt the diamond (or zincblende) structure. Assuming that all the atoms are the same size, calculate the volume fraction of the unit cell that is occupied by the atoms. How does the filling fraction of diamond compare to simple cubic and close-packed structures, and what does this tell us about the relationship between coordination number and density?
- Describe the structural basis of ferroelectricity in barium titanate.

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4.4.9: Problems

1. For each of the following close packed layer sequences, indicate the name of the structure (structure type), the coordination environment of the cations (represented by lower case letters), and the coordination environment of the anions (upper case letters). Give two additional examples (apart from the structure type itself) of compounds with the same structure.

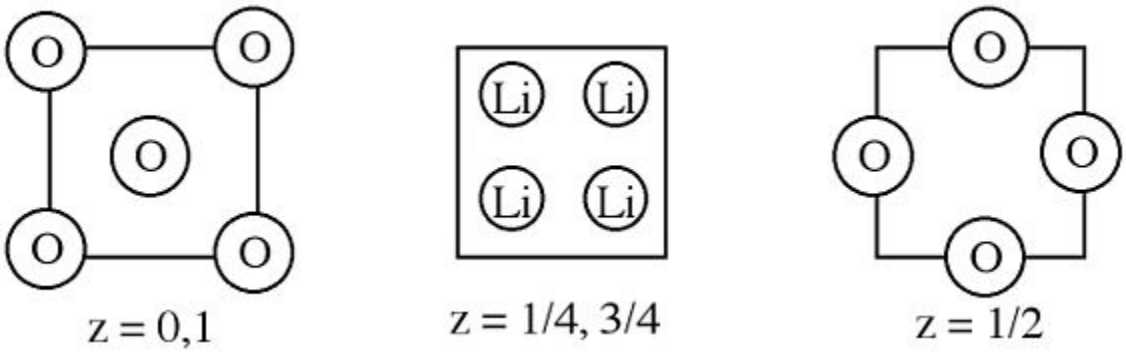
(a) AbBaAbBaAbB.....

(b) AaBbCcAaBbCc.....

(c) AcBaCbAcBaCb.....

(d) AcB | AcB | AcB |.... ("|" = van der Waals gap)

2. Below are sections of the lithium oxide unit cell.



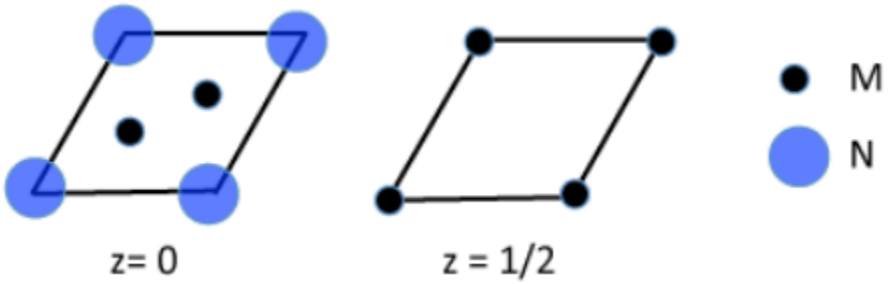
(a) Describe how to obtain (and do obtain) the empirical formula.

(b) What is the coordination number and geometry for each type of ion?

(c) Which atom is close-packed?

(d) What type and fraction of holes are filled by the other ion?

3. The hexagonal unit cell of a metal nitride is shown below in sections.



(a) What is the empirical formula of the compound?

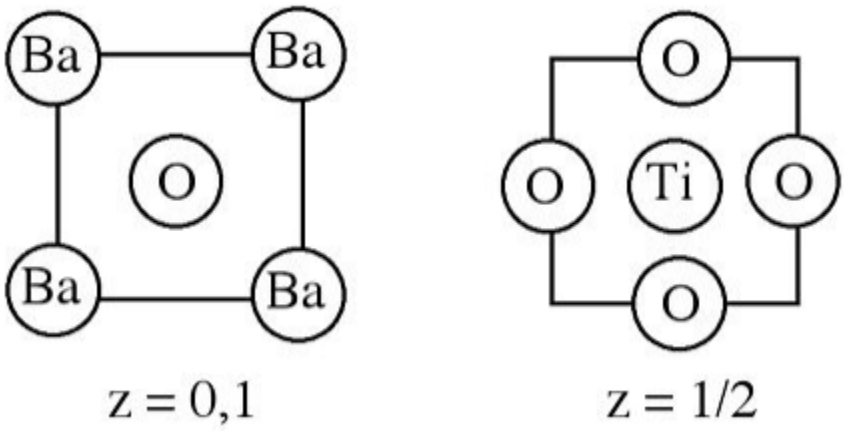
(b) How many M atoms are coordinated to each N atom?

(c) In what group of the periodic table would you expect to find M?

4. Draw the cubic Li_3Bi unit cell in sections.

5. If half the cesium is removed from the CsCl structure, such that each Cl atom is then tetrahedrally coordinated, what structure type is generated?

6. The crystal structure of barium titanate is shown below.



(a) What is the empirical formula of the compound?

(b) Which atoms (if any) are close packed?

(c) How many oxygen atoms coordinate (i) Ti^{4+} and (ii) Ba^{2+}?

(d) Why are the coordination numbers are different?

7. The structures of the disulfides (MS_2) show an apparently unusual trend, proceeding from left to right across the transition series. On the left side (TiS_2, ZrS_2, MoS_2, etc.), one finds layered structures, whereas in the middle (ReS_2, FeS_2, RuS_2) there are three-dimensional pyrite- and marcasite-type structures. On the right (PtS_2, SnS_2), there are again layered structures. Briefly explain these trends.

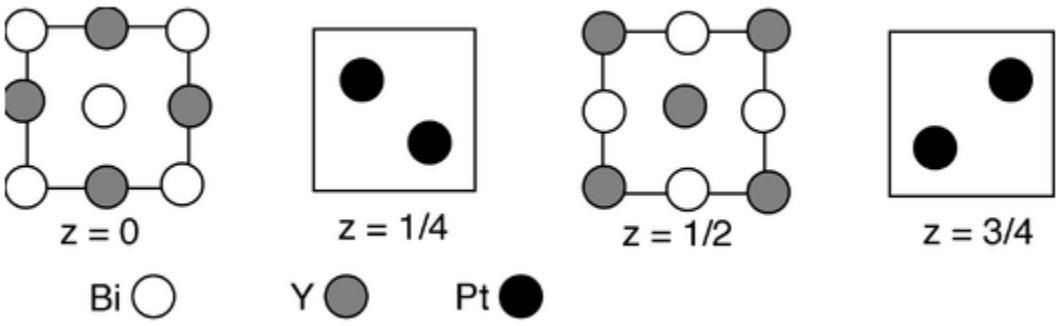
8. Explain why ionic compounds rarely have layered crystal structures.

9. Draw the zincblende structure in sections.

10. The zincblende structure is rarely found with very polar or ionic compounds. However, some polar and ionic compounds (BeO, NH_4F, etc.) have the wurtzite structure.

(a) Describe the similarities and the differences between the zincblende and wurtzite structures (in terms of coordination numbers, stacking sequence of cations and anions, etc.) (b) Why is wurtzite more ionic than zincblende?

11. A recent article by R. Cava and co-workers (*Nature Materials* 2010, *9,* 546-9) describes the unusual electronic properties of a Y-Pt-Bi alloy, the structure of which is shown in sections below:



(a) What is the stoichiometry of the compound?

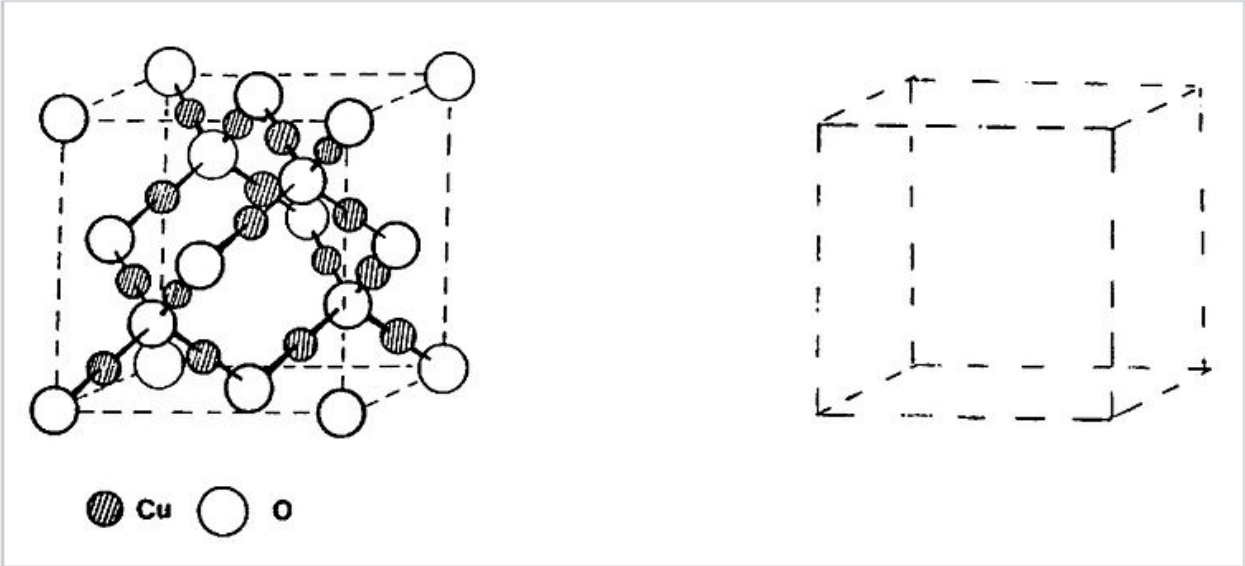
(b) How many Y and how many Pt atoms coordinate each Bi atom?

12. The fluorite structure, CaF_2, which is generated by filling all the tetrahedral holes in a FCC array, is a common MX_2 structure type.

(a) What is the coordination environment of F in a hypothetical relative of CaF_2, in which Ca forms a hcp array and F occupies all the tetrahedral sites?

(b) Suggest a reason why the structure described in (a) is very rare.

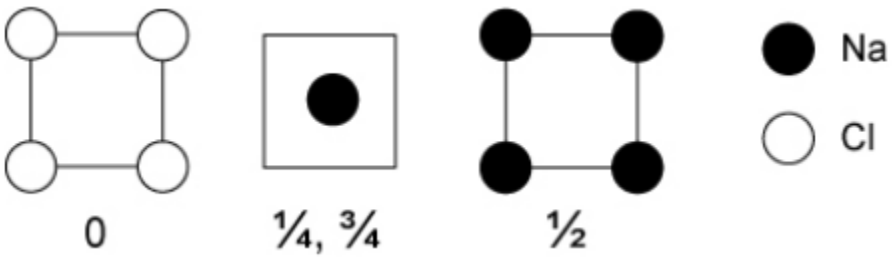
13. The cuprite (Cu_2O) structure is related to zincblende (or diamond) in that oxygen occupies both the Zn and S positions, with copper in between. This is shown schematically at the right. Actually, in cuprite there are *two* such interpenetrating networks with no bonds between them. Draw the second network in the empty cell. If you put the two halves together and take out the copper, what cubic packing lattice do you get? Is it a closest packing lattice? (*Hint #1:* start with an O atom at 1/2,1/2,1/2) (*Hint #2:* try this in pencil first)



14. Draw the rutile structure in sections of the unit cell, and verify that the stoichiometry is MX_2. What are the coordination numbers of Ti and O?

15. Stishovite is a high pressure form of SiO_2 found in meteorite craters. While normal SiO_2 has the quartz structure, in which each Si is coordinated by four O atoms, stishovite has the rutile structure. Would you expect the Si-O bond to be longer in stishovite, or in quartz? What is the bond order in each polymorph?

16. Na and Cl combine in a 1:1 ratio to make the ionic NaCl lattice. Interestingly, recent theoretical predictions (confirmed by high pressure synthesis and crystallography) have identified several other stoichiometries that form stable crystals at high pressure. These include Na_3Cl, Na_2Cl, Na_3Cl_2, $NaCl_3$, and several others.[8] The structure of one of these new sodium chlorides is shown below in sections.



a) What is the stoichiometry of this compound?

b) What are the coordination numbers of Na and Cl, and how do they compare to the coordination numbers in NaCl and Na metal?

c) Based on your answer to (b), explain why high pressure should stabilize this phase.

17. One of the new compounds discovered in the study described in problem 16 is $NaCl_3$. There are two polymorphs of this compound, one of which contains linear Cl_3^- ions. Accurate molecular orbital calculations indicate that the charge on the central Cl atom in these linear anions is close to zero. Draw a valence bond structure for the Cl_3^- ion that is consistent with these observations. Would you expect the Cl-Cl bond to be longer or shorter than the bond in Cl_2?

18. Some MX salts can exist in either the CsCl or NaCl structure. Use the Pauling formula to predict the M-X bond length in the CsCl structure of a compound that has a bond length of 3.5 Å in the NaCl structure. Would applying a high pressure stabilize the CsCl form, or the NaCl form of this compound? (*hint:* calculate the volume per formula unit)

19. Mn_3O_4 and Fe_3O_4 are both mixed-valence oxides. In both cases, there is one M^{2+} ion and two M^{3+} ions per formula unit (M = Fe, Mn).

(a) One of these is a normal spinel and one is an inverse spinel. Explain which is which, and why. (hint: think about CFSE's)

(b) For Mn_3O_4, what kind of magnetic ordering (ferri-, ferro-, or antiferromagnetic) would you expect, and why? You can assume that neighboring tetrahedral and octahedral ions in the structure are antiferromagnetically coupled.

(c) Sketch the approximate form of the χ vs. T and $1/\chi$ vs. T curves for Mn_3O_4. Label any special values of temperature on your graphs.

20. Predict whether each of the following should form a normal or inverse spinel: MgV_2O_4, VMg_2O_4, $NiGa_2O_4$, $ZnCr_2S_4$, $NiFe_2O_4$. Would kind of magnetic ordering (ferro-, ferri-, or antiferromagnetic) would you predict for $NiFe_2O_4$?

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5: CHEM 2101 TOPIC 5 - INORGANIC THERMODYNAMICS

5.1: Structure and Energetics of Solids

5.1.1: Crystal Structures and Unit Cells

5.1.2: Energetics of Ionic Solids- Lattice Energy

5.1.3: Lattice Enthalpies and Born Haber Cycles

5.1.4: Lattice Energy and Solubility

5.1.5: Bonding in Metals and Semicondoctors

5.1.6: Nanomaterials

5.1.7: Ionic Radii and Radius Ratios

5.2: Chapter 6 - Inorganic Thermodynamics

5.2.1: Enthalpy

5.2.2: Spontaneity

5.2.3: Entropy

5.2.4: Gibbs Energy

5.2.5: Lattice Energy

5.2.6: The Born-Lande' equation

5.2.7: Lattice energies and solubility

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5.1: STRUCTURE AND ENERGETICS OF SOLIDS

In the chemistry of molecular compounds, we are accustomed to the idea that properties depend strongly on structure. For example we can rationalize the polarity of the water molecule based on its shape. We also know that two molecules with the same composition (e.g., ethanol and dimethyl ether) have very different properties based on the bonding arrangements of atoms. It should come as no surprise that the properties of extended solids are also connected to their structures, and so to understand what they do we should begin with their crystal structures. Most of the metals in the periodic table have relatively simple structures and so this is a good place to begin.

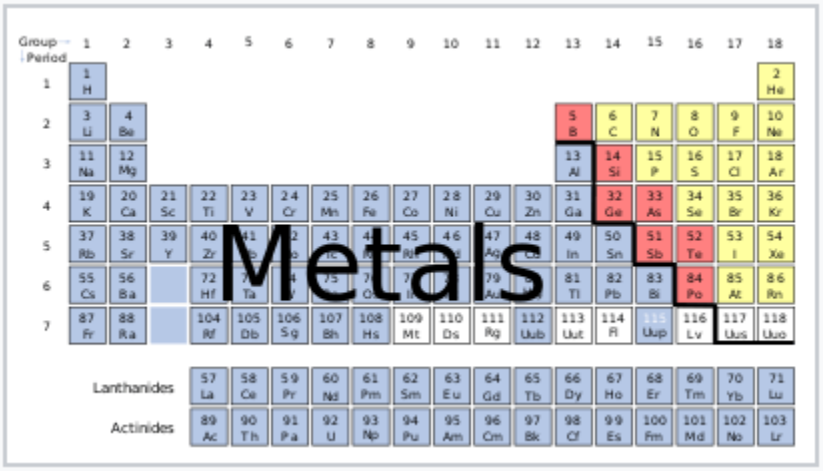


Figure 5.1.1: Over $\frac{2}{3}$ of the elements in the periodic table are metals. All elemental metals (except the three - Cs, Ga, Hg - that are liquid at or near room temperature) are crystalline solids at room temperature, and most have one of three simple crystal structures.

With ionic solids we "graduate" from simple metal structures based on sphere packings to more complex structures where there are both anions and cations. In this chapter we will try to systematize the structures of inorganic solids - metal oxides, halides, sulfides, and related compounds - and develop some rules for which structures to expect based on electronegativity differences, hard-soft acid-base rules, and other periodic trends. We will see that many of these structures are based on the simple packing of spheres.



Figure 5.1.2: The morphology of twinned crystals of iron pyrite (FeS_2) is related to the underlying cubic symmetry of the unit cell. Like NaCl, the pyrite crystal structure can be thought of as a face-centered cubic array of anions (S_2^{2-}) with cations (Fe^{2+}) occupying all the octahedral holes.

Inorganic solids often have simple crystal structures, and some of these structures are adopted by large families of ionic or covalent compounds. Examples of the most common structures include NaCl, CsCl, NiAs, zincblende, wurtzite, fluorite, perovskite, rutile, and spinel. We will develop these structures systematically from the close packed and non-close packed lattices.

Learning Objectives

- Determine the formula of an ionic solid based on the unit cell
- Predict relative lattice energies based on ion sizes and charges
- Understand how lattice energy plays a role in solubility
- Explain how particle size affects the material properties in nanomaterials

Thumbnail image shows the unit cell of the zincblende crystal structure

5.1.1: Crystal Structures and Unit Cells

5.1.2: Energetics of Ionic Solids- Lattice Energy

5.1.3: Lattice Enthalpies and Born Haber Cycles

5.1.4: Lattice Energy and Solubility

5.1.5: Bonding in Metals and Semicondoctors

5.1.6: Nanomaterials

5.1.7: Ionic Radii and Radius Ratios

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5.1.1: Crystal Structures and Unit Cells

Introduction

The term "closest packed structures" refers to the most tightly packed or space-efficient composition of crystal structures (lattices). Imagine an atom in a crystal lattice as a sphere. While cubes may easily be stacked to fill up all empty space, unfilled space will always exist in the packing of spheres. To maximize the efficiency of packing and minimize the volume of unfilled space, the spheres must be arranged as close as possible to each other. These arrangements are called **closest packed structures**. The packing of spheres can describe the solid structures of crystals. In a crystal structure, the centers of atoms, ions, or molecules lie on the lattice points. Atoms are assumed to be spherical to explain the bonding and structures of metallic crystals. These spherical particles can be packed into different arrangements. In closest packed structures, the arrangement of the spheres are densely packed in order to take up the greatest amount of space possible.

Close-Packing of Identical Spheres

Crystals are of course three-dimensional objects, but we will begin by exploring the properties of arrays in two-dimensional space. This will make it easier to develop some of the basic ideas without the added complication of getting you to visualize in 3-D — something that often requires a bit of practice. Suppose you have a dozen or so marbles. How can you arrange them in a single compact layer on a table top? Obviously, they must be in contact with each other in order to minimize the area they cover. It turns out that there are two efficient ways of achieving this:



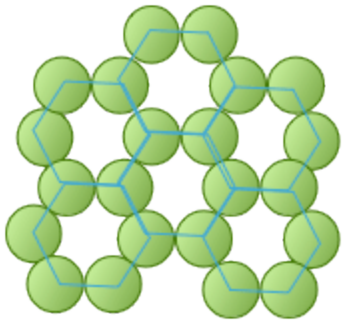
The essential difference here is that any marble within the interior of the square-packed array is in contact with four other marbles, while this number rises to six in the hexagonal-packed arrangement. It should also be apparent that the latter scheme covers a smaller area (contains less empty space) and is therefore a more efficient packing arrangement. If you are good at geometry, you can show that square packing covers 78 percent of the area, while hexagonal packing yields 91 percent coverage.

If we go from the world of marbles to that of atoms, which kind of packing would the atoms of a given element prefer?



If the atoms are identical and are bound together mainly by dispersion forces which are completely non-directional, they will favor a structure in which as many atoms can be in direct contact as possible. This will, of course, be the hexagonal arrangement.

Directed chemical bonds between atoms have a major effect on the packing. The version of hexagonal packing shown at the right occurs in the form of carbon known as *graphite* which forms 2-dimensional sheets. Each carbon atom within a sheet is bonded to three other carbon atoms. The result is just the basic hexagonal structure with some atoms missing.



The coordination number of 3 reflects the sp^2-hybridization of carbon in graphite, resulting in plane-trigonal bonding and thus the sheet structure. Adjacent sheets are bound by weak dispersion forces, allowing the sheets to slip over one another and giving rise to the lubricating and flaking properties of graphite.

Types of Holes From Close-Packing of Spheres

When a single layer of spheres is arranged into the shape of a hexagon, gaps are left uncovered. The hole formed between three spheres is called a **trigonal hole** because it resembles a triangle. In Figure 5.1.1.1, two out of the the six trigonal holes have been highlighted green.

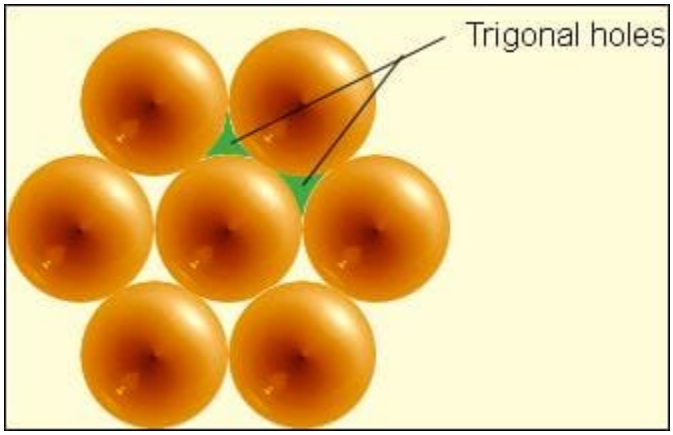


Figure 5.1.1.1: Trigonal holes (green) between close packed spheres in a single layer

Once the first layer of spheres is laid down, a second layer may be placed on top of it. The second layer of spheres may be placed to cover the trigonal holes from the first layer. Holes now exist between the first layer (the orange spheres) and the second (the lime spheres), but this time the holes are different (Figure 5.1.1.2). The triangular-shaped hole created over a orange sphere from the first layer is known as a **tetrahedral hole** because the surrounding spheres are in a tetrahedral arrangement. A hole from the second layer that also falls directly over a hole in the first layer is called an **octahedral hole** because the surrounding spheres are in an octahedral arrangement.

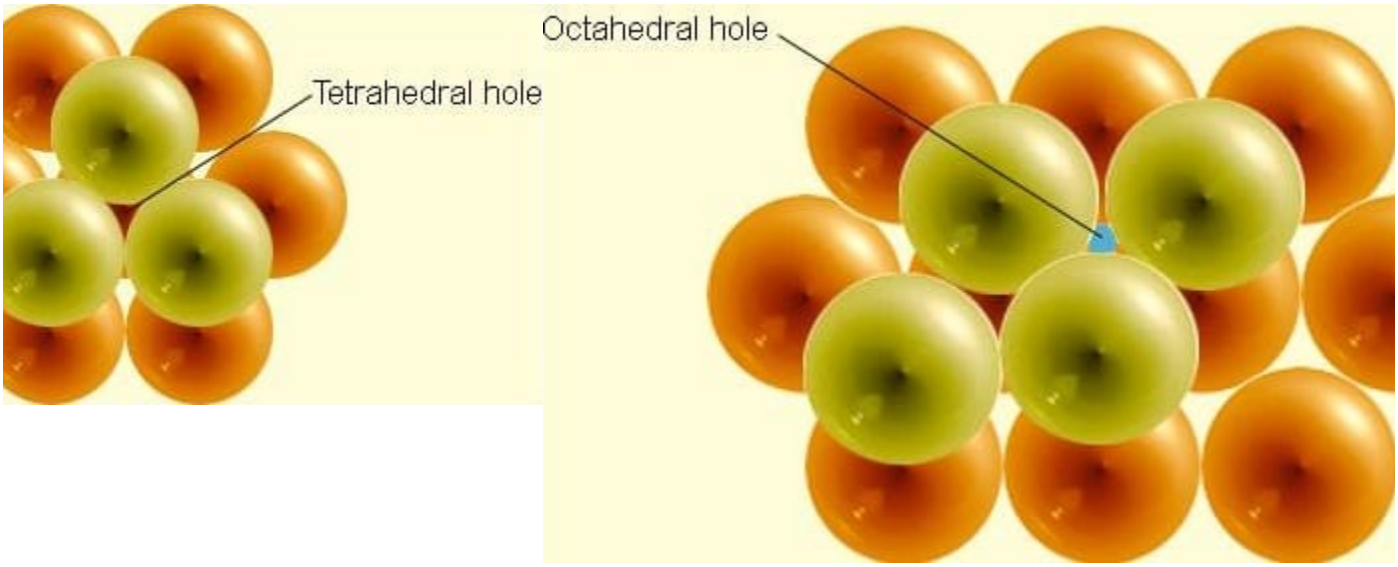


Figure 5.1.1.2: Illustrations of tetrahedral (left) and octahedral (right) holes formed between two close packed layers

Close Packed Crystal Structures

Hexagonal Close-Packed (hcp)

In a hexagonal close-packed structure, the third layer has the same arrangement of spheres as the first layer and covers all the tetrahedral holes. Since the structure repeats itself after every two layers, the stacking for hcp may be described as "a-b-a-b-a-b." The atoms in a hexagonal close-packed structure efficiently occupy 74% of space while 26% is empty space.

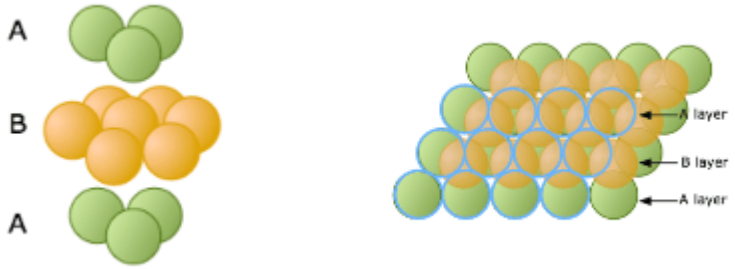


Figure 5.1.1.3: Side and top views of the layers in the hexagonal close-packed (hpc) structure.

Cubic Close-Packed (ccp)

The arrangement in a cubic closest packing also efficiently fills up 74% of space. Similar to hexagonal closest packing, the second layer of spheres is placed on to of half of the depressions of the first layer. The third layer is completely different than that first two layers and is stacked in the depressions of the second layer, thus covering all of the octahedral holes. The spheres in the third layer are not in line with those in layer A, and the structure does not repeat until a fourth layer is added. The fourth layer is the same as the first layer, so the arrangement of layers is "a-b-c-a-b-c."

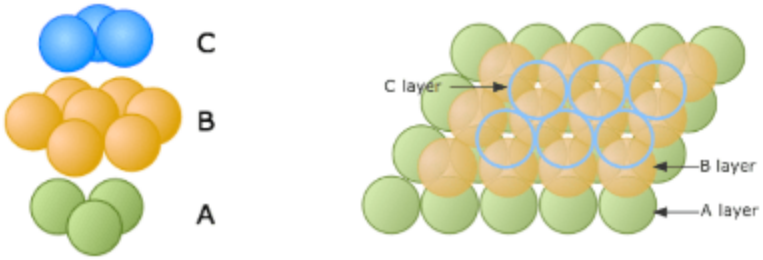


Figure 5.1.1.4: Side and top views of the layers in cubic close-packed (ccp) structure.

Coordination Number and Number of Atoms Per Unit Cell

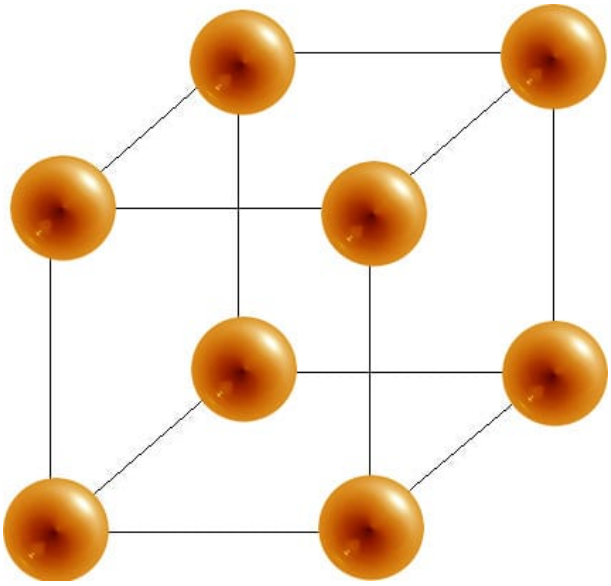
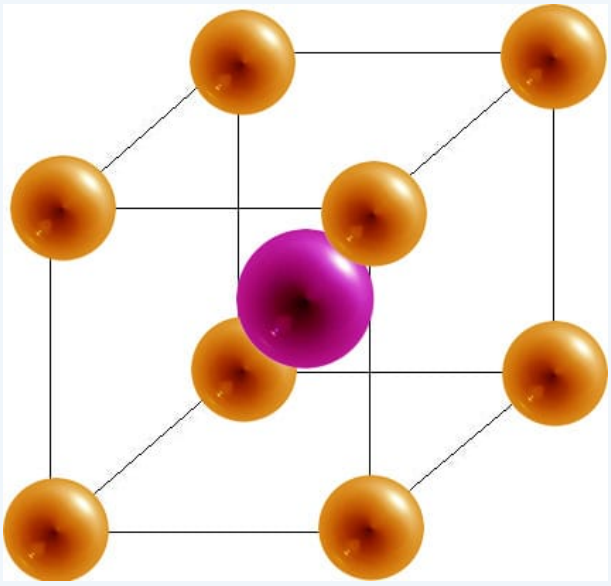
A unit cell is the smallest representation of an entire crystal. All crystal lattices are built of repeating unit cells. In a unit cell, an atom's coordination number is the number of atoms it is touching.

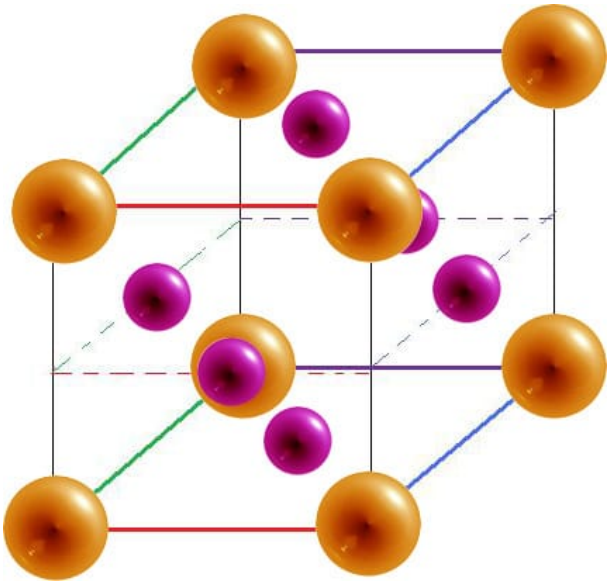
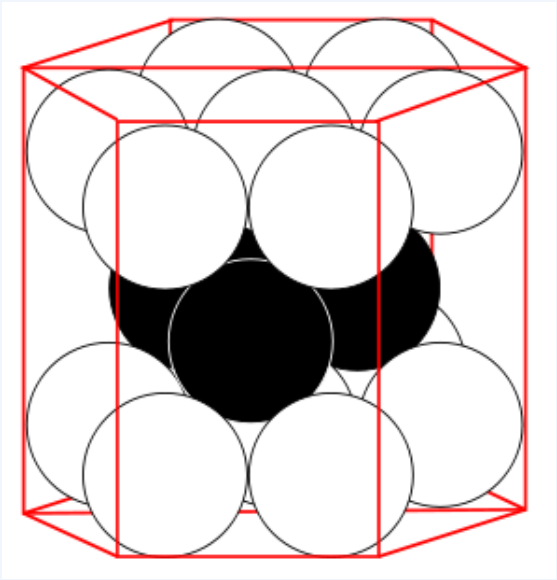
- The simple cubic has a sphere at each corner of a cube. Each sphere has a coordination number of 6 and there is 1 atom per unit cell.
- The body-centered cubic (bcc) has a sphere at each corner of a cube and one in the center. Each sphere has a coordination number 8 and there are 2 atoms per unit cell.
- The cubic closest packed, also called face-centered cubic (fcc) has has a sphere at each corner and each face of a cube. Each sphere has a coordination number of 12 and there are 4 atoms per unit cell.
- The hexagonal closest packed has spheres arranged in hexagons with one in the center. each sphere has a coordination number of 12 and there are 6 atoms per unit cell.

Atoms Per Unit Cell

The amount that an atom contributes to a unit cell depends on its position in the unit cell

- Each corner atom contributes $\frac{1}{8}$ to the unit cell in the cubic cells and $\frac{1}{6}$ to the unit cell in hcp
- Each edge atom contributes $\frac{1}{4}$ to the unit cell
- Each face atom contributes $\frac{1}{2}$ to the unit cell
- Each center atom contributes 1 to the unit cell

Unit Cell	Coordination Number	# of Atoms Per Unit Cell	% space
Simple Cubic 	6	1	52%
Body-Centered Cubic 	8	2	68%

Unit Cell	Coordination Number	# of Atoms Per Unit Cell	% space
Face-centered Cubic 	12	4	74.04%
Hexagonal Closest Packed 	12	6	74.04%

Inorganic Crystals

Many common inorganic crystals have structures that are related to cubic close packed (face-centered cubic) or hexagonal close packed sphere packings. One component of the material will pack in one of the arrangements above. The remaining component(s) will fill some or all of the holes between the layers. An interstitial atom filling a tetrahedral hole is coordinated to four packing atoms, and an atom filling an octahedral hole is coordinated to six packing atoms. In both the hexagonal close packed and cubic close packed lattices, there is one octahedral hole and two tetrahedral holes per packing atom.

Are Anions or Cations Better Packing Atoms?

We might expect that anions, which are often larger than cations, would be better suited to the positions of packing atoms. While this is often true, there are many examples of structures in which cations are the packing atoms, and others in which the distinction is arbitrary. The NaCl structure is a good example of the latter.

Rock Salt (NaCl)

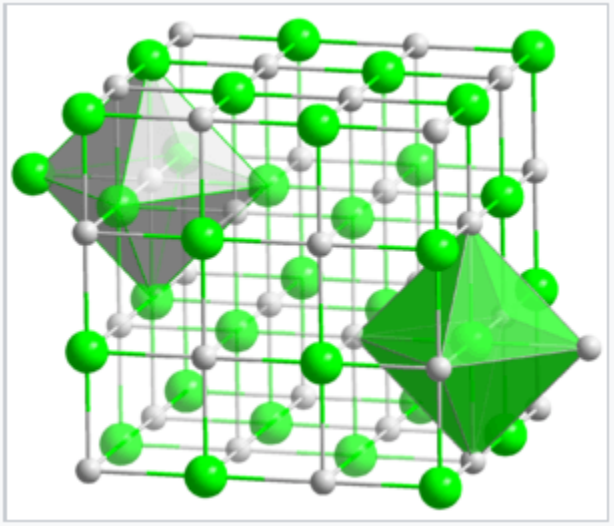


Figure 5.1.1.5: Crystal structure of NaCl. Both the Na^+ (grey) and Cl^- (green) ions are octahedrally coordinated.

In the rock salt or NaCl structure, shown in Figure 5.1.1.5, the green spheres are the Cl^- ions and the gray spheres are the Na^+ ions. The packing atoms (Na^+) are in a face centered cubic arrangement. The octahedral holes in a face-centered cubic lattice can be found at the edges and in the center of the unit cell, and they are filled by the chloride ions. Alternatively the structure can be described as the Cl^- ions in a fcc arrangement with the Na^+ ions occupying the octrahedral holes. Another way of stating this is that the structure consists of **two interpenetrating fcc lattices**, which are related to each other by a translation of half the unit cell along any of the three Cartesian axes. Thus the distinction between packing and interstitial atoms in this case is arbitrary.

NaCl is interesting in that it is a three-dimensional checkerboard, and thus there are no NaCl "molecules" that exist in the structure. When this structure was originally solved (in 1913 by using X-ray diffraction) by W. L. Bragg, his interpretation met resistance by chemists who thought that precise integer stoichiometries were a consequence of the valency of atoms in molecules. The German chemist Pfeiffer noted in 1915 that ‘the ordinary notion of valency didn’t seem to apply’, and fourteen years later, the influential chemist Armstrong still found Bragg’s proposed structure of sodium chloride ‘more than repugnant to the common sense, not chemical cricket’! Nevertheless, Bragg and his father, W. H. Bragg, persevered and used the then-new technique of X-ray diffraction to determine the structures of a number of other compounds, including diamond, zincblende, calcium fluoride, and other alkali halides. These experiments gave chemists their first real look at the atomic structure of solids, and laid the groundwork for X-ray diffraction experiments that later elucidated the structures of DNA, proteins, and many other compounds. For their work on X-ray diffraction the Braggs received the Nobel prize in Physics in 1915.

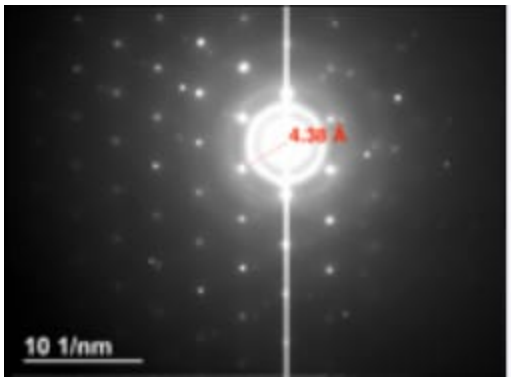


Figure 5.1.1.6: X-ray difffraction pattern for a NaCl crystal. The lattice dimensions and positions of atoms in crystals such as NaCl are inferred from diffraction patterns.

Since each type of atom in the NaCl structure forms a face-centered cubic lattice, there are four Na and four Cl atoms per NaCl unit cell. It is because of this ratio that NaCl has a 1:1 stoichiometry. The shaded green and gray octahedra in the NaCl lattice (Figure 5.1.1.5) show that the Na^+ ions are coordinated to six Cl^- ions, and vice versa.

Other materials with the NaCl structure

- Alkali Halides (except CsCl, CsBr, and CsI)
- Transition Metal Monoxides (TiO, VO,..., NiO)
- Alkali Earth Oxides and Sulfides (MgO, CaO, BaS... except BeO and MgTe)
- Carbides and Nitrides (TiC, TiN, ZrC, NbC) -these are very stable refractory, interstitial alloys (metallic)

Other Unit Cell Types

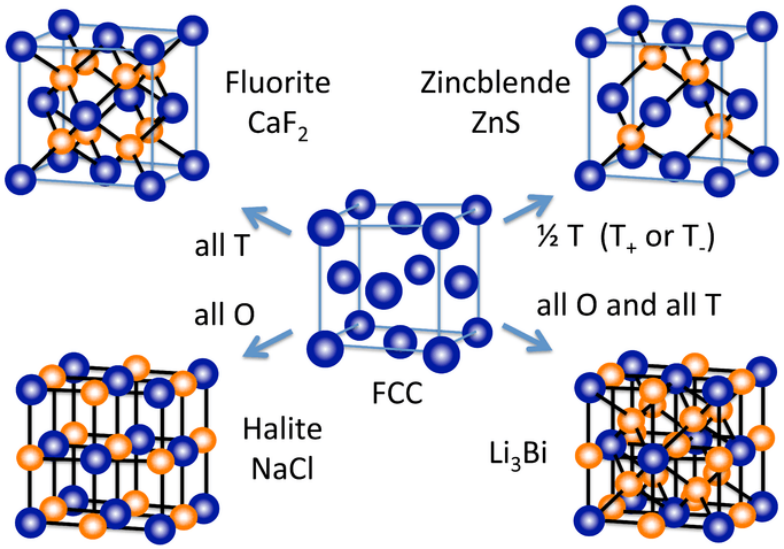


Figure 5.1.1.7: Illustration of how different unit cell types are formed by filling holes in the fcc lattice

A number of other inorganic crystal structures are formed (at least conceptually) by filling octahedral and/or tetrahedral holes in close-packed lattices. Figure 5.1.1.7 shows some of the most common structures (fluorite, NaCl, and zincblende) as well as a rather rare one (Li_3Bi) that derive from the fcc lattice. From the hcp lattice, we can make the NiAs and wurzite structures, which are the hexagonal relatives of NaCl and zincblende, respectively.

An alternative and very convenient way to represent inorganic crystal structures (especially complex structures such as Li_3Bi) is to draw the unit cell in slices along one of the unit cell axes. This kind of representation is shown at the left for the fcc lattice and

the NaCl structure. Since all atoms in these structures have z-coordinates of either 0 or 1/2, only those sections need to be drawn in order to describe the contents of the unit cell. It is a useful exercise to draw some of the fcc compound structures (above) in sections.

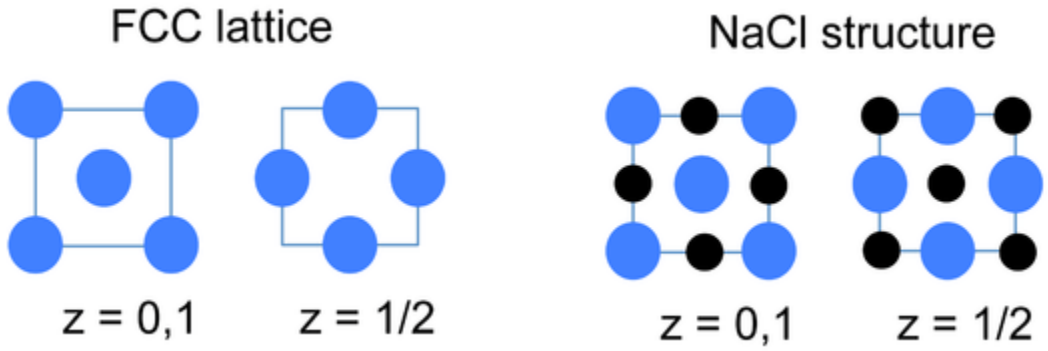


Figure 5.1.1.8: Alternative representation of the fcc lattice (left) and the NaCl structure (right). The z = 0,1 represent the bottom and top faces of the unit cell. The z = $\frac{1}{2}$ represents a slice through the center of the unit cell

Fluorite

In ccp and hcp lattices, there are two tetrahedral holes per packing atom. A stoichiometry of either M_2X or MX_2 gives a structure that fills all tetrahedral sites, while an MX structure fills only half of the sites. An example of an MX_2 structure is fluorite, CaF_2, whose structure is shown in the figure at the left. The packing atom in fluorite is Ca^{2+} and the structure is composed of three interpenetrating fcc lattices. It should be noted that the Ca^{2+} ion (gray spheres) as a packing atom defies our "rule" that anions are larger than cations and therefore must be the packing atoms. The fluorite structure is common for ionic MX_2 (MgF_2, ZrO_2, etc.) and M_2X compounds (Li_2O). In contrast, the hcp relative of the fluorite structure is quite rare because of unfavorable close contacts between like-charged ions.

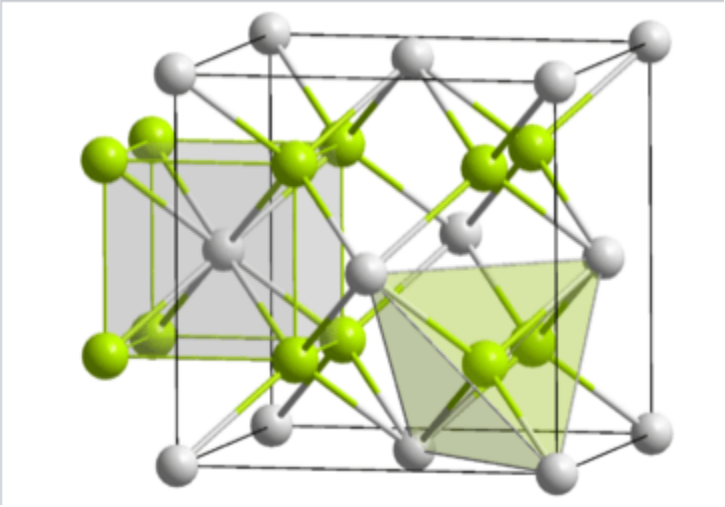


Figure 5.1.1.9: The fluorite (CaF_2) crystal structure showing the coordination environments of the Ca (grey) and F (green) atoms

In terms of geometry, Ca^{2+} is in cubic coordination with eight F^- neighbors, and the fluoride ions are tetrahedrally coordinated by four Ca^{2+} ions. The 8:4 coordination geometry is consistent with the 1:2 Ca:F stoichiometry; in all crystal structures the ratio of the coordination numbers is the inverse of the stoichiometric ratio. Looking more closely at the tetrahedral sites in fluorite, we see that they fall into two distinct groups: T_+ and T_-. If a tetrahedron is oriented with a vertex pointing upwards along the stacking axis, the site is T_+. Likewise, a tetrahedron with a vertex oriented downward is T_-. The alternation of T_+ and T_- sites allows for efficient packing of ions in the structure.

Zincblende and wurtzite

Tetrahedrally bonded compounds with a 1:1 stoichiometry (MX compounds) have only half of the tetrahedral sites (either the T_+ or T_- sites) filled. In this case, both the M and the X atoms are tetrahedrally coordinated. The zincblende and wurtzite structures of ZnS are 1:1 tetrahedral structures based on fcc and hcp lattices, respectively. Both structures are favored by p-block compounds that follow the octet rule, and these compounds are usually semiconductors or insulators. The zincblende structure, Figure 5.1.1.10 , can be thought of as two interpenetrating fcc lattices, one of anions and one of cations, offset from each other by a translation of 1/4 along the body diagonal of the unit cell. Examples of compounds with the zincblende structure include CuCl, CuI, ZnSe, HgS, BeS, CdTe, AlP, GaP, SnSb, CSi, and diamond. Using ZnS as a representative of zincblende, the coordination of both Zn and S atoms is tetrahedral.

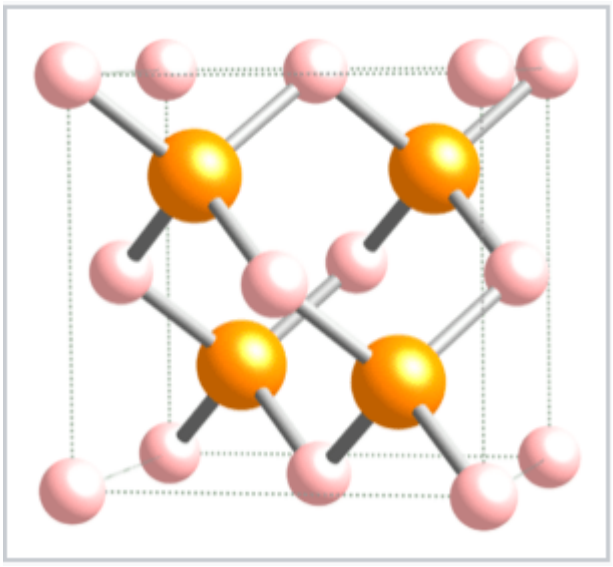


Figure 5.1.1.10: The zincblende structure of ZnS. The Zn^{2+} ions are in pink and the S^{2-} ions are in orange.

The wurtzite structure is a close relative of zincblende, based on filling half the tetrahedral holes in the hcp lattice. Like zincblende, wurtzite contains planes of fused six-membered rings in the chair conformation. Unlike zincblende, however, the rings joining these planes contain non-planar, six-membered rings. The structure aligns the anions so that they are directly above the cations in the structure, a less favorable situation sterically but a more favorable one in terms of electrostatics. As a result, the wurtzite structure tends to favor more polar or ionic compounds (e.g., ZnO, $NH_4^+F^-$) than the zincblende structure. As with zincblende, both ions are in tetrahedral (4:4) coordination and there are typically eight valence electrons in the MX compound. Examples of compounds with this structure include: BeO, ZnO, MnS, CdSe, MgTe, AlN, and NH_4F.

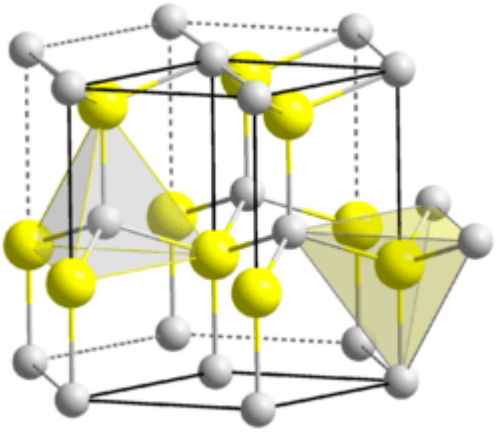


Figure 5.1.1.11: The wurtzite structure of ZnS with the tetrahedral coordination of anion and cation highlighted. The Zn^{2+} ions are in grey and the S^{2-} ions are in yellow. (Public domain; Solid State via Wikimedia Commons)

An interesting consequence of the layer stacking in the wurtzite structure is that the crystals are polar. When cleaved along the

c-axis (the stacking axis), crystals of ZnO, ZnS, and GaN have one negatively charged face and an opposite positively charged face. An applied electric field interacts with the crystal dipole, resulting in compression or elongation of the lattice along this direction. For this reason crystals of compounds in the wurtzite structure are typically piezoelectric (increasing the pressure on the material generates a voltage in the material).

Some compounds are diamorphic and can have either the zincblende or wurtzite structure. Examples of these compounds that have intermediate polarities include CdS and ZnS. SiO_2 exists in polymorphs (crystobalite and tridymite) that resemble zincblende and wurtzite with O atoms midway between each of the Si atoms. The zincblende and wurtzite structures have efficient packing arrangements for tetrahedrally bonded networks and are commonly found in compounds that have tetrahedral bonding. Water, for example, has a tetrahedral hydrogen bonding network and is wurtzite-type. The undistorted wurtzite and zincblende structures are typically found for AX compounds with eight valence electrons, which follow the octet rule. AX compounds with nine or ten electrons such as GaSe and GaAs crystallize in distorted variants of the wurtzite structure. In GaSe, the extra electrons form lone pairs and this creates layers in the structure, as can be seen in the figure below. To the right of GaSe, the structures of As, Sb, and SbAs show an ever further breakdown of the structure into layers as more valence electrons are added.

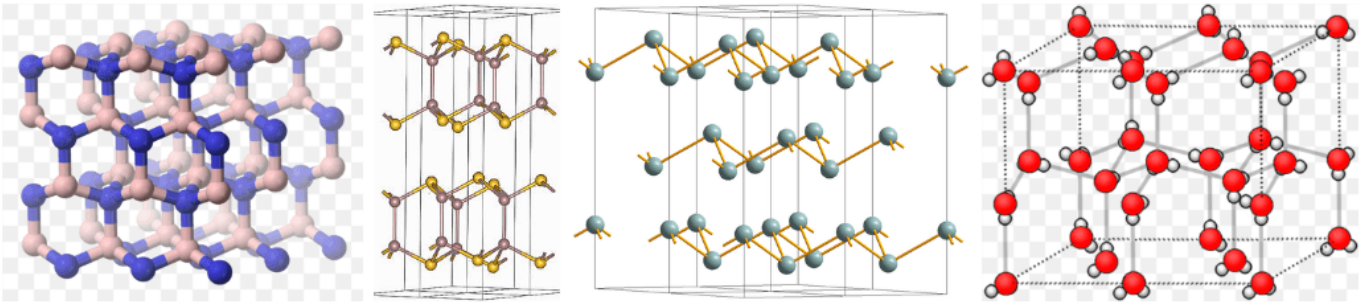


Figure 5.1.1.12: Different variations of the wurtzite crystal structure (Copyright; author via source)

Hexagonal ice is the most stable polymorph of ice, which is obtained upon freezing at 1 atmosphere pressure. This polymorph (ice-I) has a hcp wurtzite-type structure. Looking at the structure shown at the right, we see that there are irregular arrangements of the O-H---O bonds. In the structure, hydrogen bonding enforces the tetrahedral coordination of each water molecule, resulting in a relatively open structure that is less dense than liquid water. For this reason, ice floats in water.

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Contributors and Attributions

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5.1.2: Energetics of Ionic Solids- Lattice Energy

Lattice Energy

Many ionic compounds have simple structures. Because the forces holding the atoms together are primarily electrostatic, we can calculate the cohesive energy of the crystal lattice with good accuracy. Interesting questions to ask about these lattice energy calculations are:

- How accurate are lattice energy calculations?
- What do they teach us about the chemical bonds in ionic crystals?
- Can we use lattice energies to predict properties such as solubility, stability, and reactivity?
- Can we use lattice energies to predict the crystal structures of ionic compounds?

Let's start by looking at the forces that hold ionic lattices together. There are mainly two kinds of force that determine the energy of an ionic bond.

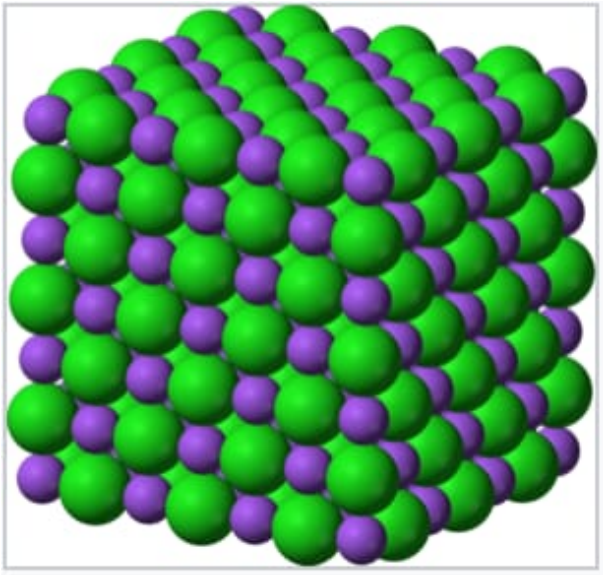


Figure 5.1.2.1: The NaCl crystal structure is the archetype for calculating lattice energies and computing enthalpies of formation from Born-Haber cycles.

Electrostatic force

Electrostatic force is the attraction and repulsion between ions described by Coulomb's Law. Two ions with charges z_+ and z_-, separated by a distance r, experience a force F:

$$\mathbf{F} = -\frac{e^2}{4\pi\varepsilon_0}\frac{z_+ z_-}{r^2} \tag{5.1.2.1}$$

where

e = 1.6022×10^{-19} C

4 π ε_0 = 1.112×10^{-10} C^2/(J m)

This force is attractive for ions of opposite charge and repulsive for ions of the same charge.

Closed-shell repulsion

When electrons in the core shells of one ion overlap with those of another ion, there is a repulsive force due to the Pauli exclusion principle. A third electron cannot enter an orbital that already contains two electrons. This force is short range, and is typically modeled as falling off exponentially or with a high power of the distance r between atoms. For example, in the Born approximation, B is a constant and ρ is a number with units of length, which is usually empirically determined from compressibility data. A typical value of ρ is 0.345 Å.

$$\mathbf{E}_{repulsion} = Bexp(\frac{-r}{\rho}) \tag{5.1.2.2}$$

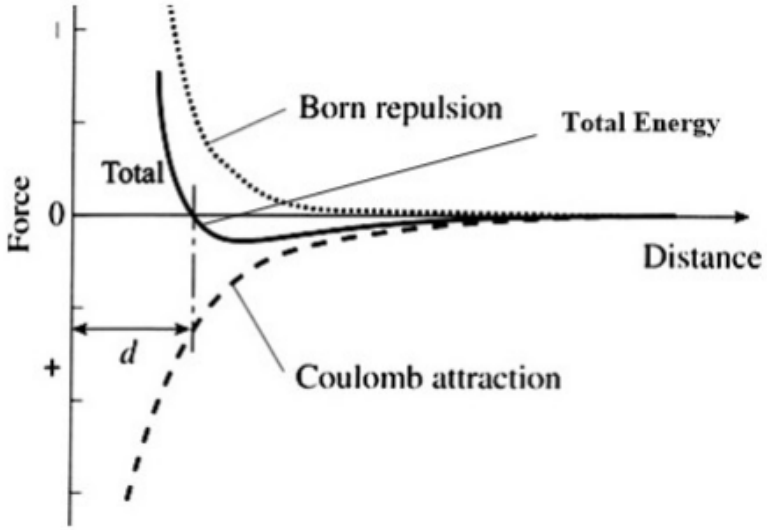


Figure 5.1.2.2: Total energy of an ionic bond (solid) determined by the combination of Coulombic attraction (dashed) and Born (closed-shell) repulsion (dotted).

The energy of the ionic bond between two atoms is then calculated as the combination of net electrostatic and the closed-shell repulsion energies, as shown in Figure 5.1.2.2. Note that for the moment we are ignoring the attractive van der Waals forces between ions. For a pair of ions, the equilibrium distance between ions is determined by the minimum in the total energy curve.

Madelung Constant

We can use the above equations to calculate the lattice energy of a crystal by summing up the interactions between all pairs of ions. Because the closed-shell repulsion force is short range, this term is typically calculated only for interactions between neighboring ions. However, the Coulomb force is long range, and must be calculated over the entire crystal. This problem was first solved in 1918 by Erwin Madelung, a German physicist.

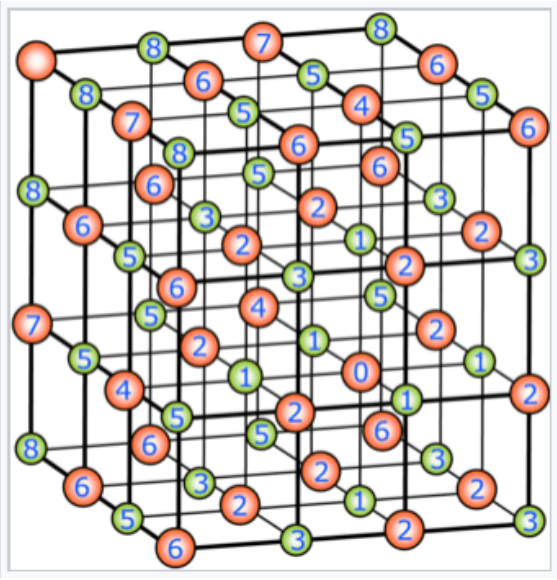


Figure 5.1.2.3: The Madelung constant is calculated by summing up electrostatic interactions with ion labeled 0 in the expanding spheres method. Each number designates the order in which it is summed. For example, ions labeled 1 represent the six nearest neighbors (attractive interaction), ions labeled 2 are the 12 next nearest neighbors (repulsive interaction) and so on.

Consider an ion in the NaCl structure labeled "0" in Figure 5.1.2.3. We can see that the nearest neighbor interactions (+ -) with ions labeled "1" are attractive, the next nearest neighbor interactions (- - and + +) are repulsive, and so on. In the NaCl structure, counting from the ion in the center of the unit cell, there are 6 nearest neighbors (on the faces of the cube), 12 next nearest neighbors (on the edges of the cube), 8 in the next shell (at the vertices of the cube), and so on. Their distances from ion "0" increase progressively: r_o, $\sqrt{2}\, r_o$, $\sqrt{3}\, r_o$, and so on, where r_o is the nearest neighbor distance.

We can now write the electrostatic energy at ion "0" as:

$$\mathbf{E}_{elec} = -6\frac{e^2}{4\pi\varepsilon_0}\frac{z_+z_-}{r_o} + 12\frac{e^2}{4\pi\varepsilon_0}\frac{z_+z_-}{\sqrt{2}r_o} - 8\frac{e^2}{4\pi\varepsilon_0}\frac{z_+z_-}{\sqrt{3}r_o} + ... \tag{5.1.2.3}$$

Factoring out constants and the nearest-neighbor bond distance r_o we obtain:

$$\mathbf{E}_{elec} = \frac{e^2}{4\pi\varepsilon_0}\frac{z_+z_-}{r_o}(6 - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{\sqrt{4}} + ...) \tag{5.1.2.4}$$

Where the sum in parentheses, which is unitless, slowly converges to a value of A = 1.74756. Generalizing this formula for any three-dimensional ionic crystal we get a function:

$$\mathbf{E}_{elec} = \frac{e^2}{4\pi\varepsilon_0}\frac{z_+z_-}{r_o}NA \tag{5.1.2.5}$$

where N is Avogadro's number (because we are calculating energy per mole of ions) and A is called the *Madelung constant*. The **Madelung constant** depends only on the geometrical arrangement of the ions and so it varies between different types of crystal structures, but within a given structure type it does not change. Thus MgO and NaCl have the same Madelung constant because they both have the NaCl structure.

Table 5.1.2.1: 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	6 : 3	

Compound	Crystal Lattice	M	A : C	Type
MgF_2	Tetragonal	2.381		
ZnS (wurtzite)	Hexagonal	1.64132	4 : 4	Wurtzite
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.				

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 5.1.2.6) 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

$$U = \frac{N_A M Z^2 e^2}{4\pi\epsilon_o r}\left(1 - \frac{1}{n}\right) \tag{5.1.2.6}$$

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 5.1.2.3).

Table 5.1.2.2: 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

Example 5.1.2.1: NaCl

Estimate the lattice energy for NaCl.

Solution
Using the values giving in the discussion above, the estimation is given by

$$U_{NaCl} = \frac{(6.022 \times 10^{23}/mol)(1.74756)(1.6022 \times 10^{-19})^2(1.747558)}{4\pi\,(8.854 \times 10^{-12} C^2/m)(282 \times 10^{-12}\ m)}\left(1 - \frac{1}{9.1}\right)$$
$$= -756\,kJ/mol$$

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.



Figure 5.1.2.4: Lithium fluoride (shown here as a large single crystal in a beaker of water) is the only alkali halide that is not freely soluble in water. The lattice energy of LiF is the most negative of the alkali fluorides because Li^+ and F^- are both small ions and lattice energy is proportional to $1/r_0$.

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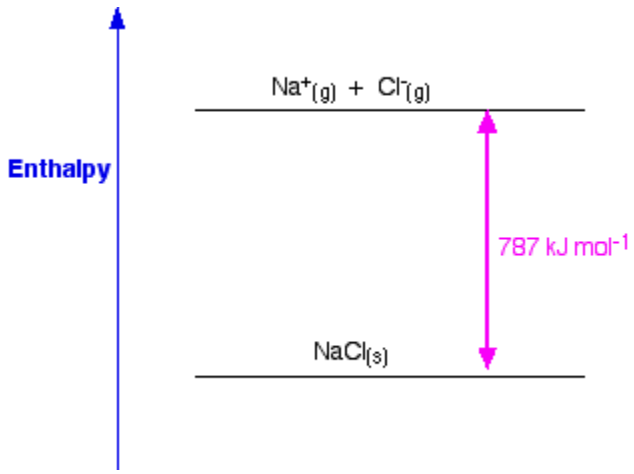
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5.1.3: Lattice Enthalpies and Born Haber Cycles

Lattice enthalpy is a measure of the strength of the forces between the ions in an ionic solid. The greater the **lattice enthalpy**, the stronger the forces. This page introduces lattice enthalpies (lattice energies) and Born-Haber cycles.

Defining Lattice Enthalpy

There are two different ways of defining lattice enthalpy which directly contradict each other, and you will find both in common use. In fact, there is a simple way of sorting this out, but many sources do not use it. Lattice enthalpy is a measure of the strength of the forces between the ions in an ionic solid. The greater the lattice enthalpy, the stronger the forces. 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. You can show this on a simple enthalpy diagram.



For sodium chloride, the solid is more stable than the gaseous ions by 787 kJ mol^{-1}, and that is a measure of the strength of the attractions between the ions in the solid. Remember that energy (in this case heat energy) is released when bonds are made, and is required to break bonds.

So lattice enthalpy could be described in either of two ways.

- It could be described as the enthalpy change when 1 mole of sodium chloride (or whatever) was formed from its scattered gaseous ions. In other words, you are looking at a downward arrow on the diagram.
- Or, it could be described as the enthalpy change when 1 mole of sodium chloride (or whatever) is broken up to form its scattered gaseous ions. In other words, you are looking at an upward arrow on the diagram.

Both refer to the same enthalpy diagram, but one looks at it from the point of view of making the lattice, and the other from the point of view of breaking it up. Unfortunately, both of these are often described as "lattice enthalpy".

Definitions

- 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**.

This is an absurdly confusing situation which is easily resolved by never using the term "lattice enthalpy" without qualifying it.

- You should talk about "lattice dissociation enthalpy" if you want to talk about the amount of energy needed to split up a lattice

into its scattered gaseous ions. For NaCl, the lattice dissociation enthalpy is +787 kJ mol^{-1}.
- You should talk about "lattice formation enthalpy" if you want to talk about the amount of energy released when a lattice is formed from its scattered gaseous ions. For NaCl, the lattice formation enthalpy is -787 kJ mol^{-1}.

That immediately removes any possibility of confusion.

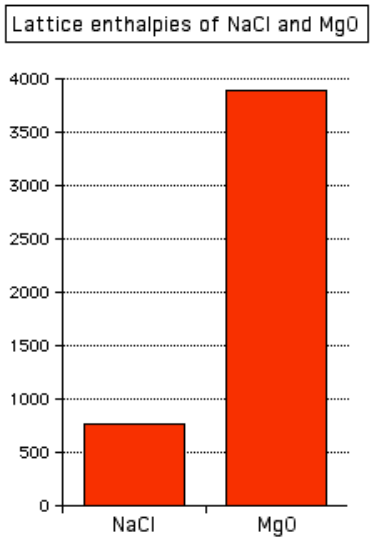
Factors affecting Lattice Enthalpy

The two main factors affecting lattice enthalpy are

- The charges on the ions and
- The ionic radii (which affects the distance between the ions).

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.

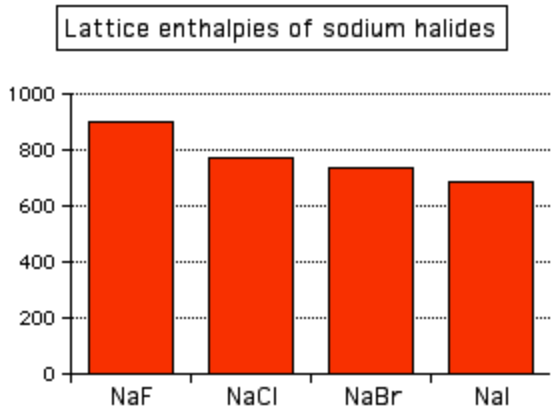


You can see that the lattice enthalpy of magnesium oxide is much greater than that of sodium chloride. That's because in magnesium oxide, 2+ ions are attracting 2- ions; in sodium chloride, the attraction is only between 1+ and 1- ions.

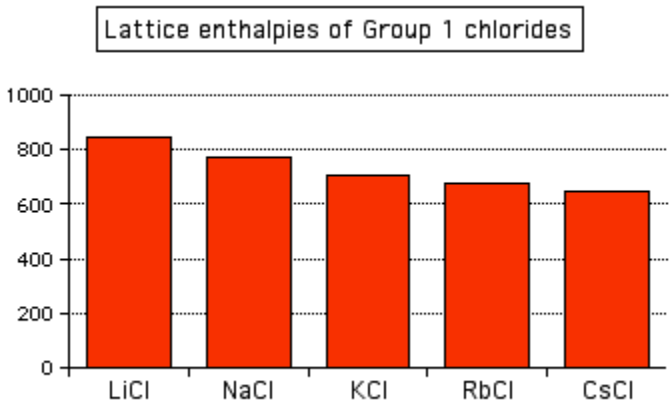
The Radius of the Ions

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:



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.



Calculating Lattice Enthalpy

It is impossible to measure the enthalpy change starting from a solid crystal and converting it into its scattered gaseous ions. It is even more difficult to imagine how you could do the reverse - start with scattered gaseous ions and measure the enthalpy change when these convert to a solid crystal. Instead, lattice enthalpies always have to be calculated, and there are two entirely different ways in which this can be done.

1. You can can use a Hess's Law cycle (in this case called a Born-Haber cycle) involving enthalpy changes which can be measured. Lattice enthalpies calculated in this way are described as experimental values.
2. Or you can do physics-style calculations working out how much energy would be released, for example, when ions considered as point charges come together to make a lattice. These are described as theoretical values. In fact, in this case, what you are actually calculating are properly described as lattice energies.

Born-Haber Cycles

Standard Atomization Enthalpies

Before we start talking about Born-Haber cycles, we need to define the **atomization enthalpy**, ΔH_a^o. The standard atomization enthalpy 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:

$$\frac{1}{2}Cl_2(g) \rightarrow Cl(g) \quad \Delta H_a^o = +122\,kJ\,mol^{-1}$$

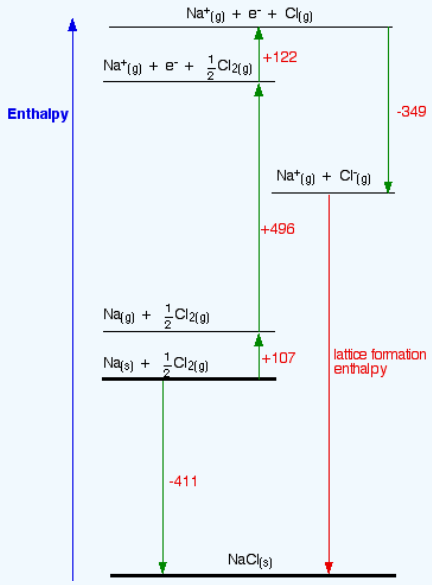
$$\frac{1}{2}Br_2(l) \rightarrow Br(g) \quad \Delta H_a^o = +122\,kJ\,mol^{-1}$$

$$Na(s) \rightarrow Na(g) \quad \Delta H_a^o = +107\,kJ\,mol^{-1}$$

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.

Example 5.1.3.1: Born-Haber Cycle for NaCl

Consider a Born-Haber cycle for sodium chloride, and then talk it through carefully afterwards. You will see that I have arbitrarily decided to draw this for lattice formation enthalpy. If you wanted to draw it for lattice dissociation enthalpy, the red arrow would be reversed - pointing upwards.



Focus to start with on the higher of the two thicker horizontal lines. We are starting here with the elements sodium and chlorine in their standard states. Notice that we only need half a mole of chlorine gas in order to end up with 1 mole of NaCl. The arrow pointing down from this to the lower thick line represents the enthalpy change of formation of sodium chloride.

The Born-Haber cycle now imagines this formation of sodium chloride as happening in a whole set of small changes, most of which we know the enthalpy changes for - except, of course, for the lattice enthalpy that we want to calculate.

- The +107 is the atomization enthalpy of sodium. We have to produce gaseous atoms so that we can use the next stage in the cycle.
- The +496 is the first ionization energy of sodium. Remember that first ionization energies go from gaseous atoms to gaseous singly charged positive ions.
- The +122 is the atomization enthalpy of chlorine. Again, we have to produce gaseous atoms so that we can use the next stage in the cycle.
- The -349 is the first electron affinity of chlorine. Remember that first electron affinities go from gaseous atoms to gaseous singly charged negative ions.
- And finally, we have the positive and negative gaseous ions that we can convert into the solid sodium chloride using the lattice formation enthalpy.

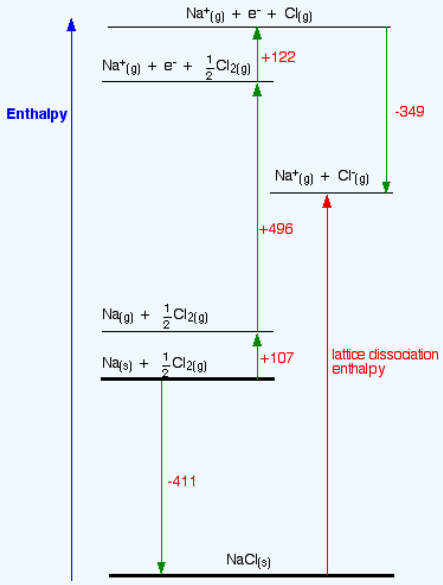
Now we can use Hess' Law and find two different routes around the diagram which we can equate. As drawn, the two routes are obvious. The diagram is set up to provide two different routes between the thick lines. So, from the cycle we get the calculations directly underneath it . . .

$$-411 = +107 + 496 + 122 - 349 + LE$$

$$LE = -411 - 107 - 496 - 122 + 349$$

$$LE = -787 \text{ kJ mol}^{-1}$$

How would this be different if you had drawn a lattice dissociation enthalpy in your diagram? Your diagram would now look like this:



The only difference in the diagram is the direction the lattice enthalpy arrow is pointing. It does, of course, mean that you have to find two new routes. You cannot use the original one, because that would go against the flow of the lattice enthalpy arrow. This time both routes would start from the elements in their standard states, and finish at the gaseous ions.

$$-411 + LE = +107 + 496 + 122 - 349$$

$$LE = +107 + 496 + 122 - 349 + 411$$

$$LE = +787 \text{ kJ mol}^{-1}$$

Once again, the cycle sorts out the sign of the lattice enthalpy.

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.

Example 5.1.3.2: Born-Haber Cycle for $MgCl_2$

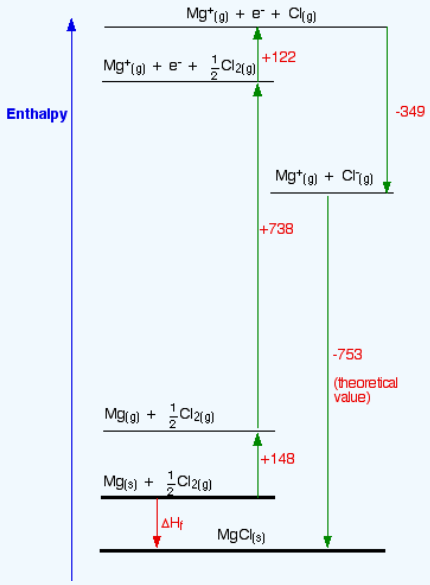
The question arises as to why, from an energetics point of view, magnesium chloride is $MgCl_2$ rather than MgCl or $MgCl_3$ (or any other formula you might like to choose). It turns out that $MgCl_2$ is the formula of the compound which has the most negative enthalpy change of formation - in other words, 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 and contrast the enthalpy change of formation for the imaginary compounds MgCl and $MgCl_3$. That means that we will have to use theoretical values of their lattice enthalpies. We ca not use experimental ones, because these compounds obviously do not exist! I'm taking theoretical values for lattice enthalpies for these compounds that I found on the web. I can't confirm these, but all the other values used by that source were accurate. The exact values do not matter too much anyway, because the results are so dramatically clear-cut.

1. The Born-Haber cycle for MgCl

We will start with the compound MgCl, because that cycle is just like the NaCl one we have already looked at.

$$Mg\,(s) + \tfrac{1}{2}\,Cl_2\,(g) \rightarrow MgCl\,(s)$$



Find two routes around this without going against the flow of any arrows. That's easy:

$$\Delta H_f = +148 + 738 + 122 - 349 - 753$$

$$\Delta H_f = -94 \text{ kJ mol}^{-1}$$

So the compound MgCl is definitely energetically **more stable** than its elements. I have drawn this cycle very roughly to scale, but that is going to become more and more difficult as we look at the other two possible formulae. So I am going to rewrite it as a table. 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

2. 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

$$Mg\,(s) + \tfrac{3}{2}\,Cl_2\,(g) \rightarrow MgCl_3\,(s)$$

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.

Contributors and Attributions

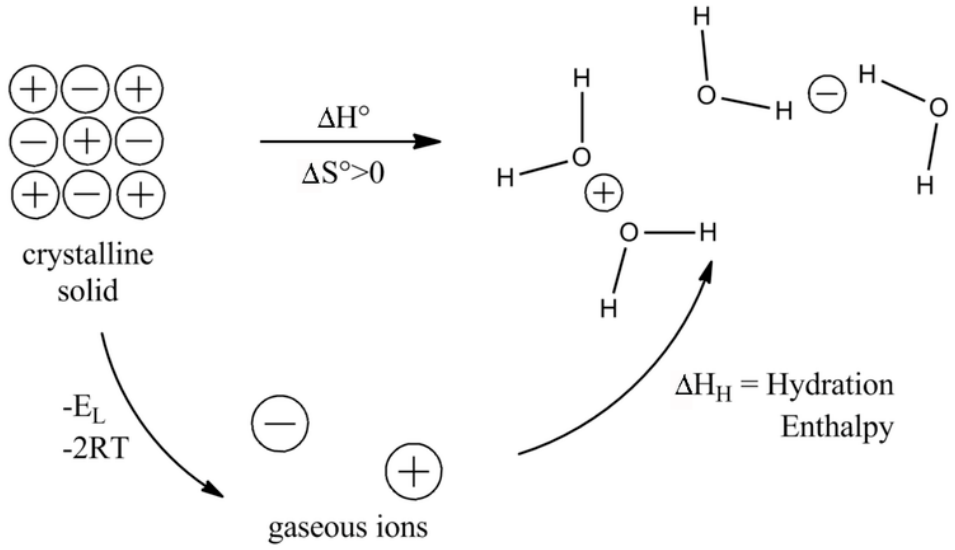
- Jim Clark (Chemguide.co.uk)

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5.1.4: Lattice Energy and Solubility

Lattice energies can also help predict compound solubilities. Let's consider a Born-Haber cycle for dissolving a salt in water. We can imagine this as the sum of two processes: (1) the vaporization of the salt to produce gaseous ions, characterized by the lattice enthalpy, and (2) the hydration of those ions to produce the solution. The enthalpy change for the overall process is the sum of those two steps. We know that the entropy change for dissolution of a solid is positive, so the solubility depends on the enthalpy change for the overall process.



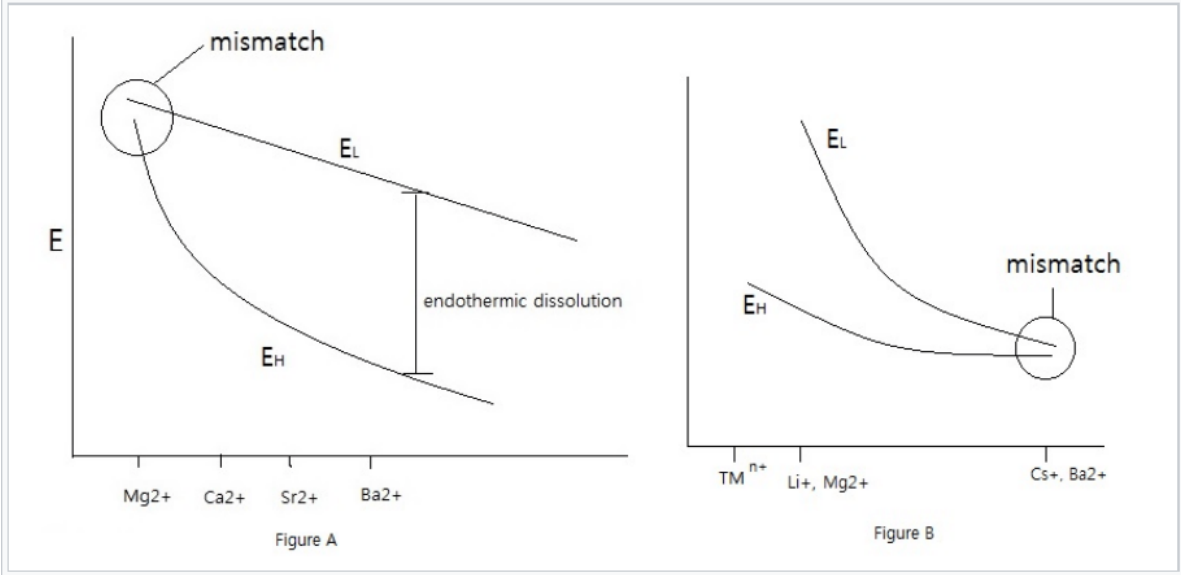
Here we need to consider the trends in both the lattice energy E_L and the hydration energy E_H. The lattice energy depends on the sum of the anion and cation radii ($r_+ + r_-$), whereas the hydration energy has separate anion and cation terms. Generally the solvation of small ions (typically cations) dominates the hydration energy because of the $1/r^2$ dependence.

$$E_L \alpha \frac{1}{r_+ + r_-} \tag{5.1.4.1}$$

$$E_H \alpha \frac{1}{r_+^2} + \frac{1}{r_-^2} \tag{5.1.4.2}$$

For salts that contain large anions, E_L doesn't change much as r_+ changes. That is because the anion dominates the $r_+ + r_-$ term in the denominator of the formula for E_L. On the other hand, E_H changes substantially with r_+, especially for small cations.

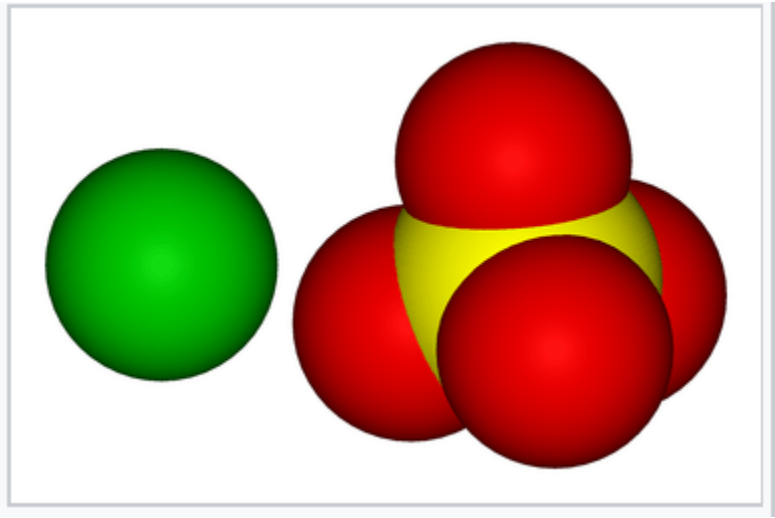
As a result, sulfate salts of small divalent cations, such as $MgSO_4$ (epsom salts), are soluble, whereas the lower hydration energy of Ba^{2+} in $BaSO_4$ makes that salt insoluble ($K_{sp} = 10^{-10}$).



Left: E_L diagram for sulfate salts. The large SO_4^{2-} ion is size-mismatched to small cations such as Mg^{2+}, which have large hydration energies, resulting soluble salts. With larger cations such as Ba^{2+}, which have lower E_H, the lattice energy exceeds the solvation enthalpy and the salts are insoluble.. Right: In the case of small anions such as F^- and OH^-, the lattice energy dominates with small cations such as transition metal ions (TM^{n+}), Mg^{2+}, and Li^+. Anion-cation size mismatch occurs with larger cations, such as Cs^+ and Ba^{2+}, which make soluble fluoride salts.

For small anions, E_L is more sensitive to r_+, whereas E_H does not depend on r_+ as strongly. For fluorides and hydroxides, LiF is slightly soluble whereas CsF is very soluble, and $Mg(OH)_2$ is insoluble whereas $Ba(OH)_2$ is very soluble.

Putting both trends together, we see that **low solubility** is most often encountered when the **anion and cation match well in their sizes**, especially when one or both are **multiply charged**.



Space-filling models showing the van der Waals surfaces of Ba^{2+} and SO_4^{2-}. The similarity in size of the two ions contributes to the low solubility of $BaSO_4$ in water.

Combining all our conclusions about solubility, we note the following trends:

1) Increasing **size mismatch** between the anion and cation leads to greater solubility, so CsF and LiI are the most soluble alkali halides.

2) Increasing **covalency** leads to lower solubility in the salts (due to larger E_L. For example, AgF, AgCl, AgBr, and AgI exhibit progressively lower solubility because of increasing covalency.

$$\mathrm{AgF} > \mathrm{AgCl} > \mathrm{AgBr} > \mathrm{AgI}$$

3) Increasing the **charge on the anion** lowers the solubility because the increase in E_L is large relative to the increase in E_H.

4) Small, polyvalent cations (having large E_H) make **soluble salts with large, univalent anions** such as I^-, NO_3^-, ClO_4^-, PF_6^-, and acetate.

Examples: Salts of transition metal and lanthanide ions

- Ln^{3+}: Nitrate salts are soluble, but oxides and hydroxides are insoluble.
- Fe^{3+}: Perchlorate is soluble, but sulfate is insoluble.

5) Multiple charged anions such as O^{2-}, S^{2-}, PO_4^{3-}, and SO_4^{2-} make insoluble salts with most M^{2+}, M^{3+}, and M^{4+} metals.

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5.1.5: Bonding in Metals and Semicondoctors

Band Theory

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. One way to conceptualize band theory is to view is as an extension of molecular orbital theory where the number of atomic orbitals mixed is increased to an infinite number and the energy difference between the molecular orbitals formed approaches 0 (Figure 5.1.5.1).

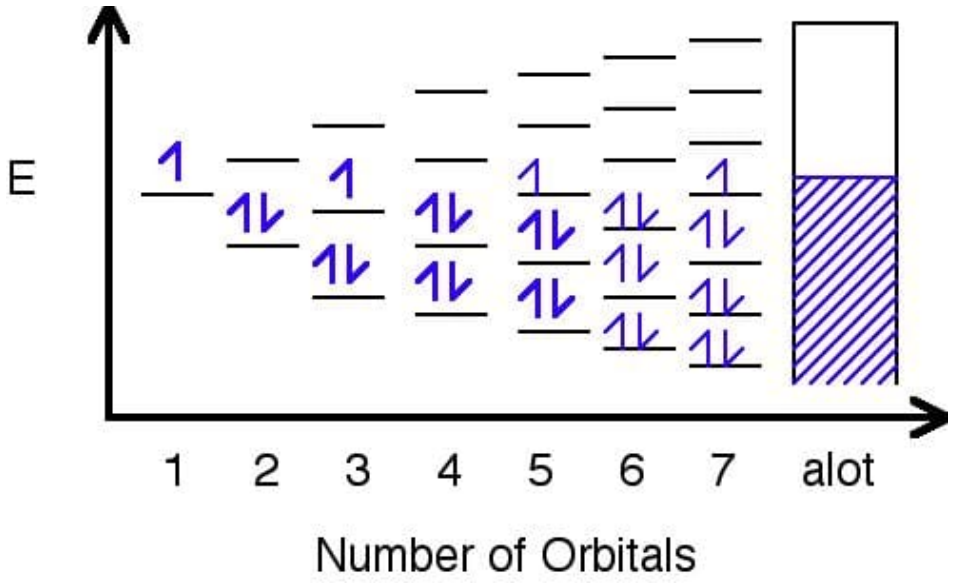


Figure 5.1.5.1: In this image, orbitals are represented by the black horizontal lines, and they are being filled with an increasing number of electrons as their amount increases. Eventually, as more orbitals are added, the space in between them decreases to hardly anything, and as a result, a band is formed where the orbitals have been filled.

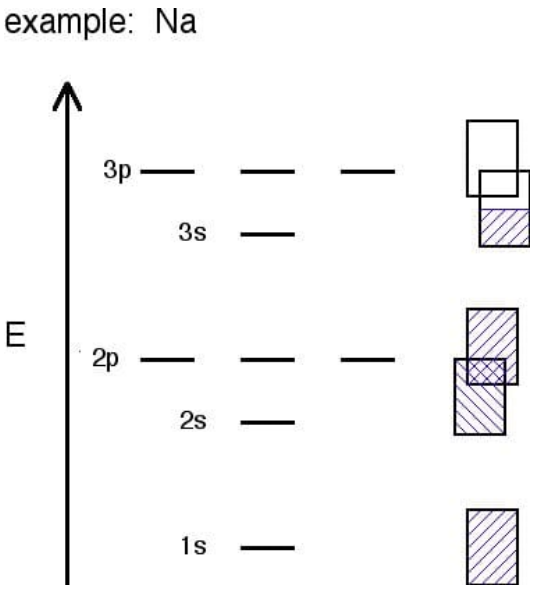


Figure 5.1.5.2: Bands diagram of sodium metal. Filled bands are blue and empty bands are white. Because the 3s orbital is half filled in Na, the band formed form the 3s orbitals is also half filled.

Different metals will produce different combinations of filled and half filled bands depending on their valence electron

configuration. Sodium's bands are shown in Figure 5.1.5.2. 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 band is 1/2 full... and so on.

In order for the material to conduct electricity, electrons should be in the conduction band where they are able to move freely through the material. The probability of finding an electron in the conduction band is shown by the equation:

$$P = \frac{1}{e^{\frac{\Delta E}{k_b T}} + 1} \tag{5.1.5.1}$$

The ΔE in the equation stands for the energy gap between the valence and conduction bands. k_b is the Boltzmann constant and T is temperature in K. That equation and the table below show that the larger the band 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 don't have sufficient energy to make the jump up to the conduction band.

Table 5.1.5.1: Band Gaps and Conduction Band Electron Densities for Group 4 Elements

ELEMENT	ΔE(kJ/mol) of energy gap	# of electrons/cm^3 in conduction band	material type
C (diamond)	524	10^{-27}	insulator
Si	117	10^{9}	semiconductor
Ge	66	10^{13}	semiconductor

Conductors, Insulators and Semiconductors

The conductivity of materials is directly related to the band gap and the probability of having electrons in the conduction band. Materials can be divided into three classes based on their band gaps (Figure 5.1.5.3).

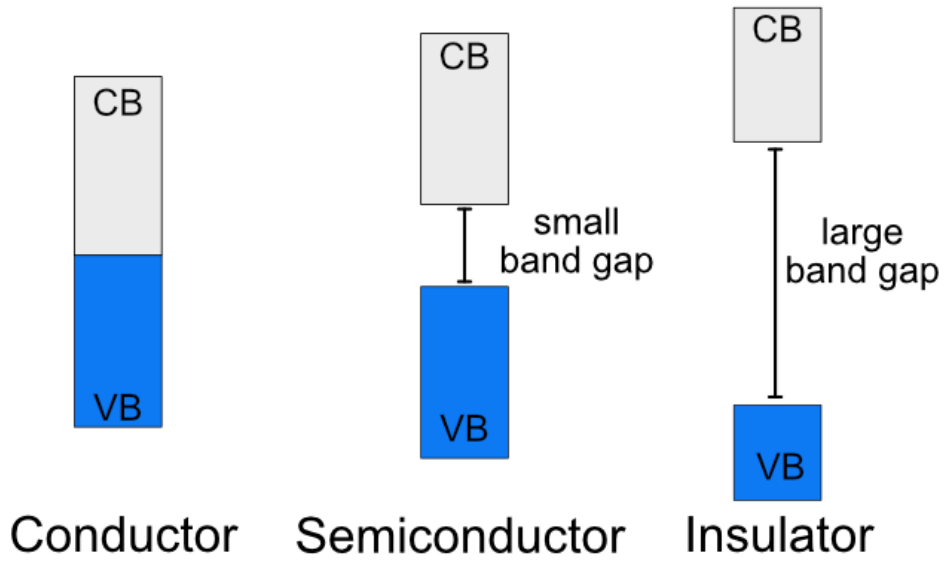


Figure 5.1.5.3: Illustration of the energy difference between the valence band (VB) and conduction band (CB) in conductors, semiconductors and insulators. (CC BY-NC-SA; Catherine McCusker)

Conductors

Conductors have no band gap between their valence and conduction bands, since they overlap. There is no barrier for electrons to move from the valence to conduction band. Electrons can move freely through the material, which makes it able to conduct electricity. When the temperature of a conductor increases, the resistivity increases (and the conductivity decreases). Conductivity and resistivity are inversely proportional to each other. When conductivity is low, resistivity is high. When resistivity is low, conductivity is high. Since conductivity is the measure of how easily electricity flows, electrical resistivity measures how much a material resists the flow of electricity. As electrons move through a material, they come into contact with nuclei in the material. Collisions slow the electrons down. Each collision increases the resistivity of the material, and as temperature increases the electron are more likely to have collisions.

Insulators

Insulators have a large band gap between the valence and conduction bands. In insulators electrons do not have sufficient energy to jump from the valence band to the conduction band and the probability of finding an electron in the conduction band approaches 0. An insulator material won't conduct any electricity at any temperature.

Semiconductors

Semiconductors are an intermediate between conductors and insulators. They have a small energy gap between the valence band and the conduction band. Some electrons have sufficient energy that they can make the jump up to the conduction band. Semiconductors can conduct electricity, but not as easily as conductors. The probability of finding electrons in the conduction band of a semiconductor, and therefore it's ability to conduct electricity, will vary with the band gap and the temperature. Unlike conductors, semiconductors are more conductive at higher temperatures because more electrons have the energy to jump into the conduction band. There are two types of semiconductors: **intrinsic** and **extrinsic**.

Intrinsic Semiconductors

An intrinsic semiconductor is a pure material with a small band gap. For every electron that jumps into the conduction band, the missing electron will generate a hole that can move freely in the valence band. Both conduction band electrons and valence band holes can contribute to conducting electricity. The number of holes will equal the number of electrons that have jumped.

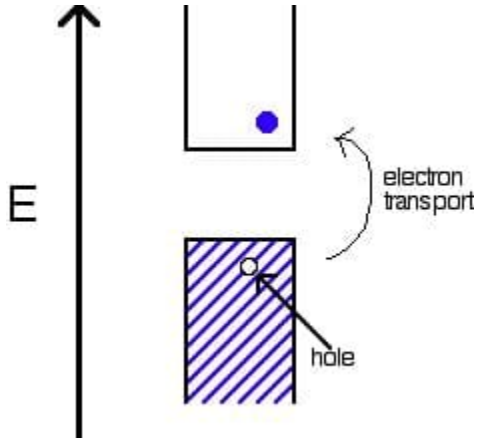


Figure 5.1.5.4: Illustration of an intrinsic semiconductor. The electron in the conduction band (blue dot) leaves behind a vacancy (hole) in the valence band (white dot).

Extrinsic Semiconductors

Extrinsic semiconductors are not good conductors in their pure forms, they have larger band gaps than intrinsic semiconductors. In extrinsic semiconductors, the conductivity is controlled by purposefully adding small amounts of 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 valence band holes will not equal the number of conduction band electrons. Silicon is one of the most common extrinsic semiconductors. If silicon is doped with an atom with fewer electron, such as boron, electron from the silicon valence band can hop to the boron atoms, leaving holes in the valence band to conduct electricity. If silicon is doped with an atom with more electrons, such as phosphorus, the extra electron from the phosphorus atoms can jump into the silicon conduction band.

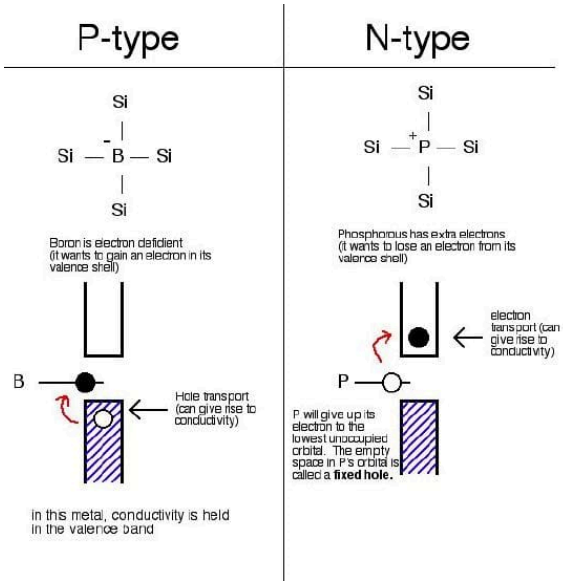


Figure 5.1.5.5: P-type (left) n-type (right) silicon semiconductors. In the p-type an electron from the valence band can jump to a vacancy on boron, leaving a hole in the valence band. In the n-type an electron from the phosphorus dopant can jump into the conduction band.

Exercise 5.1.5.1

Describe the difference between a valence band and a conduction band

Answer available at the end of this section.

Exercise 5.1.5.2

A conductor material and a semiconductor material have the same conductivity at 100 K. Which will be more conductive when the temperature is increased to 200 K?

Answer available at the end of this section.

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Contributors and Attributions

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Answers

Exercise 5.1.5.1

The valence band is the highest band with electrons in it, the equivalent of the HOMO in MO theory. The conduction band is the highest band with no electrons in it, the equivalent of the LUMO in MO theory.

Exercise 5.1.5.2

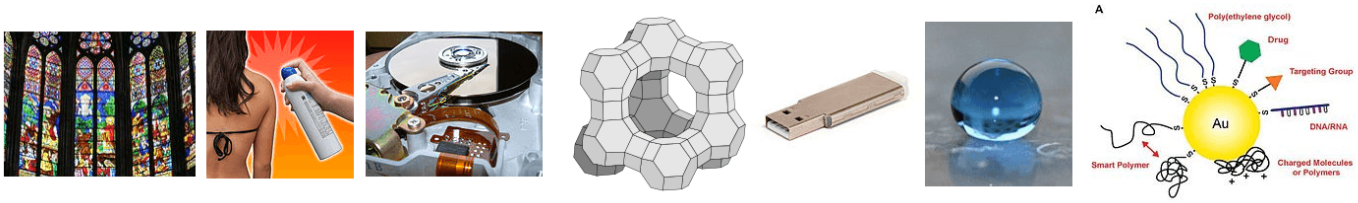
The conductivity of conductors will decrease as the temperature increases and the conductivity of semiconductors will increase as the temperature increases. Therefore at higher temperature the semiconductor material will have higher conductivity.

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5.1.6: 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 section we will learn about the basic science of nanomaterials, i.e., what it is about their size that makes them different.



Surface Area

Nanoparticles have a substantial fraction of their atoms on the surface, as shown in Figure 5.1.6.1. 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. In some cases, such as TiO_2, it can change which polymorph is most stable. The most stable form of bulk TiO_2 is rutile, but in TiO_2 nanoparticles, the most stable polymorph is anatase. Heterogeneous catalysts, for example, are often based on nanoparticles because the catalytically reactive atoms are those that are on the surface of the particle, and this allows for the most reactive surface sites with the smallest amount of material.

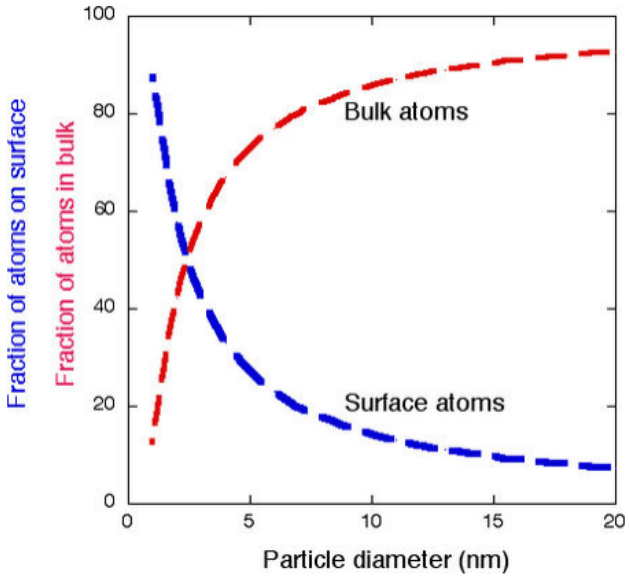


Figure 5.1.6.1: Plot of how the ratio of surface to bulk atoms changes with particle size.

Surface Energy

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 surface of the crystal 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 5.1.6.1

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 surface of a gold crystal?.

Solution

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 crystal face is 4.3 x 10^4 m^2.

Now we multiply this area by the surface energy:

$(4.3 \times 10^4 \frac{m^2}{mol}) \times (1.5 \frac{J}{mol}) \times (\frac{1kJ}{1000J}) = +\mathbf{65kJ}$ 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 the above 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.

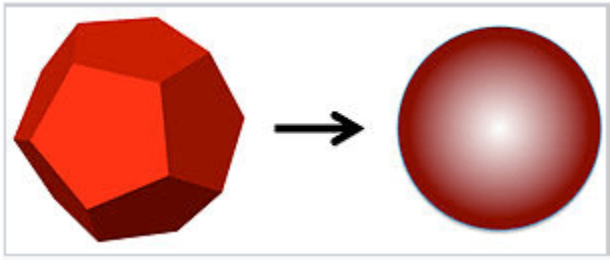


Figure 5.1.6.2: A faceted solid nanocrystal melts into a spherical droplet in order to minimize its surface energy.

Let's consider melting a silver nanocrystal that is 2 nm in diameter, meaning that about $\frac{1}{2}$ 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:

$$\Delta H^o_{fusion} \approx \Delta H^o_{fusion,\ bulk} - (\frac{1}{2})(0.25)(\frac{1}{4})\Delta H^o_{vap} = \Delta H^o_{fusion,\ bulk} - 0.025\Delta H^o_{vap,\ bulk} \tag{5.1.6.1}$$

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:

$$\Delta H^o_{fusion} \approx 11.3 - (0.025)(25) = 5.1 \frac{kJ}{mol} \tag{5.1.6.2}$$

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. 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 larger crystals of the same material.

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.

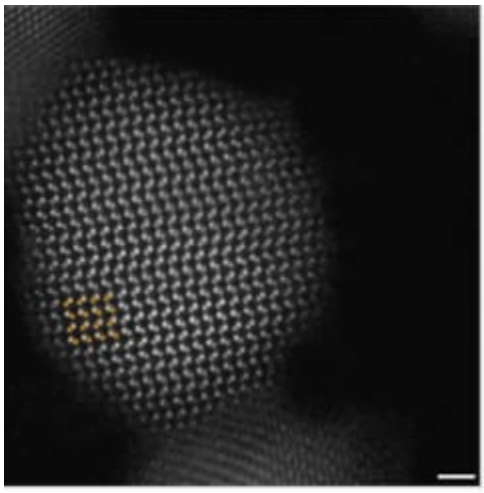


Figure 5.1.6.3: Atomic resolution image of a CdSe nanoparticle.

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 in Figure 5.1.6.3. The band gap in many of these quantum dots is in a range where absorption of visible light can promote an electron from the valence band to the conduction band as shown in Figure 5.1.6.4. Relaxation of that electron back into the valence band results in emission. The quantum yield for band gap emission of semiconductor quantum dots is typically high, giving rise to the bright emission colors shown in (Figure 5.1.6.5) 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.

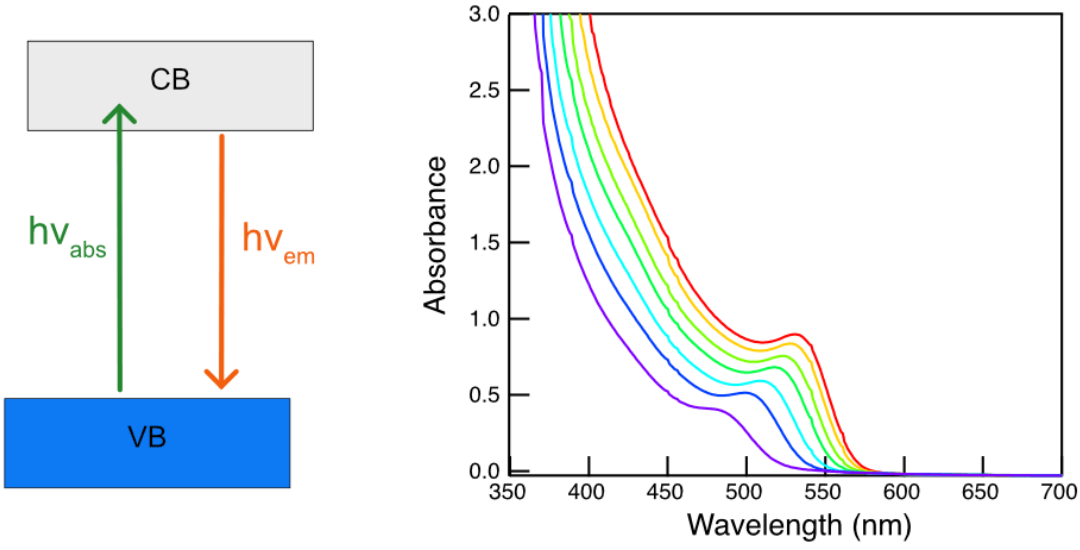


Figure 5.1.6.4: Diagram (left) showing the band gap absorption and emission of visible light in quantum dots. UV-visible spectrum (right) of a series of CdSe quantum dots. (CC BY-NC-SA, Catherine McCusker)

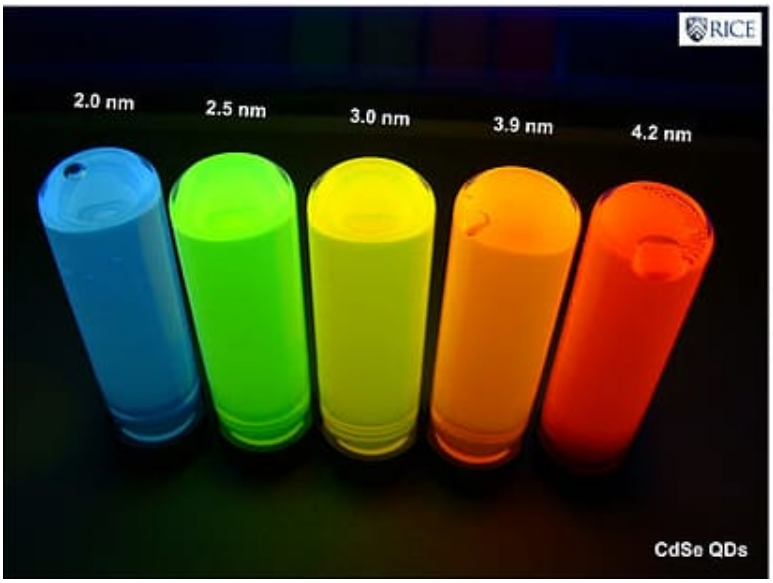


Figure 5.1.6.5: Emission colors of CdSe nanoparticles of different sizes. Smaller particles emit blue light because the exciton energy increases as the size decreases.

Size dependence

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 band gap of a semiconductor quantum dot is given approximately by:

$$E_{gap} = E_{gap,bulk} + \frac{h^2}{8\mu R^2} - \frac{1.8e^2}{4R\pi\varepsilon\varepsilon_0} + ... \tag{5.1.6.3}$$

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.

Definition: Exciton

A conduction band electron and its valence band hole together form an exciton. Excitons are formed when an electron is promoted from the valence band to the conduction band of a material.

Synthesis

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:

$$\mathrm{CdCl_{2\,(aq)} + H_2Se_{(g)} = CdSe_{(s)} + 2\,HCl_{(aq)}}$$

$$\mathrm{Pb(NO_3)_2 + H_2S_{(g)} = PbS_{(s)} + 2\,HNO_{3\,(aq)}}$$

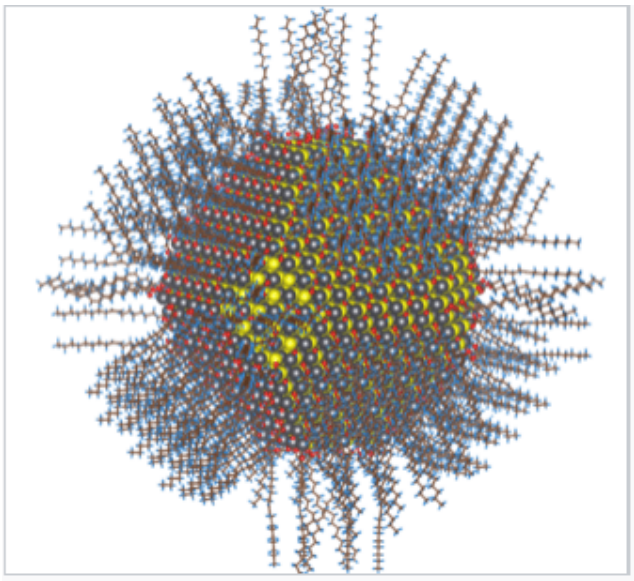


Figure 5.1.6.6: Complete atomistic model of a 5 nm diameter colloidal lead sulfide nanoparticle with surface passivation by oleic acid, oleyl and hydroxyl groups.

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. 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 in Figure 5.1.6.7.

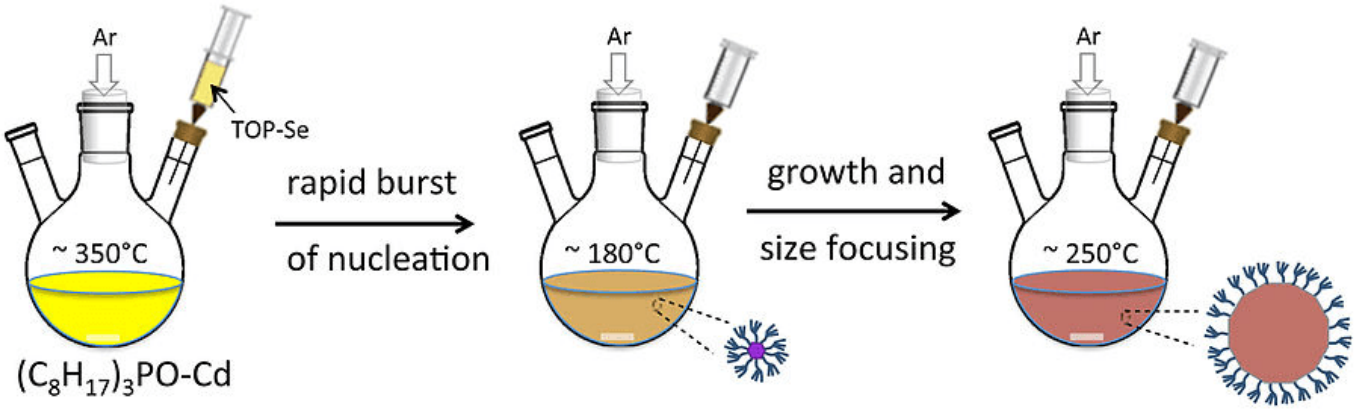


Figure 5.1.6.7: Illustration of the steps of CdSe nanoparticle synthesis

The synthesis is carried out in a coordinating, high boiling solvent that is a mixture of trioctylphosphine (TOP) and trioctylphosphine oxide (TOPO). IAt the start of the reaction, a selenium source is rapidly injected into the hot (350 °C) reaction mixture containing Cd. 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. Because the nanoparticles are capped with a ligand shell of TOP, they can be precipitated and re-suspended in organic solvents.

The high temperature synthesis of semiconductor quantum dots has been applied to a broad variety of materials. 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.

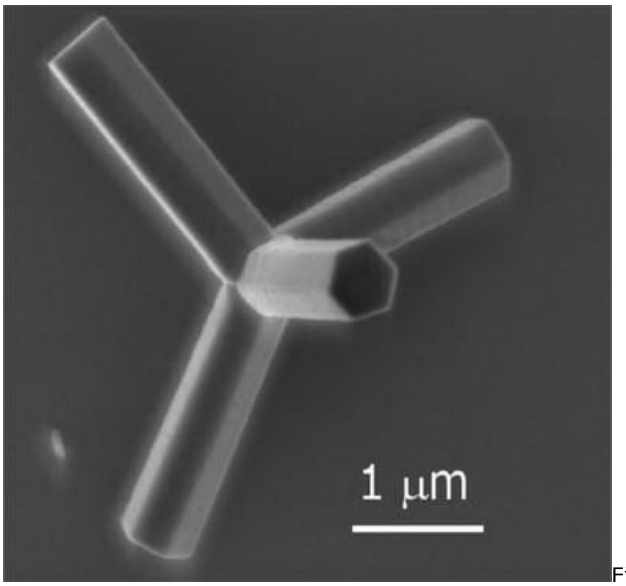
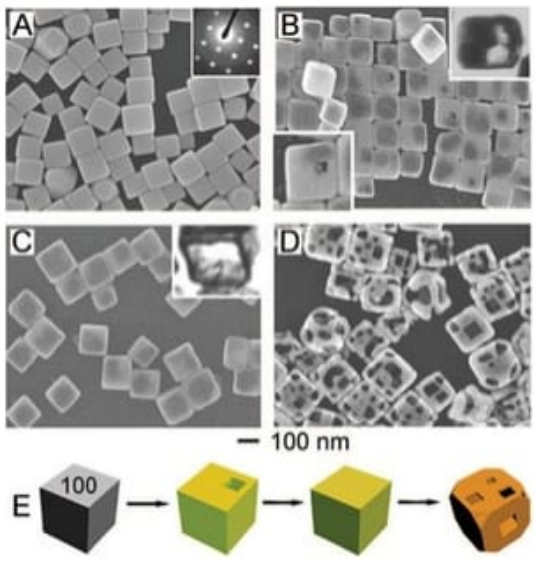


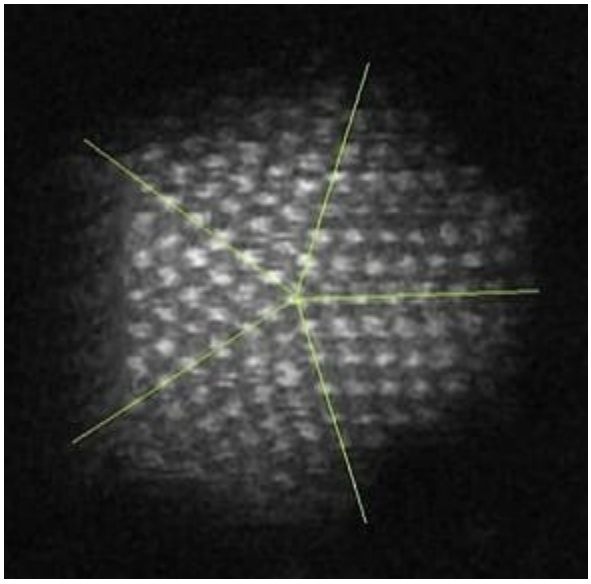
Figure 5.1.6.1: Scanning electron microscope (SEM) image of a ZnO tetrapod nanocrystal. (CC BY-NC-ND 3.0; ScienceDirect via https://doi.org/10.1016/S1369-7021(07)70079-2)

Metal nanoparticles



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**:

$$F = kx \tag{5.1.6.4}$$

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:

$$k = \frac{ne^2}{\varepsilon_0} \tag{5.1.6.5}$$

The **resonant frequency** of the plasma oscillation is given by:

$$\omega_p = (\frac{k}{m})^{\frac{1}{2}} = (\frac{ne^2}{m_e\varepsilon_0}^{\frac{1}{2}} \tag{5.1.6.6}$$

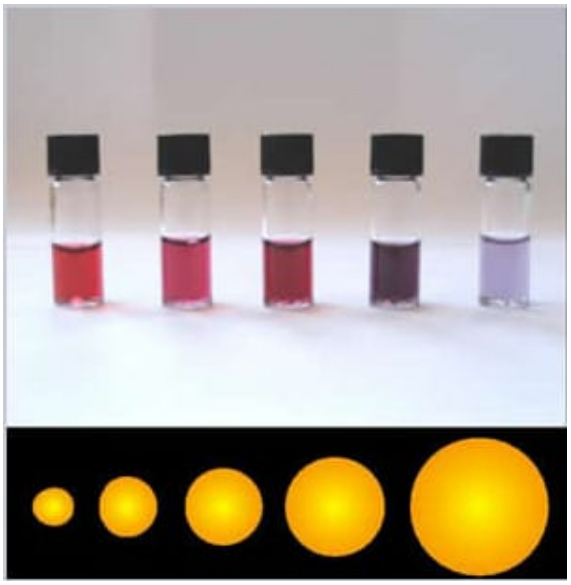
where m_e is the electron mass. For most metals, the plasmon resonance is in the ultraviolet part of the spectrum, but for a few metals like Au, Ag, and Cu it is in the visible.



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:

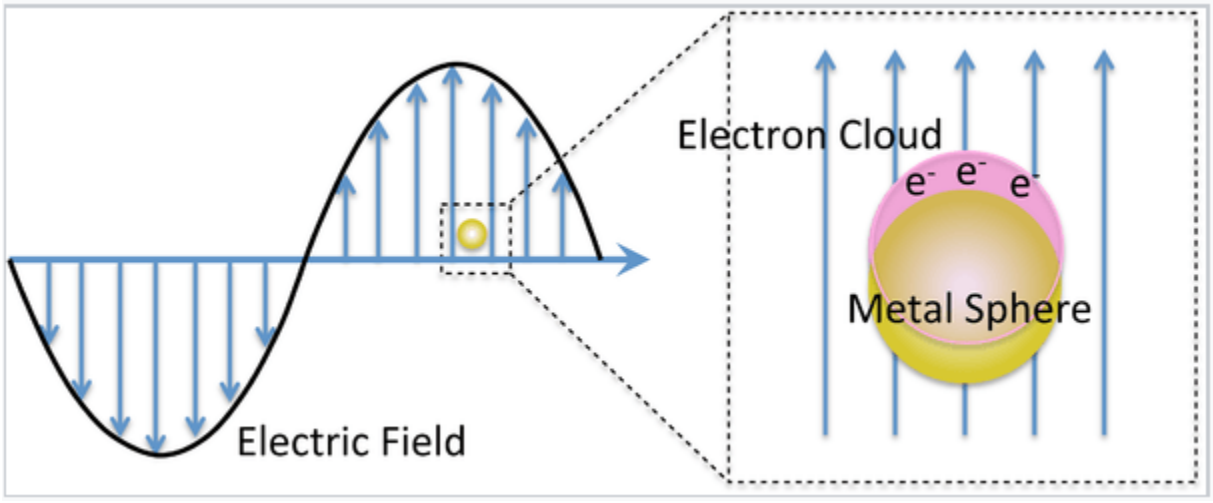
- The **local electric field** of the incoming light wave is greatly **enhanced** at the particle surface. This gives rise to huge enhancement factors in optical processes such as **Raman scattering** and **fluorescence**. Thus, certain analytical spectroscopic techniques are greatly enhanced by LSPR.
- 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:

$$\varepsilon = \varepsilon^{'} + i\varepsilon^{''} \tag{5.1.6.7}$$

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:

$$\sigma_{absorption} = \frac{9\omega}{c}\epsilon_{diel}^{\frac{3}{2}} V \frac{\epsilon_{metal}^{''}}{(\epsilon_{metal}^{'} + 2\epsilon_{diel})^2 + (\epsilon_{metal}^{''})^2} \tag{5.1.6.8}$$

and the **cross-section for scattering** is:

$$\sigma_{scattering} = \frac{3}{2\pi}(\frac{\omega^4}{c})\epsilon_{diel}^2 V^2 \frac{(\epsilon_{metal}^{'} - \epsilon_{diel})^2 + (\epsilon_{metal}^{''})^2}{(\epsilon_{metal}^{'} + 2\epsilon_{diel})^2 + (\epsilon_{metal}^{''})^2} \tag{5.1.6.9}$$

The sum of these two is the **cross-section for extinction**:

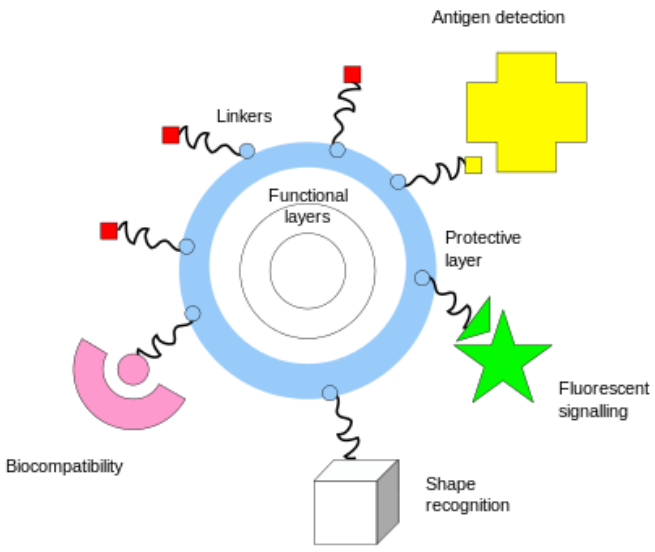
$$\sigma_{extinction} = \sigma_{absorption} + \sigma_{scattering} \tag{5.1.6.10}$$

These cross-sections become large when the (ε'_{metal} + $2\varepsilon_{diel}$) term in the denominator becomes small. This occurs when

$$\epsilon_{metal}^{'} \simeq -2\epsilon_{diel} \tag{5.1.6.11}$$

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.

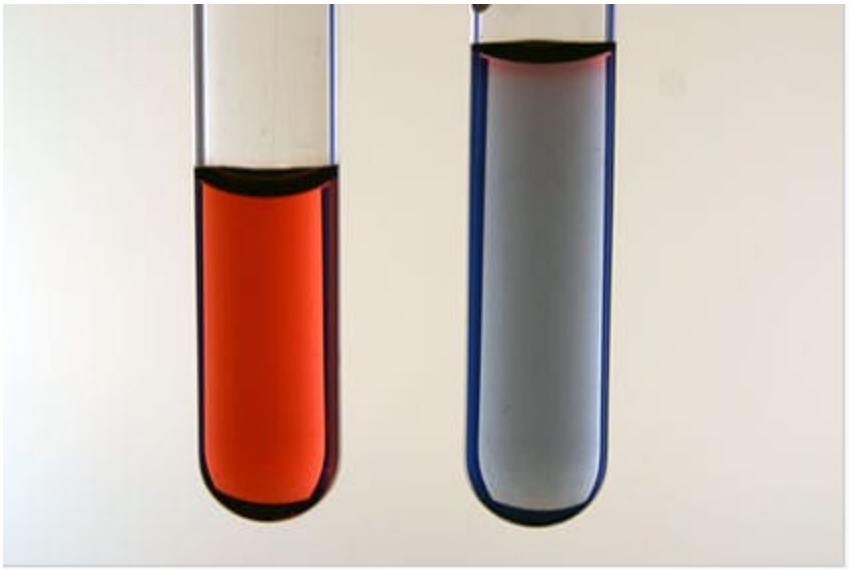
It is important to note that the cross-section for **scattering** is proportional to the **square of the volume** of the particle, V^2, whereas the absorption is proportional to V. This means that very small gold particles (< 5 nm) are strongly absorbing but not strongly scattering. Larger particles (>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.

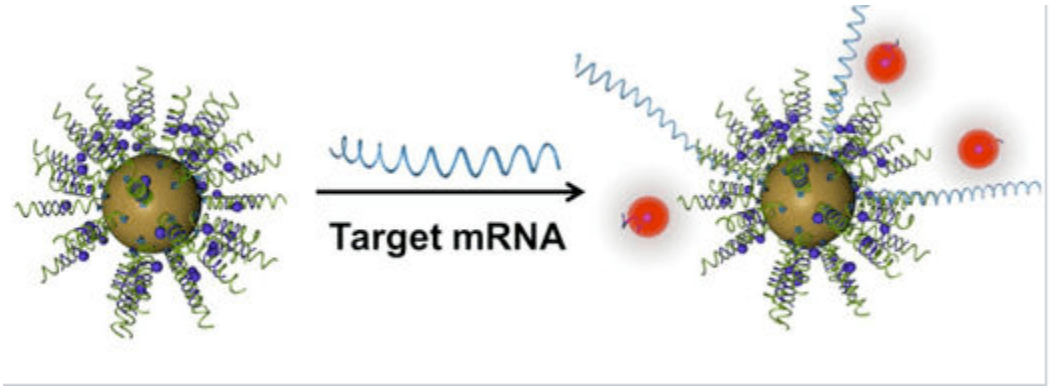
Functionalization of gold nanoparticles with thiol-terminated single-stranded DNA was the basis of one of the first nanoparticle sensors, developed by the Mirkin group at Northwestern University. **DNA-coated nanoparticles** have the characterstic wine-

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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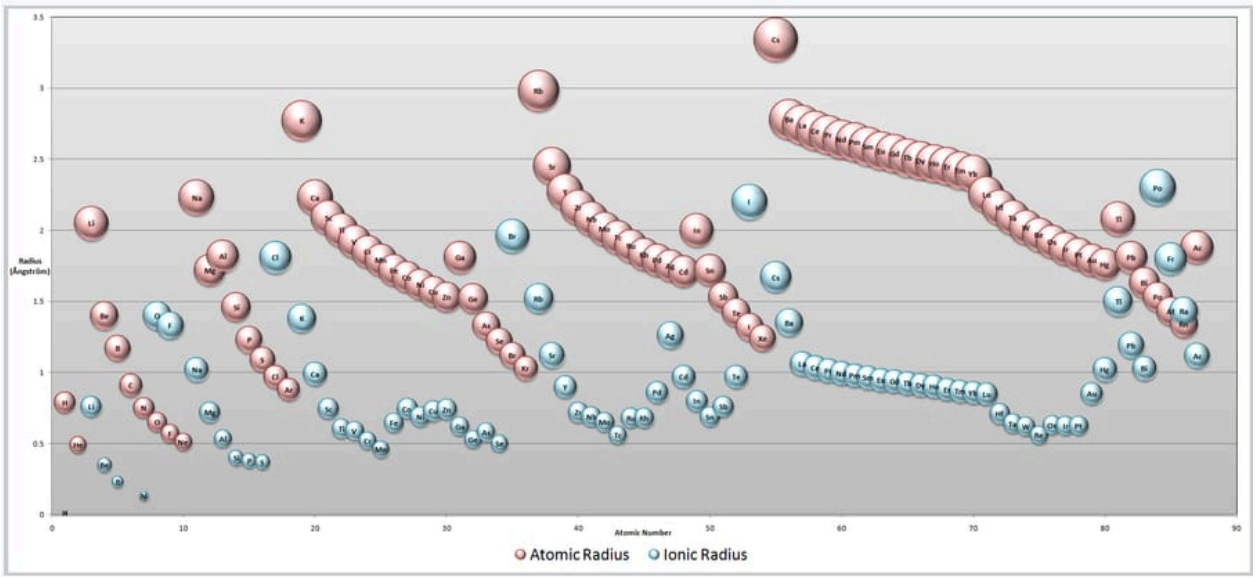
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5.1.7: Ionic Radii and Radius Ratios

Atoms in crystals are held together by electrostatic forces, van der Waals interactions, and covalent bonding. It follows that arrangements of atoms that can maximize the strength of these attractive interactions should be most favorable and lead to the most commonly observed crystal structures.

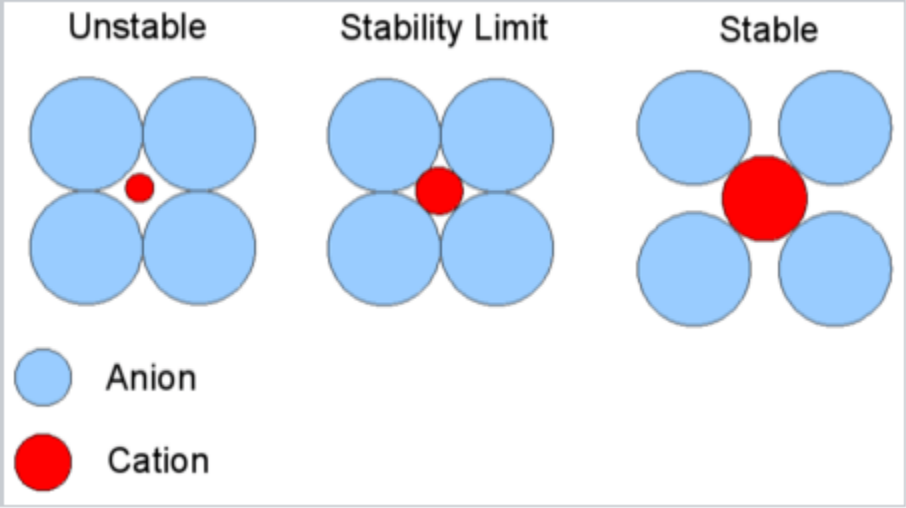
Radius ratio rules

Early crystallographers had trouble solving the structures of inorganic solids using X-ray diffraction because some of the mathematical tools for analyzing the data had not yet been developed. Once a trial structure was proposed, it was relatively easy to calculate the diffraction pattern, but it was difficult to go the other way (from the diffraction pattern to the structure) if nothing was known *a priori* about the arrangement of atoms in the unit cell. It was (and still is!) important to develop some guidelines for guessing the coordination numbers and bonding geometries of atoms in crystals. The first such rules were proposed by Linus Pauling, who considered how one might pack together oppositely charged spheres of different radii. Pauling proposed from geometric considerations that the quality of the "fit" depended on the **radius ratio** of the anion and the cation.



Atomic and Ionic Radii. Note that cations are always smaller than the neutral atom (pink) of the same element, whereas anions are larger. Going from left to right across any row of the periodic table, neutral atoms and cations contract in size because of increasing nuclear charge. (click for larger image)

The basic idea of radius ratio rules is illustrated at the right. We consider that the anion is the packing atom in the crystal and the smaller cation fills interstitial sites ("holes"). Cations will find arrangements in which they can contact the largest number of anions. If the cation can touch all of its nearest neighbor anions, as shown at the right for a small cation in contact with larger anions, then the fit is good. If the cation is too small for a given site, that coordination number will be unstable and it will prefer a lower coordination structure. The table below gives the ranges of cation/anion radius ratios that give the best fit for a given coordination geometry.



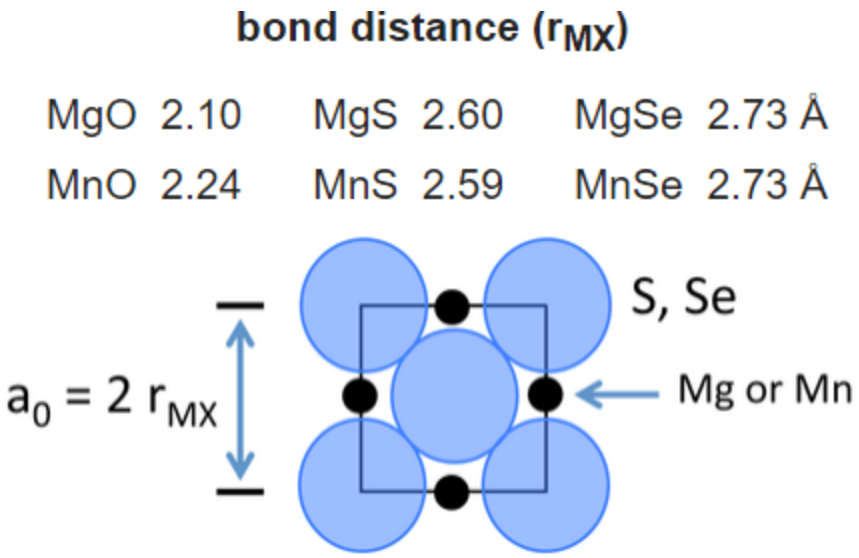
Critical Radius Ratio. This diagram is for coordination number six: 4 anions in the plane are shown, 1 is above the plane and 1 is below. The stability limit is at r_C/r_A = 0.414

Coordination number	**Geometry**	**ρ = r_{cation}/r_{anion}**
2	linear	0 - 0.155
3	triangular	0.155 - 0.225
4	tetrahedral	0.225 - 0.414
4	square planar	0.414 - 0.732
6	octahedral	0.414 - 0.732
8	cubic	0.732 - 1.0
12	cuboctahedral	1.0

There are unfortunately several challenges with using this idea to predict crystal structures:

- We don't know the radii of individual ions
- Atoms in crystals are not really ions - there is a varying degree of covalency depending electronegativity differences
- Bond distances (and therefore ionic radii) depend on bond strength and coordination number (remember Pauling's rule D(n) = D(1) - 0.6 log n)
- Ionic radii depend on oxidation state (higher charge => smaller cation size, larger anion size)

We can build up a table of ionic radii by assuming that the bond length is the sum of the radii ($r_+ + r_-$) if the ions are in contact in the crystal. Consider for example the compounds MgX and MnX, where X = O, S, Se. All of these compounds crystallize in the NaCl structure:



For the two larger anions (S^{2-} and Se^{2-}), the unit cell dimensions are the same for both cations. This suggests that the anions are in contact in these structures. From geometric considerations, the anion radius in this case is given by:

Extra close brace or missing open brace

and thus the radii of the S^{2-} and Se^{2-} ions are 1.84 and 1.93 Å, respectively. Once the sizes of these anions are fixed, we can obtain a self-consistent set of cation and anion radii from the lattice constants of many MX compounds.

How well does this model work? Let's consider the structures of tetravalent metal oxides (MO_2), using Pauling radii and the predictions of the radius ratio model:

Oxide MO_2	**Radius ratio**	**Predicted coord. no.**	**Observed coord no. (structure)**
CO_2	~0.1	2	2 (linear molecule)
SiO_2	0.32	4	4 (various tetrahedral structures)
GeO_2	0.43	4	4 (silica-like structures)
"	0.54	6	6 (rutile)
TiO_2	0.59	6	6 (rutile)
ZrO_2	0.68	6	7 (baddleyite)
"	0.77	8	8 (fluorite)
ThO_2	0.95	8	8 (fluorite)

Note that cations have different radii depending on their coordination numbers, and thus different radius ratios are calculated for Ge^{4+} with coordination numbers 4 and 6, and for Zr^{4+} with coordination numbers 6 and 8.

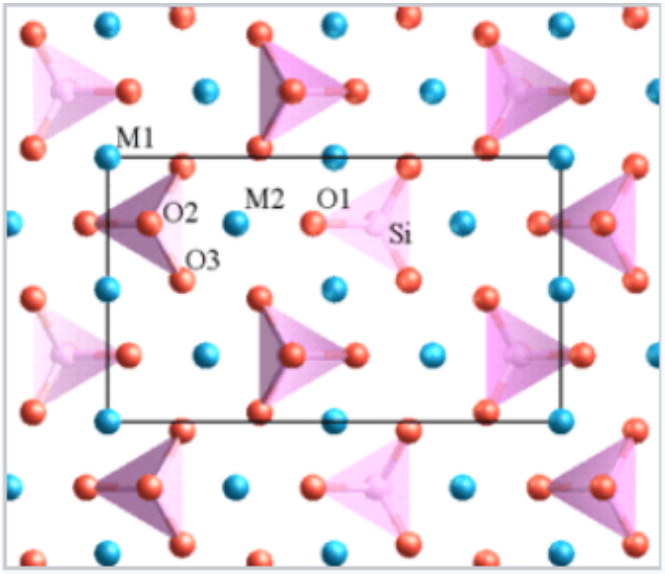
For this series of oxides, the model appears to work quite well. The correct coordination number is predicted in all cases, and borderline cases such as GeO_2 and ZrO_2 are found in structures with different coordination numbers. The model also correctly predicts the structures of BeF_2 (SiO_2 type), MgF_2 (rutile), and CaF_2 (fluorite).

What about the alkali halides NaCl, KBr, LiI, CsF, etc.? All of them have the NaCl structure except for CsCl, CsBr, and CsI, which have the CsCl (8-8) structure. In this case the radius ratio model fails rather badly. The Li^+ salts LiBr and LiI are predicted to have tetrahedral structures, and KF is predicted to have an 8-8 structure like CsCl. We can try adjusting the radii (e.g., making the cations larger and anions smaller), but the best we can do with the alkali halides is predict about half of their structures correctly. Since the alkali halides are clearly ionic compounds, this failure suggests that there is something very wrong with the radius ratio

model, and its success with MO_2 compounds was coincidental.

In addition to the radius ratio rule, Linus Pauling developed other useful rules that are helpful in rationalizing and also predicting the structures of inorganic compounds. Pauling's rules[1] state that:

- Stable structures are **locally electroneutral**. For example, in the structure of the double perovskite Sr_2FeMoO_6, MO_6 (M = Fe^{2+}, Mo^{6+}) octahedra share all their vertices, and Sr^{2+} ions fill the cubooctahedral cavities that are flanked by eight MO_6 octahedra.[2] Each O^{2-} ion is coordinated to one Fe^{2+} and one Mo^{6+} ion in order to achieve local electroneutrality, and thus the FeO_6 and MoO_6 octahedra alternate in the structure.
- **Cation-cation repulsion** should be minimized. Anion polyhedra can share vertices (as in the perovskite structure) without any energetic penalty. Shared polyhedral edges, and especially shared faces, cause cation-cation repulsion and should be avoided. For example, in rutile, the most stable polymorph of TiO_2, the TiO_6 octahedra share vertices and two opposite edges, forming ribbons in the structure. In anatase TiO_2, each octahedron shares four edges so the anatase polymorph is less thermodynamically stable.
- **Highly charged cations** in anion polyhedra tend not to share edges or even vertices, especially when the coordination number is low. For example, in orthosilicates such as olivine (M_2SiO_4), there are isolated SiO_4^{4-} tetrahedra.



Structure of olivine. M (Mg or Fe) = blue spheres, Si = pink tetrahedra, O = red spheres.

As we will soon see, all of Pauling's rules are justified on the basis of lattice energy considerations. In ionic compounds, the arrangement of atoms that maximizes anion-cation interactions while minimizing cation-cation and anion-anion contacts is energetically the best.

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5.2.1: Enthalpy

Learning Objectives

- State the first law of thermodynamics
- Define enthalpy and explain its classification as a state function
- Write and balance thermochemical equations
- Calculate enthalpy changes for various chemical reactions
- Explain Hess's law and use it to compute reaction enthalpies

Thermochemistry is a branch of chemical thermodynamics, the science that deals with the relationships between heat, work, and other forms of energy in the context of chemical and physical processes. As we concentrate on thermochemistry in this chapter, we need to consider some widely used concepts of thermodynamics.

Substances act as reservoirs of energy, meaning that energy can be added to them or removed from them. Energy is stored in a substance when the kinetic energy of its atoms or molecules is raised. The greater kinetic energy may be in the form of increased translations (travel or straight-line motions), vibrations, or rotations of the atoms or molecules. When thermal energy is lost, the intensities of these motions decrease and the kinetic energy falls. The total of all possible kinds of energy present in a substance is called the internal energy (*U*), sometimes symbolized as *E*.

As a system undergoes a change, its internal energy can change, and energy can be transferred from the system to the surroundings, or from the surroundings to the system. Energy is transferred into a system when it absorbs heat (*q*) from the surroundings or when the surroundings do work (*w*) on the system. For example, energy is transferred into room-temperature metal wire if it is immersed in hot water (the wire absorbs heat from the water), or if you rapidly bend the wire back and forth (the wire becomes warmer because of the work done on it). Both processes increase the internal energy of the wire, which is reflected in an increase in the wire's temperature. Conversely, energy is transferred out of a system when heat is lost from the system, or when the system does work on the surroundings.

The relationship between internal energy, heat, and work can be represented by the equation:

$$\Delta U = q + w \tag{5.2.1.1}$$

as shown in Figure $5.2.1.1$. This is one version of the first law of thermodynamics, and it shows that the internal energy of a system changes through heat flow into or out of the system (positive q is heat flow in; negative *q* is heat flow out) or work done on or by the system. The work, *w*, is positive if it is done on the system and negative if it is done by the system.

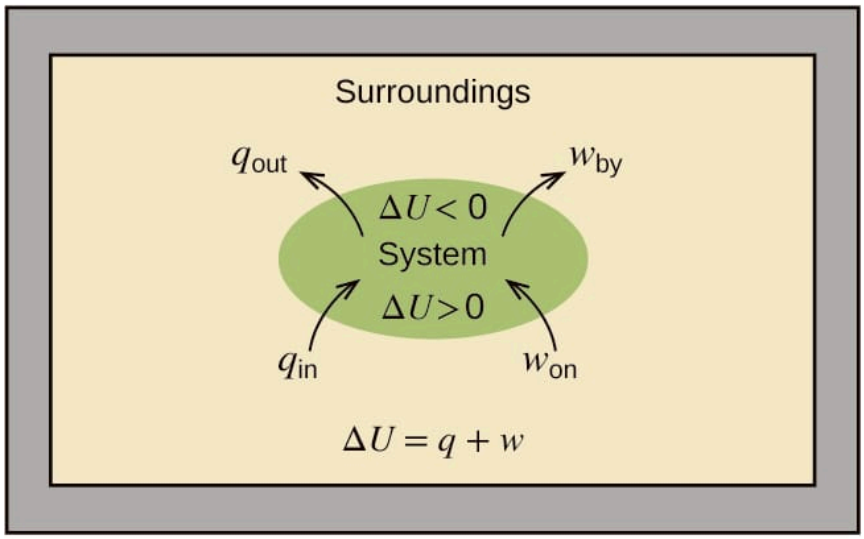


Figure 5.2.1.1: The internal energy, U, of a system can be changed by heat flow and work. If heat flows into the system, q_{in}, or work is done on the system, w_{on}, its internal energy increases, $\Delta U > 0$. If heat flows out of the system, q_{out}, or work is done by the system, w_{by}, its internal energy decreases, $\Delta U < 0$.

A type of work called expansion work (or pressure-volume work) occurs when a system pushes back the surroundings against a restraining pressure, or when the surroundings compress the system. An example of this occurs during the operation of an internal combustion engine. The reaction of gasoline and oxygen is exothermic. Some of this energy is given off as heat, and some does work pushing the piston in the cylinder. The substances involved in the reaction are the system, and the engine and the rest of the universe are the surroundings. The system loses energy by both heating and doing work on the surroundings, and its internal energy decreases. (The engine is able to keep the car moving because this process is repeated many times per second while the engine is running.) We will consider how to determine the amount of work involved in a chemical or physical change in the chapter on thermodynamics.

As discussed, the relationship between internal energy, heat, and work can be represented as $\Delta U = q + w$. Internal energy is a type of quantity known as a state function (or state variable), whereas heat and work are not state functions. The value of a state function depends only on the state that a system is in, and not on how that state is reached. If a quantity is not a state function, then its value *does* depend on how the state is reached. An example of a state function is altitude or elevation. If you stand on the summit of Mt. Kilimanjaro, you are at an altitude of 5895 m, and it does not matter whether you hiked there or parachuted there. The distance you traveled to the top of Kilimanjaro, however, is not a state function. You could climb to the summit by a direct route or by a more roundabout, circuitous path (Figure 5.2.1.2). The distances traveled would differ (distance is not a state function) but the elevation reached would be the same (altitude is a state function).

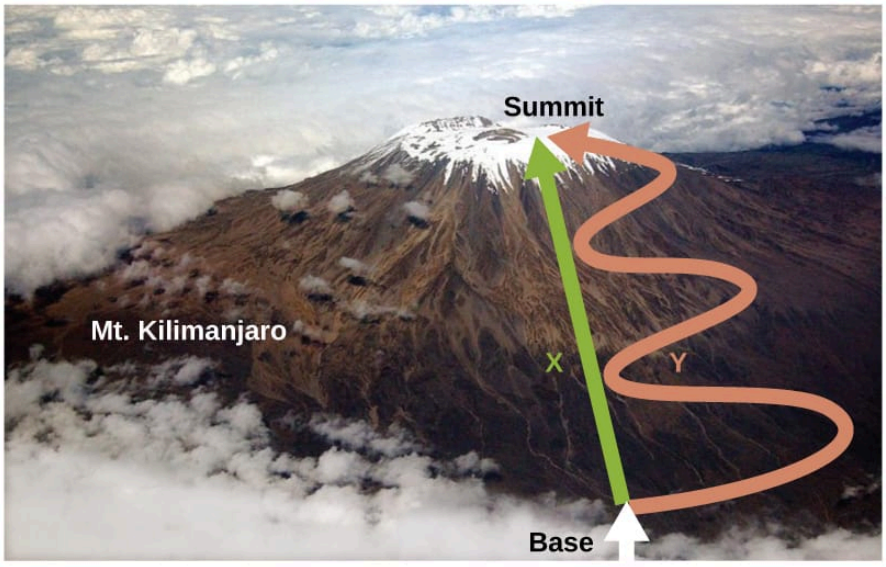


Figure 5.2.1.2: Paths X and Y represent two different routes to the summit of Mt. Kilimanjaro. Both have the same change in elevation (altitude or elevation on a mountain is a state function; it does not depend on path), but they have very different distances traveled (distance walked is not a state function; it depends on the path). (credit: modification of work by Paul Shaffner)

An aerial photo depicts a view of Mount Kilimanjaro. A straight, green arrow labeled X is drawn from the term “base,” written at the bottom of the mountain, to the term “Summit,” written at the top of the mountain. Another arrow labeled Y is draw from the base to the summit alongside the green arrow, but this arrow is pink and has three large S-shaped curves along its length.

Chemists ordinarily use a property known as enthalpy (H) to describe the thermodynamics of chemical and physical processes. Enthalpy is defined as the sum of a system’s internal energy (U) and the mathematical product of its pressure (P) and volume (V):

$$H = U + PV \tag{5.2.1.2}$$

Since it is derived from three state functions (U, P, and V), enthalpy is also a state function. Enthalpy values for specific substances cannot be measured directly; only enthalpy changes for chemical or physical processes can be determined. For processes that take place at constant pressure (a common condition for many chemical and physical changes), the enthalpy change (ΔH) is:

$$\Delta H = \Delta U + P\Delta V \tag{5.2.1.3}$$

The mathematical product $P\Delta V$ represents work (w), namely, expansion or pressure-volume work as noted. By their definitions, the arithmetic signs of ΔV and w will always be opposite:

$$P\Delta V = -w \tag{5.2.1.4}$$

Substituting Equation 5.2.1.4 and the definition of internal energy (Equation 5.2.1.1) into Equation 5.2.1.3 yields:

$$\Delta H = \Delta U + P\Delta V \tag{5.2.1.5}$$

$$= q_{\mathrm{p}} + \cancel{w} - \cancel{w} \tag{5.2.1.6}$$

$$= q_{\mathrm{p}} \tag{5.2.1.7}$$

where q_p is the heat of reaction under conditions of constant pressure.

And so, if a chemical or physical process is carried out at constant pressure with the only work done caused by expansion or contraction, then the heat flow (q_{p}) and enthalpy change (ΔH) for the process are equal.

The heat given off when you operate a Bunsen burner is equal to the enthalpy change of the methane combustion reaction that takes place, since it occurs at the essentially constant pressure of the atmosphere. On the other hand, the heat produced by a reaction measured in a bomb calorimeter is not equal to ΔH because the closed, constant-volume metal container prevents expansion work from occurring. Chemists usually perform experiments under normal atmospheric conditions, at constant external pressure with $q = \Delta H$, which makes enthalpy the most convenient choice for determining heat.

The following conventions apply when we use ΔH:

1. Chemists use a thermochemical equation to represent the changes in both matter and energy. In a thermochemical equation, the enthalpy change of a reaction is shown as a ΔH value following the equation for the reaction. This ΔH value indicates the amount of heat associated with the reaction involving the number of moles of reactants and products as shown in the chemical equation. For example, consider this equation:

$$\mathrm{H_2\,(g)} + \tfrac{1}{2}\,\mathrm{O_2\,(g)} \longrightarrow \mathrm{H_2O\,(l)} \quad \Delta H = -286\ \mathrm{kJ} \tag{5.2.1.8}$$

   This equation indicates that when 1 mole of hydrogen gas and 12 mole of oxygen gas at some temperature and pressure change to 1 mole of liquid water at the same temperature and pressure, 286 kJ of heat are released to the surroundings. If the coefficients of the chemical equation are multiplied by some factor, the enthalpy change must be multiplied by that same factor (ΔH is an extensive property).

Multiple \label

2. The enthalpy change of a reaction depends on the physical state of the reactants and products of the reaction (whether we have gases, liquids, solids, or aqueous solutions), so these must be shown. For example, when 1 mole of hydrogen gas and 12 mole of oxygen gas change to 1 mole of liquid water at the same temperature and pressure, 286 kJ of heat are released. If gaseous water forms, only 242 kJ of heat are released.

$$\mathrm{H_2\,(g)} + \tfrac{1}{2}\,\mathrm{O_2\,(g)} \longrightarrow \mathrm{H_2O\,(g)} \quad \Delta H = -242\ k\,\mathrm{J} \tag{5.2.1.9}$$

3. A negative value of an enthalpy change, Δ*H*, indicates an exothermic reaction; a positive value of Δ*H* indicates an endothermic reaction. If the direction of a chemical equation is reversed, the arithmetic sign of its Δ*H* is changed (a process that is endothermic in one direction is exothermic in the opposite direction).

Example 5.2.1.1: Measurement of an Enthalpy Change

When 0.0500 mol of HCl(*aq*) reacts with 0.0500 mol of NaOH(*aq*) to form 0.0500 mol of NaCl(*aq*), 2.9 kJ of heat are produced. What is ΔH, the enthalpy change, per mole of acid reacting, for the acid-base reaction run under the conditions described ?

$$\mathrm{HCl\,(aq) + NaOH\,(aq)} \rightarrow \mathrm{NaCl\,(aq) + H_2O\,(l)}$$

Solution

For the reaction of 0.0500 mol acid (HCl), q = –2.9 kJ. This ratio

$$\frac{-2.9\ \mathrm{kJ}}{0.0500\ \mathrm{mol\ HCl}}$$

can be used as a conversion factor to find the heat produced when 1 mole of HCl reacts:

$$\Delta H = 1\ \cancel{\mathrm{mol\ HCl}} \times \frac{-2.9\ \mathrm{kJ}}{0.0500\ \cancel{\mathrm{mol\ HCl}}} = -58\ \mathrm{kJ}$$

The enthalpy change when 1 mole of HCl reacts is –58 kJ. Since that is the number of moles in the chemical equation, we write the thermochemical equation as:

$$\mathrm{HCl_{(aq)} + NaOH_{(aq)} \longrightarrow NaCl_{(aq)} + H_2O_{(l)}} \quad \Delta H = -58\ \mathrm{kJ}$$

Exercise 5.2.1.1

When 1.34 g Zn(s) reacts with 60.0 mL of 0.750 M HCl(aq), 3.14 kJ of heat are produced. Determine the enthalpy change per mole of zinc reacting for the reaction:

$$\mathrm{Zn_{(s)} + 2\,HCl_{(aq)} \longrightarrow ZnCl_{(aq)} + H_{2(g)}}$$

Answer available at the end of this section.

Be sure to take both stoichiometry and limiting reactants into account when determining the Δ*H* for a chemical reaction.

Example 5.2.1.2: Another Example of the Measurement of an Enthalpy Change

A gummy bear contains 2.67 g sucrose, $C_{12}H_{22}O_{11}$. When it reacts with 7.19 g potassium chlorate, $KClO_3$, 43.7 kJ of heat are produced. Determine the enthalpy change for the reaction

$$\mathrm{C_{12}H_{22}O_{11}}(aq) + 8\,\mathrm{KClO_3}(aq) \longrightarrow 12\,\mathrm{CO_2}(g) + 11\,\mathrm{H_2O}(l) + 8\,\mathrm{KCl}(aq)$$

Solution

We have $2.67\ \cancel{g} \times \dfrac{1\ \mathrm{mol}}{342.3\ \cancel{g}} = 0.00780\ \mathrm{mol\ C_{12}H_{22}O_{11}}$ available, and

$$7.19\ \cancel{g} \times \frac{1\ \mathrm{mol}}{122.5\ \cancel{g}} = 0.0587\ \mathrm{mol\ KClO_3}\ \text{available.}$$

Since

$$0.0587\ \mathrm{mol\ KClO_3} \times \frac{1\ \mathrm{mol\ C_{12}H_{22}O_{11}}}{8\ \mathrm{mol\ KClO_3}} = 0.00734\ \mathrm{mol}\ {}_{12}\mathrm{CH_{22}O_{11}}$$

is needed, $C_{12}H_{22}O_{11}$ is the excess reactant and $KClO_3$ is the limiting reactant.

The reaction uses 8 mol $KClO_3$, and the conversion factor is $\dfrac{-43.7\ \mathrm{kJ}}{0.0587\ \mathrm{mol\ KClO_3}}$, so we have $\Delta H = 8\ \mathrm{mol} \times \dfrac{-43.7\ \mathrm{kJ}}{0.0587\ \mathrm{mol\ KClO_3}} = -5960\ \mathrm{kJ}$. The enthalpy change for this reaction is –5960 kJ, and the thermochemical equation is:

$$\mathrm{C_{12}H_{22}O_{11}} + 8\,\mathrm{KClO_3} \longrightarrow 12\,\mathrm{CO_2} + 11\,\mathrm{H_2O} + 8\,\mathrm{KCl} \quad \Delta H = -5960\ k\,\mathrm{J}$$

Exercise 5.2.1.2

When 1.42 g of iron reacts with 1.80 g of chlorine, 3.22 g of $\mathrm{FeCl_{2(s)}}$ and 8.60 kJ of heat is produced. What is the enthalpy change for the reaction when 1 mole of $\mathrm{FeCl_2\,(s)}$ is produced?

Answer available at the end of this section.

Enthalpy changes are typically tabulated for reactions in which both the reactants and products are at the same conditions. A standard state is a commonly accepted set of conditions used as a reference point for the determination of properties under other different conditions. For chemists, the IUPAC standard state refers to materials under a pressure of 1 bar and solutions at 1 M, and **does not specify a temperature** (it used too). Many thermochemical tables list values with a standard state of 1 atm. Because the Δ*H* of a reaction changes very little with such small changes in pressure (1 bar = 0.987 atm), Δ*H* values (except for the most precisely measured values) are essentially the same under both sets of standard conditions. We will include a superscripted "o" in the enthalpy change symbol to designate standard state. Since the usual (but not technically standard) temperature is 298.15 K, we will use a subscripted "298" to designate this temperature. Thus, the symbol (ΔH°_{298}) is used to indicate an enthalpy change for a process occurring under these conditions. (The symbol Δ*H* is used to indicate an enthalpy change for a reaction occurring under nonstandard conditions.)

The enthalpy changes for many types of chemical and physical processes are available in the reference literature, including those for combustion reactions, phase transitions, and formation reactions. As we discuss these quantities, it is important to pay attention to the *extensive* nature of enthalpy and enthalpy changes. Since the enthalpy change for a given reaction is proportional

to the amounts of substances involved, it may be reported on that basis (i.e., as the ΔH for specific amounts of reactants). However, we often find it more useful to divide one extensive property (ΔH) by another (amount of substance), and report a per-amount *intensive* value of ΔH, often "normalized" to a per-mole basis. (Note that this is similar to determining the intensive property specific heat from the extensive property heat capacity, as seen previously.)

Enthalpy of Combustion

Standard enthalpy of combustion (ΔH°_C) is the enthalpy change when 1 mole of a substance burns (combines vigorously with oxygen) under standard state conditions; it is sometimes called "heat of combustion." For example, the enthalpy of combustion of ethanol, –1366.8 kJ/mol, is the amount of heat produced when one mole of ethanol undergoes complete combustion at 25 °C and 1 atmosphere pressure, yielding products also at 25 °C and 1 atm.

$$\mathrm{C_2H_5OH}(l) + 3\,\mathrm{O_2}(g) \longrightarrow 2\,\mathrm{CO_2} + 3\,\mathrm{H_2O}(l) \quad \Delta H^\circ_{298} = -1366.8\ \mathrm{kJ} \tag{5.2.1.10}$$

Enthalpies of combustion for many substances have been measured; a few of these are listed in Table 5.2.1.1. Many readily available substances with large enthalpies of combustion are used as fuels, including hydrogen, carbon (as coal or charcoal), and hydrocarbons (compounds containing only hydrogen and carbon), such as methane, propane, and the major components of gasoline.

Table 5.2.1.1: Standard Molar Enthalpies of Combustion

Substance	Combustion Reaction	Enthalpy of Combustion $\Delta H^\circ_c \left(\frac{\mathrm{kJ}}{\mathrm{mol}} \text{ at } 25^\circ\mathrm{C}\right)$
carbon	$\mathrm{C}(s) + \mathrm{O_2}(g) \longrightarrow \mathrm{CO_2}(g)$	–393.5
hydrogen	$\mathrm{H_2}(g) + \frac{1}{2}\mathrm{O_2}(g) \longrightarrow \mathrm{H_2O}(l)$	–285.8
magnesium	$\mathrm{Mg}(s) + \frac{1}{2}\mathrm{O_2}(g) \longrightarrow \mathrm{MgO}(s)$	–601.6
sulfur	$\mathrm{S}(s) + \mathrm{O_2}(g) \longrightarrow \mathrm{SO_2}(g)$	–296.8
carbon monoxide	$\mathrm{CO}(g) + \frac{1}{2}\mathrm{O_2}(g) \longrightarrow \mathrm{CO_2}(g)$	–283.0
methane	$\mathrm{CH_4}(g) + 2\,\mathrm{O_2}(g) \longrightarrow \mathrm{CO_2}(g) + 2\,\mathrm{H_2O}(l)$	–890.8
acetylene	$\mathrm{C_2H_2}(g) + \frac{5}{2}\mathrm{O_2}(g) \longrightarrow 2\,\mathrm{CO_2}(g) + \mathrm{H_2O}(l)$	–1301.1
ethanol	$\mathrm{C_2H_5OH}(l) + 3\,\mathrm{O_2}(g) \longrightarrow \mathrm{CO_2}(g) + 3\,\mathrm{H_2O}(l)$	–1366.8
methanol	$\mathrm{CH_3OH}(l) + \frac{3}{2}\mathrm{O_2}(g) \longrightarrow \mathrm{CO_2}(g) + 2\,\mathrm{H_2O}(l)$	–726.1
isooctane	$\mathrm{C_8H_{18}}(l) + \frac{25}{2}\mathrm{O_2}(g) \longrightarrow 8\,\mathrm{CO_2}(g) + 9\,\mathrm{H_2O}(l)$	–5461

Example 5.2.1.3: Using Enthalpy of Combustion

As Figure 5.2.1.3 suggests, the combustion of gasoline is a highly exothermic process. Let us determine the approximate amount of heat produced by burning 1.00 L of gasoline, assuming the enthalpy of combustion of gasoline is the same as that of isooctane, a common component of gasoline. The density of isooctane is 0.692 g/mL.



Figure 5.2.1.3: The combustion of gasoline is very exothermic. (credit: modification of work by “AlexEagle”/Flickr)

Solution

Starting with a known amount (1.00 L of isooctane), we can perform conversions between units until we arrive at the desired amount of heat or energy. The enthalpy of combustion of isooctane provides one of the necessary conversions. Table 5.2.1.1 gives this value as –5460 kJ per 1 mole of isooctane (C_8H_{18}).

Using these data,

$$1.00\ \cancel{\text{L}\ {}_8\text{CH}_{18}} \times \frac{1000\ \cancel{\text{mL}\ {}_8\text{CH}_{18}}}{1\ \cancel{\text{L}\ {}_8\text{CH}_{18}}} \times \frac{0.692\ \cancel{\text{g}\ \text{C}_8\text{H}_{18}}}{1\ \cancel{\text{mL}\ {}_8\text{CH}_{18}}} \times \frac{1\ \cancel{\text{mol}\ {}_8\text{CH}_{18}}}{114\ \cancel{\text{g}\ \text{C}_8\text{H}_{18}}} \times \frac{-5460\ \text{kJ}}{1\ \cancel{\text{mol}\ {}_8\text{CH}_{18}}} = -3.31 \times 10^4\ \text{kJ}$$

The combustion of 1.00 L of isooctane produces 33,100 kJ of heat. (This amount of energy is enough to melt 99.2 kg, or about 218 lbs, of ice.)

Note: If you do this calculation one step at a time, you would find:

$$1.00\ \text{L}\ {}_8\text{CH}_{18} \longrightarrow 1.00 \times 10^3\ \text{mL}\ {}_8\text{CH}_{18}$$
$$1.00 \times 10^3\ \text{mL}\ {}_8\text{CH}_{18} \longrightarrow 692\ \text{g}\ \text{C}_8\text{H}_{18}$$
$$692\ \text{g}\ \text{C}_8\text{H}_{18} \longrightarrow 6.07\ \text{mol}\ {}_8\text{CH}_{18}$$
$$692\ \text{g}\ \text{C}_8\text{H}_{18} \longrightarrow -3.31 \times 10^4\ \text{kJ}$$

Exercise 5.2.1.3

How much heat is produced by the combustion of 125 g of acetylene?

Answer available at the end of this section.

Emerging Algae-Based Energy Technologies (Biofuels)

As reserves of fossil fuels diminish and become more costly to extract, the search is ongoing for replacement fuel sources for the future. Among the most promising biofuels are those derived from algae (Figure 5.2.1.4). The species of algae used are nontoxic, biodegradable, and among the world’s fastest growing organisms. About 50% of algal weight is oil, which can be readily converted into fuel such as biodiesel. Algae can yield 26,000 gallons of biofuel per hectare—much more energy per acre than other crops. Some strains of algae can flourish in brackish water that is not usable for growing other crops. Algae can produce biodiesel, biogasoline, ethanol, butanol, methane, and even jet fuel.

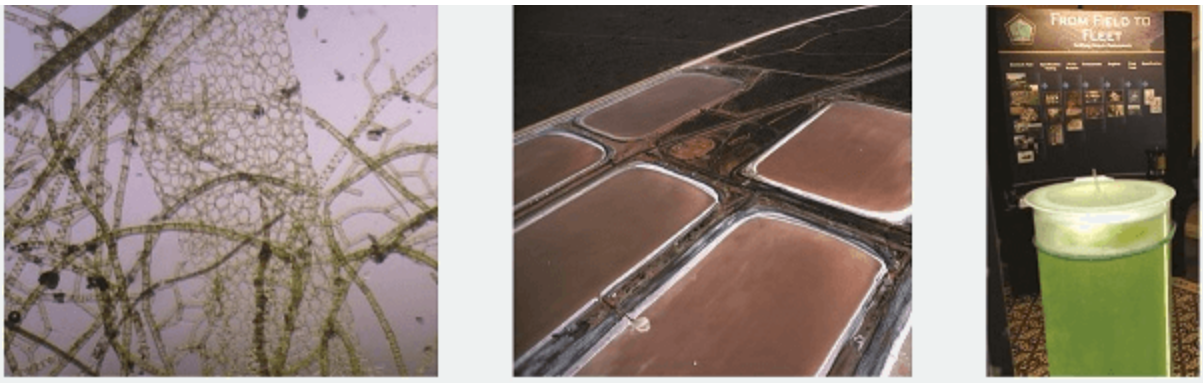


Figure 5.2.1.4: (a) Tiny algal organisms can be (b) grown in large quantities and eventually (c) turned into a useful fuel such as biodiesel. (credit a: modification of work by Micah Sittig; credit b: modification of work by Robert Kerton; credit c: modification of work by John F. Williams)

According to the US Department of Energy, only 39,000 square kilometers (about 0.4% of the land mass of the US or less than $\frac{1}{7}$ of the area used to grow corn) can produce enough algal fuel to replace all the petroleum-based fuel used in the US. The cost of algal fuels is becoming more competitive—for instance, the US Air Force is producing jet fuel from algae at a total cost of under $5 per gallon. The process used to produce algal fuel is as follows: grow the algae (which use sunlight as their energy source and CO_2 as a raw material); harvest the algae; extract the fuel compounds (or precursor compounds); process as necessary (e.g., perform a transesterification reaction to make biodiesel); purify; and distribute (Figure 5.2.1.5).

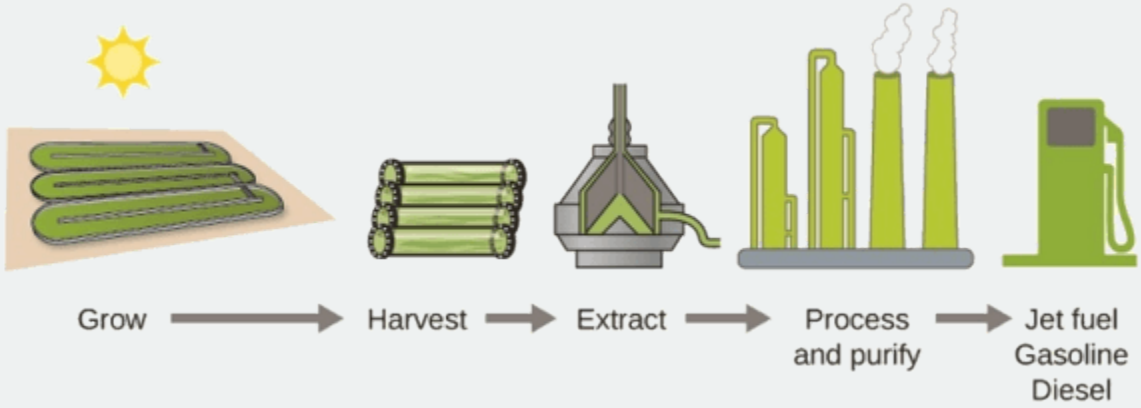


Figure 5.2.1.5: Algae convert sunlight and carbon dioxide into oil that is harvested, extracted, purified, and transformed into a variety of renewable fuels.

Standard Enthalpy of Formation

A standard enthalpy of formation ΔH_f° is an enthalpy change for a reaction in which exactly 1 mole of a pure substance is formed from free elements in their most stable states under standard state conditions. These values are especially useful for computing or predicting enthalpy changes for chemical reactions that are impractical or dangerous to carry out, or for processes for which it is difficult to make measurements. If we have values for the appropriate standard enthalpies of formation, we can determine the enthalpy change for any reaction, which we will practice in the next section on Hess's law.

The standard enthalpy of formation of $CO_2(g)$ is –393.5 kJ/mol. This is the enthalpy change for the exothermic reaction:

$$\mathrm{C}(s)+\mathrm{O}_2(g) \longrightarrow \mathrm{CO}_2(g) \quad \Delta H_f^\circ = \Delta H_{298}^\circ = -393.5\,k\,\mathrm{J} \tag{5.2.1.11}$$

starting with the reactants at a pressure of 1 atm and 25 °C (with the carbon present as graphite, the most stable form of carbon under these conditions) and ending with one mole of CO_2, also at 1 atm and 25 °C. For nitrogen dioxide, $NO_{2(g)}$, ΔH_f° is 33.2 kJ/mol. This is the enthalpy change for the reaction:

$$\frac{1}{2}\mathrm{N_2}(g)+\mathrm{O_2}(g) \longrightarrow \mathrm{NO_2}(g) \quad \Delta H_\mathrm{f}^\circ = \Delta H_{298}^\circ = +33.2\ k\,\mathrm{J} \tag{5.2.1.12}$$

A reaction equation with $\frac{1}{2}$ mole of N_2 and 1 mole of O_2 is correct in this case because the standard enthalpy of formation always refers to 1 mole of product, $NO_2(g)$.

You will find a table of standard enthalpies of formation of many common substances in Tables T1 and T2. These values indicate that formation reactions range from highly exothermic (such as –2984 kJ/mol for the formation of P_4O_{10}) to strongly endothermic (such as +226.7 kJ/mol for the formation of acetylene, C_2H_2). By definition, the standard enthalpy of formation of an element in its most stable form is equal to zero under standard conditions, which is 1 atm for gases and 1 M for solutions.

Example 5.2.1.4: Evaluating an Enthalpy of Formation

Ozone, $O_3(g)$, forms from oxygen, $O_2(g)$, by an endothermic process. Ultraviolet radiation is the source of the energy that drives this reaction in the upper atmosphere. Assuming that both the reactants and products of the reaction are in their standard states, determine the standard enthalpy of formation, $\Delta H_\mathrm{f}^\circ$ of ozone from the following information:

$$3\,\mathrm{O_2}(g) \longrightarrow 2\,\mathrm{O_3}(g) \quad \Delta H_{298}^\circ = +286\ k\,\mathrm{J}$$

Solution $\Delta H_\mathrm{f}^\circ$ is the enthalpy change for the formation of one mole of a substance in its standard state from the elements in their standard states. Thus, $\Delta H_\mathrm{f}^\circ$ for $O_3(g)$ is the enthalpy change for the reaction:

$$\frac{3}{2}\mathrm{O_2}(g) \longrightarrow \mathrm{O_3}(g)$$

For the formation of 2 mol of $O_3(g)$, $\Delta H_{298}^\circ = +286\ \ k\,\mathrm{J}$. This ratio, $\left(\frac{286\ \mathrm{kJ}}{2\ \mathrm{mol\ O_3}}\right)$, can be used as a conversion factor to find the heat produced when 1 mole of $O_3(g)$ is formed, which is the enthalpy of formation for $O_3(g)$:

$$\Delta H^\circ \text{ for 1 mole of } \mathrm{O_3}(g) = 1\ \cancel{\mathrm{mol\ O_3}} \times \frac{286\ \mathrm{kJ}}{2\ \cancel{\mathrm{mol\ O_3}}} = 143\ \mathrm{kJ}$$

Therefore, $\Delta H_\mathrm{f}^\circ[\mathrm{O_3}(g)] = +143\ \ k\,\mathrm{J/mol}$.

Exercise 5.2.1.4

Hydrogen gas, H_2, reacts explosively with gaseous chlorine, Cl_2, to form hydrogen chloride, $HCl(g)$. What is the enthalpy change for the reaction of 1 mole of $H_2(g)$ with 1 mole of $Cl_2(g)$ if both the reactants and products are at standard state conditions? The standard enthalpy of formation of $HCl(g)$ is –92.3 kJ/mol.

Answer available at the end of this section.

Example 5.2.1.5: Writing Reaction Equations for $\Delta H_\mathrm{f}^\circ$

Write the heat of formation reaction equations for:

a. $\mathrm{C_2H_5OH}_{(l)}$
b. $\mathrm{Ca_3(PO_4)_2}_{(s)}$

Solution

Remembering that $\Delta H_\mathrm{f}^\circ$ reaction equations are for forming 1 mole of the compound from its constituent elements under standard conditions, we have:

a. $2\,\mathrm{C}(s,\ \text{graphite}) + 3\,\mathrm{H_2}(g) + \frac{1}{2}\mathrm{O_2}(g) \longrightarrow \mathrm{C_2H_5OH}(l)$

b. $3\,\mathrm{Ca}(s) + \frac{1}{2}\mathrm{P}_4(s) + 4\,\mathrm{O}_2(g) \longrightarrow \mathrm{Ca}_3(\mathrm{PO}_4)_2(s)$

Note: The standard state of carbon is graphite, and phosphorus exists as P_4.

Exercise 5.2.1.5

Write the heat of formation reaction equations for:

a. $\mathrm{C_2H_5OC_2H_{5(l)}}$
b. $\mathrm{Na_2CO_{3(s)}}$

Answer a available at the end of this section.

Hess's Law

There are two ways to determine the amount of heat involved in a chemical change: measure it experimentally, or calculate it from other experimentally determined enthalpy changes. Some reactions are difficult, if not impossible, to investigate and make accurate measurements for experimentally. And even when a reaction is not hard to perform or measure, it is convenient to be able to determine the heat involved in a reaction without having to perform an experiment.

This type of calculation usually involves the use of Hess's law, which states: If a process can be written as the sum of several stepwise processes, the enthalpy change of the total process equals the sum of the enthalpy changes of the various steps. Hess's law is valid because enthalpy is a state function: Enthalpy changes depend only on where a chemical process starts and ends, but not on the path it takes from start to finish. For example, we can think of the reaction of carbon with oxygen to form carbon dioxide as occurring either directly or by a two-step process. The direct process is written:

$$\mathrm{C}_{(s)} + \mathrm{O}_{2(g)} \longrightarrow \mathrm{CO}_{2(g)} \quad \Delta H^\circ_{298} = -394\ \mathrm{kJ} \tag{5.2.1.13}$$

In the two-step process, first carbon monoxide is formed:

$$\mathrm{C}_{(s)} + \frac{1}{2}\mathrm{O}_{2(g)} \longrightarrow \mathrm{CO}_{(g)} \quad \Delta H^\circ_{298} = -111\ \mathrm{kJ} \tag{5.2.1.14}$$

Then, carbon monoxide reacts further to form carbon dioxide:

$$\mathrm{CO}(g) + \frac{1}{2}\mathrm{O}_2(g) \longrightarrow \mathrm{CO}_2(g) \quad \Delta H^\circ_{298} = -283\ \mathrm{kJ} \tag{5.2.1.15}$$

The equation describing the overall reaction is the sum of these two chemical changes:

$$\begin{aligned} &\text{Step 1: } \mathrm{C}(s) + \frac{1}{2}\mathrm{O}_2(g) \longrightarrow \mathrm{CO}(g) \\ &\text{Step 2: } \mathrm{CO}(g) + \frac{1}{2}\mathrm{O}_2(g) \longrightarrow \mathrm{CO}_2(g) \\ \hline &\text{Sum: } \mathrm{C}(s) + \frac{1}{2}\mathrm{O}_2(g) + \mathrm{CO}(g) + \frac{1}{2}\mathrm{O}_2(g) \longrightarrow \mathrm{CO}(g) + \mathrm{CO}_2(g) \end{aligned}$$

Because the CO produced in Step 1 is consumed in Step 2, the net change is:

$$\mathrm{C}_{(s)} + \mathrm{O}_{2(g)} \longrightarrow \mathrm{CO}_{2(g)} \tag{5.2.1.16}$$

According to Hess's law, the enthalpy change of the reaction will equal the sum of the enthalpy changes of the steps. We can apply the data from the experimental enthalpies of combustion in Table 5.2.1.1 to find the enthalpy change of the entire reaction from its two steps:

$$\begin{array}{ll} \mathrm{C}(s)+\frac{1}{2}\mathrm{O_2}(g)\longrightarrow \mathrm{CO}(g) & \Delta H^\circ_{298}=-111\ \mathrm{kJ} \\ \mathrm{CO}(g)+\frac{1}{2}\mathrm{O_2}(g)\longrightarrow \mathrm{CO_2}(g) & \Delta H^\circ_{298}=-283\ \mathrm{kJ} \\ \hline \mathrm{C}(s)+\mathrm{O_2}(g)\longrightarrow \mathrm{CO_2}(g) & \Delta H^\circ_{298}=-394\ \mathrm{kJ} \end{array}$$

The result is shown in Figure 5.2.1.6. We see that ΔH of the overall reaction is the same whether it occurs in one step or two. This finding (overall ΔH for the reaction = sum of Δ*H* values for reaction "steps" in the overall reaction) is true in general for chemical and physical processes.

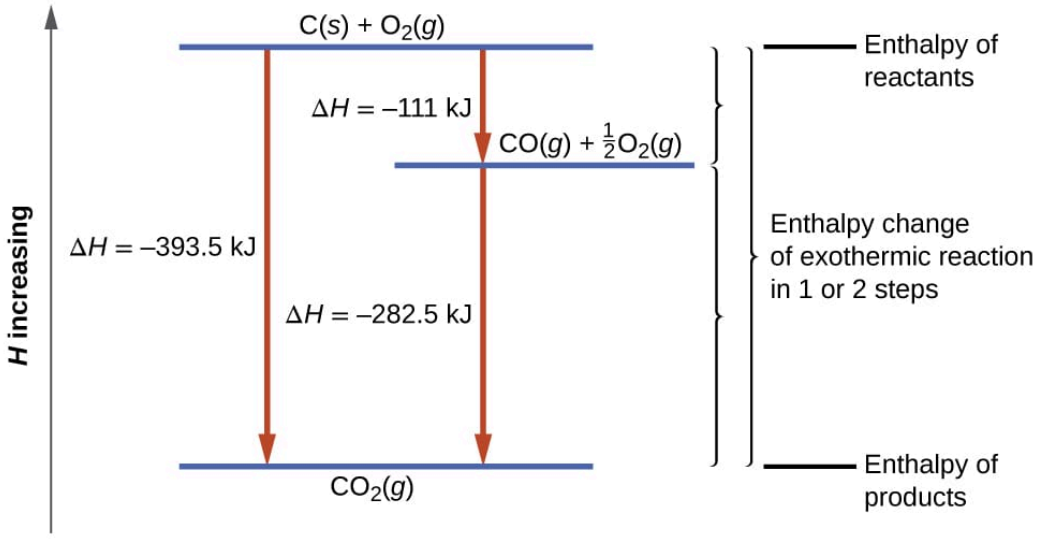


Figure 5.2.1.6: The formation of CO_2(g) from its elements can be thought of as occurring in two steps, which sum to the overall reaction, as described by Hess's law. The horizontal blue lines represent enthalpies. For an exothermic process, the products are at lower enthalpy than are the reactants.

Before we further practice using Hess's law, let us recall two important features of Δ*H*.

1. Δ*H* is directly proportional to the quantities of reactants or products. For example, the enthalpy change for the reaction forming 1 mole of NO_2(*g*) is +33.2 kJ:

$$\frac{1}{2}\mathrm{N_2}(g)+\mathrm{O_2}(g)\longrightarrow \mathrm{NO_2}(g)\quad \Delta H=+33.2\ \mathrm{kJ} \tag{5.2.1.17}$$

   When 2 moles of NO_2 (twice as much) are formed, the Δ*H* will be twice as large:

$$\mathrm{N_2}(g)+2\,\mathrm{O_2}(g)\longrightarrow 2\,\mathrm{NO_2}(g)\quad \Delta H=+66.4\ \mathrm{kJ} \tag{5.2.1.18}$$

   In general, if we multiply or divide an equation by a number, then the enthalpy change should also be multiplied or divided by the same number.

2. Δ*H* for a reaction in one direction is equal in magnitude and opposite in sign to Δ*H* for the reaction in the reverse direction. For example, given that:

$$\mathrm{H_2}(g)+\mathrm{Cl_2}(g)\longrightarrow 2\,\mathrm{HCl}(g)\quad \Delta H=-184.6\ \mathrm{kJ} \tag{5.2.1.19}$$

   Then, for the "reverse" reaction, the enthalpy change is also "reversed":

$$2\,\mathrm{HCl}(g)\longrightarrow \mathrm{H_2}(g)+\mathrm{Cl_2}(g)\quad \Delta H=+184.6\ \mathrm{kJ} \tag{5.2.1.20}$$

Example 5.2.1.6: Stepwise Calculation of ΔH_f°

Using Hess's Law Determine the enthalpy of formation, ΔH_f°, of $FeCl_3$(s) from the enthalpy changes of the following two-step process that occurs under standard state conditions:

$$\mathrm{Fe}(s)+\mathrm{Cl_2}(g) \longrightarrow \mathrm{FeCl_2}(s) \quad \Delta H°= -341.8\ \mathrm{kJ}$$

$$\mathrm{FeCl_2}(s) + \frac{1}{2}\mathrm{Cl_2}(g) \longrightarrow \mathrm{FeCl_3}(s) \quad \Delta H°= -57.7\ kJ$$

Solution

We are trying to find the standard enthalpy of formation of FeCl3(s), which is equal to ΔH° for the reaction:

$$\mathrm{Fe}(s) + \frac{3}{2}\mathrm{Cl_2}(g) \longrightarrow \mathrm{FeCl_3}(s) \quad \Delta H_\mathrm{f}^\circ = ?$$

Looking at the reactions, we see that the reaction for which we want to find Δ*H*° is the sum of the two reactions with known Δ*H* values, so we must sum their Δ*H*s:

$$\begin{array}{ll} \mathrm{Fe}(s)+\mathrm{Cl_2}(g) \longrightarrow \mathrm{FeCl_2}(s) & \Delta H°= -341.8\ \mathrm{kJ} \\ \mathrm{FeCl_2}(s) + \frac{1}{2}\mathrm{Cl_2}(g) \longrightarrow \mathrm{FeCl_3}(s) & \Delta H°= -57.7\ \mathrm{kJ} \\ \hline \mathrm{Fe}(s) + \frac{1}{2}\mathrm{Cl_2}(g) \longrightarrow \mathrm{FeCl_3}(s) & \Delta H°= -399.5\ \mathrm{kJ} \end{array}$$

The enthalpy of formation, $\Delta H_\mathrm{f}^\circ$, of $FeCl_3$(s) is –399.5 kJ/mol.

Exercise 5.2.1.6

Calculate ΔH for the process:

$$\mathrm{N_2}(g) + 2\,\mathrm{O_2}(g) \longrightarrow 2\,\mathrm{NO_2}(g)$$

from the following information:

$$\mathrm{N_2}(g) + \mathrm{O_2}(g) \longrightarrow 2\,\mathrm{NO}(g) \quad \Delta H = 180.5\ \mathrm{kJ}$$

$$\mathrm{NO}(g) + \frac{1}{2}\mathrm{O_2}(g) \longrightarrow \mathrm{NO_2}(g) \quad \Delta H = -57.06\ \mathrm{kJ}$$

Answer available at the end of this section.

Here is a less straightforward example that illustrates the thought process involved in solving many Hess's law problems. It shows how we can find many standard enthalpies of formation (and other values of Δ*H*) if they are difficult to determine experimentally.

Example 5.2.1.7: A More Challenging Problem

Using Hess's Law Chlorine monofluoride can react with fluorine to form chlorine trifluoride:

$$\text{(i) } \mathrm{ClF}(g) + \mathrm{F_2}(g) \longrightarrow \mathrm{ClF_3}(g) \quad \Delta H\,° = \ ?$$

Use the reactions here to determine the ΔH° for reaction (i):

$$\text{(ii) } 2\,\mathrm{OF_2}(g) \longrightarrow \mathrm{O_2}(g) + 2\,\mathrm{F_2}(g) \quad \Delta H_{(ii)}^\circ = -49.4\ \mathrm{kJ}$$

$$\text{(iii) } 2\,\mathrm{ClF}(g) + \mathrm{O_2}(g) \longrightarrow \mathrm{Cl_2O}(g) + \mathrm{OF_2}(g) \quad \Delta H_{(iii)}^\circ = +205.6\ \mathrm{kJ}$$

$$\text{(iv) } \mathrm{ClF_3}(g) + \mathrm{O_2}(g) \longrightarrow \tfrac{1}{2}\mathrm{Cl_2O}(g) + \frac{3}{2}\mathrm{OF_2}(g) \quad \Delta H_{(iv)}^\circ = +266.7\ \mathrm{kJ}$$

Solution

Our goal is to manipulate and combine reactions (ii), (iii), and (iv) such that they add up to reaction (i). Going from left to right in (i), we first see that $\mathrm{ClF}_{(g)}$ is needed as a reactant. This can be obtained by multiplying reaction (iii) by $\frac{1}{2}$, which means that the ΔH° change is also multiplied by $\frac{1}{2}$:

$$\mathrm{ClF}(g) + \frac{1}{2}\mathrm{O_2}(g) \longrightarrow \frac{1}{2}\mathrm{Cl_2O}(g) + \frac{1}{2}\mathrm{OF_2}(g) \quad \Delta H° = \frac{1}{2}(205.6) = +102.8\ k\,\mathrm{J}$$

Next, we see that $\mathrm{F_2}$ is also needed as a reactant. To get this, reverse and halve reaction (ii), which means that the ΔH° changes sign and is halved:

$$\frac{1}{2}\mathrm{O_2}(g) + \mathrm{F_2}(g) \longrightarrow \mathrm{OF_2}(g) \quad \Delta H° = +24.7\ k\,\mathrm{J}$$

To get $\mathrm{ClF_3}$ as a product, reverse (iv), changing the sign of ΔH°:

$$\frac{1}{2}\mathrm{Cl_2O}(g) + \frac{3}{2}\mathrm{OF_2}(g) \longrightarrow \mathrm{ClF_3}(g) + \mathrm{O_2}(g) \quad \Delta H° = -266.7\ \mathrm{kJ}$$

Now check to make sure that these reactions add up to the reaction we want:

$$\begin{array}{ll}
\mathrm{ClF}(g) + \frac{1}{2}\mathrm{O_2}(g) \longrightarrow \frac{1}{2}\mathrm{Cl_2O}(g) + \frac{1}{2}\mathrm{OF_2}(g) & \Delta H° = +102.8\ \mathrm{kJ} \\
\frac{1}{2}\mathrm{O_2}(g) + \mathrm{F_2}(g) \longrightarrow \mathrm{OF_2}(g) & \Delta H° = +24.7\ \mathrm{kJ} \\
\frac{1}{2}\mathrm{Cl_2O}(g) + \frac{3}{2}\mathrm{OF_2}(g) \longrightarrow \mathrm{ClF_3}(g) + \mathrm{O_2}(g) & \Delta H° = -266.7\ \mathrm{kJ} \\
\hline
\mathrm{ClF}(g) + \mathrm{F_2} \longrightarrow \mathrm{ClF_3}(g) & \Delta H° = -139.2\ \mathrm{kJ}
\end{array}$$

Reactants $\frac{1}{2}\mathrm{O_2}$ and $\frac{1}{2}\mathrm{O_2}$ cancel out product O_2; product $\frac{1}{2}\mathrm{Cl_2O}$ cancels reactant $\frac{1}{2}\mathrm{Cl_2O}$; and reactant $\frac{3}{2}\mathrm{OF_2}$ is cancelled by products $\frac{1}{2}\mathrm{OF_2}$ and OF_2. This leaves only reactants ClF(g) and F_2(g) and product ClF_3(g), which are what we want. Since summing these three modified reactions yields the reaction of interest, summing the three modified ΔH° values will give the desired ΔH°:

$$\Delta H^\circ = (+102.8\ \mathrm{kJ}) + (24.7\ \mathrm{kJ}) + (-266.7\ \mathrm{kJ}) = -139.2\ \mathrm{kJ}$$

Exercise 5.2.1.7

Aluminum chloride can be formed from its elements:

$$\text{(i)}\ 2\,\mathrm{Al}(s) + 3\,\mathrm{Cl_2}(g) \longrightarrow 2\,\mathrm{AlCl_3}(s) \quad \Delta H^\circ = \ ?$$

Use the reactions here to determine the ΔH° for reaction (i):

$$\text{(ii)}\ \mathrm{HCl}(g) \longrightarrow \mathrm{HCl}(aq) \quad \Delta H^\circ_{(ii)} = -74.8\ \mathrm{kJ}$$

$$\text{(iii)}\ \mathrm{H_2}(g) + \mathrm{Cl_2}(g) \longrightarrow 2\,\mathrm{HCl}(g) \quad \Delta H^\circ_{(iii)} = -185\ \mathrm{kJ}$$

$$\text{(iv)}\ \mathrm{AlCl_3}(aq) \longrightarrow \mathrm{AlCl_3}(s) \quad \Delta H^\circ_{(iv)} = +323\ \mathrm{kJ/mol}$$

$$\text{(v)}\ 2\,\mathrm{Al}(s) + 6\,\mathrm{HCl}(aq) \longrightarrow 2\,\mathrm{AlCl_3}(aq) + 3\,\mathrm{H_2}(g) \quad \Delta H^\circ_{(v)} = -1049\ \mathrm{kJ}$$

Answer available at the end of this section.

We also can use Hess's law to determine the enthalpy change of any reaction if the corresponding enthalpies of formation of the reactants and products are available. The stepwise reactions we consider are: (i) decompositions of the reactants into their component elements (for which the enthalpy changes are proportional to the negative of the enthalpies of formation of the reactants), followed by (ii) re-combinations of the elements to give the products (with the enthalpy changes proportional to the enthalpies of formation of the products). The standard enthalpy change of the overall reaction is therefore equal to: (ii) the sum of the standard enthalpies of formation of all the products plus (i) the sum of the negatives of the standard enthalpies of formation

of the reactants. This is usually rearranged slightly to be written as follows, with $\sum$ representing "the sum of" and *n* standing for the stoichiometric coefficients:

$$\Delta H^\circ_{\text{reaction}} = \sum n \times \Delta H^\circ_{\text{f}}(\text{products}) - \sum n \times \Delta H^\circ_{\text{f}}(\text{reactants}) \tag{5.2.1.21}$$

The following example shows in detail why this equation is valid, and how to use it to calculate the enthalpy change for a reaction of interest.

Example 5.2.1.8: Using Hess's Law

What is the standard enthalpy change for the reaction:

$$3\,NO_2(g) + H_2O(l) \longrightarrow 2\,HNO_3(aq) + NO(g) \quad \Delta H° = ?$$

Solution 1: Using the Equation

Alternatively, we could use the special form of Hess's law given previously:

$$\Delta H^\circ_{\text{reaction}} = \sum n \times \Delta H^\circ_{\text{f}}(\text{products}) - \sum n \times \Delta H^\circ_{\text{f}}(\text{reactants})$$

$$= \left[2\ \cancel{\text{mol HNO}_3} \times \frac{-207.4\ \text{kJ}}{\cancel{\text{mol HNO}_3\,(aq)}} + 1\ \cancel{\text{mol NO}\,(g)} \times \frac{+90.2\ \text{kJ}}{\cancel{\text{mol NO}\,(g)}}\right]$$

$$- \left[3\ \cancel{\text{mol NO}_2(g)} \times \frac{+33.2\ \text{kJ}}{\cancel{\text{mol NO}_2\,(g)}} + 1\ \cancel{\text{mol H}_2\text{O}\,(l)} \times \frac{-285.8\ \text{kJ}}{\cancel{\text{mol H}_2\text{O}\,(l)}}\right]$$

$$= 2(-207.4\ \text{kJ}) + 1(+90.2\ \text{kJ}) - 3(+33.2\ \text{kJ}) - 1(-285.8\ \text{kJ})$$

$$= -138.4\ \text{kJ}$$

Solution 2: Supporting Why the General Equation Is Valid

We can write this reaction as the sum of the decompositions of 3NO_2(*g*) and 1H_2O(*l*) into their constituent elements, and the formation of 2 HNO_3(*aq*) and 1 NO(*g*) from their constituent elements. Writing out these reactions, and noting their relationships to the $\Delta H^\circ_{\text{f}}$ values for these compounds (from Tables T1 and T2), we have:

$$3\,NO_2(g) \longrightarrow \frac{3}{2}N_2(g) + 3O_2(g) \quad \Delta H^\circ_1 = -99.6\ \text{kJ}$$

$$H_2O(l) \longrightarrow H_2(g) + \frac{1}{2}O_2(g) \quad \Delta H^\circ_2 = +285.8\ kJ\ [-1 \times \Delta H^\circ_{\text{f}}(H_2O)]$$

$$H_2(g) + N_2(g) + 3O_2(g) \longrightarrow 2\,HNO_3(aq) \quad \Delta H^\circ_3 = -414.8\ kJ\ [2 \times \Delta H^\circ_{\text{f}}(HNO_3\ )]$$

$$\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \longrightarrow NO(g) \quad \Delta H^\circ_4 = +90.2\ kJ\ [1 \times (NO)]$$

Summing these reaction equations gives the reaction we are interested in:

$$3\,NO_2(g) + H_2O(l) \longrightarrow 2\,HNO_3(aq) + NO(g)$$

Summing their enthalpy changes gives the value we want to determine:

$$\Delta H^\circ_{\text{rxn}} = \Delta H^\circ_1 + \Delta H^\circ_2 + \Delta H^\circ_3 + \Delta H^\circ_4 = (-99.6\ \text{kJ}) + (+285.8\ \text{kJ}) + (-414.8\ \text{kJ}) + (+90.2\ \text{kJ})$$
$$= -138.4\ \text{kJ}$$

So the standard enthalpy change for this reaction is $\Delta H°$ = –138.4 kJ.

Note that this result was obtained by:

1. multiplying the $\Delta H^\circ_{\text{f}}$ of each product by its stoichiometric coefficient and summing those values,
2. multiplying the $\Delta H^\circ_{\text{f}}$ of each reactant by its stoichiometric coefficient and summing those values, and then

3. subtracting the result found in step 2 from the result found in step 1.

This is also the procedure in using the general equation, as shown.

Exercise 5.2.1.8

Calculate the heat of combustion of 1 mole of ethanol, $C_2H_5OH(l)$, when $H_2O(l)$ and $CO_2(g)$ are formed. Use the following enthalpies of formation: $C_2H_5OH(l)$, –278 kJ/mol; $H_2O(l)$, –286 kJ/mol; and $CO_2(g)$, –394 kJ/mol.

Answer available at the end of this section.

Summary

If a chemical change is carried out at constant pressure and the only work done is caused by expansion or contraction, *q* for the change is called the enthalpy change with the symbol Δ*H*, or ΔH°_{298} for reactions occurring under standard state conditions. The value of Δ*H* for a reaction in one direction is equal in magnitude, but opposite in sign, to Δ*H* for the reaction in the opposite direction, and Δ*H* is directly proportional to the quantity of reactants and products. Examples of enthalpy changes include enthalpy of combustion, enthalpy of fusion, enthalpy of vaporization, and standard enthalpy of formation. The standard enthalpy of formation, ΔH°_f, is the enthalpy change accompanying the formation of 1 mole of a substance from the elements in their most stable states at 1 bar (standard state). Many of the processes are carried out at 298.15 K. If the enthalpies of formation are available for the reactants and products of a reaction, the enthalpy change can be calculated using Hess's law: If a process can be written as the sum of several stepwise processes, the enthalpy change of the total process equals the sum of the enthalpy changes of the various steps.

Key Equations

- $\Delta U = q + w$
- $\Delta H^\circ_{\text{reaction}} = \sum n \times \Delta H^\circ_f(\text{products}) - \sum n \times \Delta H^\circ_f(\text{reactants})$

Footnotes

1. 1 For more on algal fuel, see www.theguardian.com/environme...n-fuel-problem.

Glossary

chemical thermodynamics
: area of science that deals with the relationships between heat, work, and all forms of energy associated with chemical and physical processes

enthalpy (*H*)
: sum of a system's internal energy and the mathematical product of its pressure and volume

enthalpy change (Δ*H*)
: heat released or absorbed by a system under constant pressure during a chemical or physical process

expansion work (pressure-volume work)
: work done as a system expands or contracts against external pressure

first law of thermodynamics
: internal energy of a system changes due to heat flow in or out of the system or work done on or by the system

Hess's law
: if a process can be represented as the sum of several steps, the enthalpy change of the process equals the sum of the enthalpy changes of the steps

hydrocarbon
compound composed only of hydrogen and carbon; the major component of fossil fuels

internal energy (*U*)
total of all possible kinds of energy present in a substance or substances

standard enthalpy of combustion (ΔH_c°)
heat released when one mole of a compound undergoes complete combustion under standard conditions

standard enthalpy of formation (ΔH_f°)
enthalpy change of a chemical reaction in which 1 mole of a pure substance is formed from its elements in their most stable states under standard state conditions

standard state
set of physical conditions as accepted as common reference conditions for reporting thermodynamic properties; 1 bar of pressure, and solutions at 1 molar concentrations, usually at a temperature of 298.15 K

state function
property depending only on the state of a system, and not the path taken to reach that state

Answers

Exercise 5.2.1.1
ΔH = −153 kJ

Exercise 5.2.1.2
ΔH = −338 kJ

Exercise 5.2.1.3
6.25×10^3 kJ

Exercise 5.2.1.4
For the reaction

$$\mathrm{H_2}(g)+\mathrm{Cl_2}(g) \longrightarrow 2\,\mathrm{HCl}(g) \quad \Delta H_{298}^\circ = -184.6\ \mathrm{kJ}$$

Exercise 5.2.1.5
$4\,\mathrm{C}(s,\ \text{graphite}) + 5\,\mathrm{H_2}(g) + \frac{1}{2}\mathrm{O_2}(g) \longrightarrow \mathrm{C_2H_5OC_2H_5}(l)$;
$2\,\mathrm{Na}(s) + \mathrm{C}(s,\ \text{graphite}) + \frac{3}{2}\mathrm{O_2}(g) \longrightarrow \mathrm{Na_2CO_3}(s)$

Exercise 5.2.1.6
66.4 kJ

Exercise 5.2.1.7
−1407 kJ

Exercise 5.2.1.8
−1368 kJ/mol

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5.2.2: Spontaneity

Learning Objectives

- Distinguish between spontaneous and nonspontaneous processes
- Describe the dispersal of matter and energy that accompanies certain spontaneous processes

In this section, consider the differences between two types of changes in a system: Those that occur spontaneously and those that occur only with the continuous input of energy. In doing so, we'll gain an understanding as to why some systems are naturally inclined to change in one direction under certain conditions. We'll also gain insight into how the spontaneity of a process affects the distribution of energy and matter within the system.

Spontaneous and Nonspontaneous Processes

Processes have a natural tendency to occur in one direction under a given set of conditions. Water will naturally flow downhill, but uphill flow requires outside intervention such as the use of a pump. A spontaneous process is one that occurs naturally under certain conditions. A nonspontaneous process, on the other hand, will not take place unless it is "driven" by the continual input of energy from an external source. A process that is spontaneous in one direction under a particular set of conditions is nonspontaneous in the reverse direction. At room temperature and typical atmospheric pressure, for example, ice will spontaneously melt, but water will not spontaneously freeze.

The spontaneity of a process is *not* correlated to the speed of the process. A spontaneous change may be so rapid that it is essentially instantaneous or so slow that it cannot be observed over any practical period of time. To illustrate this concept, consider the decay of radioactive isotopes, a topic more thoroughly treated in the chapter on nuclear chemistry. Radioactive decay is by definition a spontaneous process in which the nuclei of unstable isotopes emit radiation as they are converted to more stable nuclei. All the decay processes occur spontaneously, but the rates at which different isotopes decay vary widely. Technetium-99m is a popular radioisotope for medical imaging studies that undergoes relatively rapid decay and exhibits a half-life of about six hours. Uranium-238 is the most abundant isotope of uranium, and its decay occurs much more slowly, exhibiting a half-life of more than four billion years (Figure 5.2.2.1).

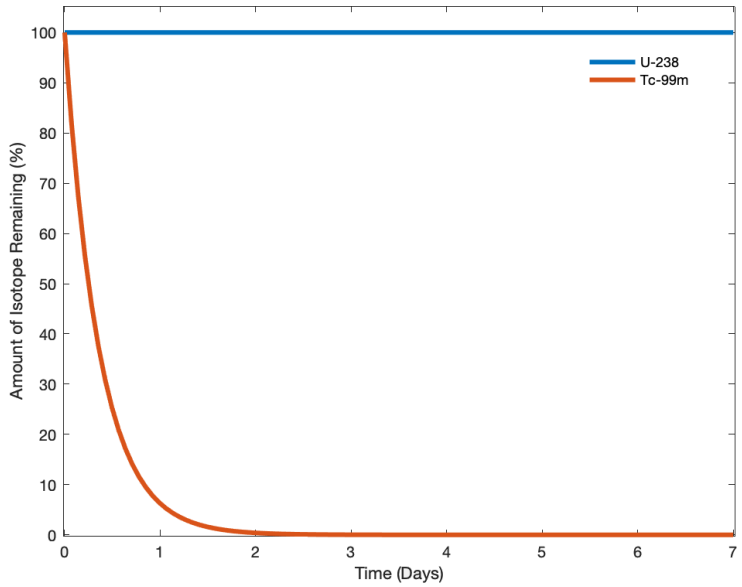


Figure 5.2.2.1: Both U-238 and Tc-99m undergo spontaneous radioactive decay, but at drastically different rates. Over the course of one week, essentially all of a Tc-99m sample and none of a U-238 sample will have decayed. (CC by 4.0; Morgan Johnson via LibreTexts)

Two curves are shown to represent U-238 and Tc-99m respectively. The vertical axes represents the percentage of isotope remaining and the horizontal axes is the time that has elapsed in days.

As another example, consider the conversion of diamond into graphite (Figure 5.2.2.2).

$$\mathrm{C\,(s,\,diamond)} \longrightarrow \mathrm{C\,(s,\,graphite)} \tag{5.2.2.1}$$

The phase diagram for carbon indicates that graphite is the stable form of this element under ambient atmospheric pressure, while diamond is the stable allotrope at very high pressures, such as those present during its geologic formation. Thermodynamic calculations of the sort described in the last section of this chapter indicate that the conversion of diamond to graphite at ambient pressure occurs spontaneously, yet diamonds are observed to exist, and persist, under these conditions. Though the process is spontaneous under typical ambient conditions, its rate is extremely slow, and so for all practical purposes diamonds are indeed "forever." Situations such as these emphasize the important distinction between the thermodynamic and the kinetic aspects of a process. In this particular case, diamonds are said to be *thermodynamically unstable* but *kinetically stable* under ambient conditions.

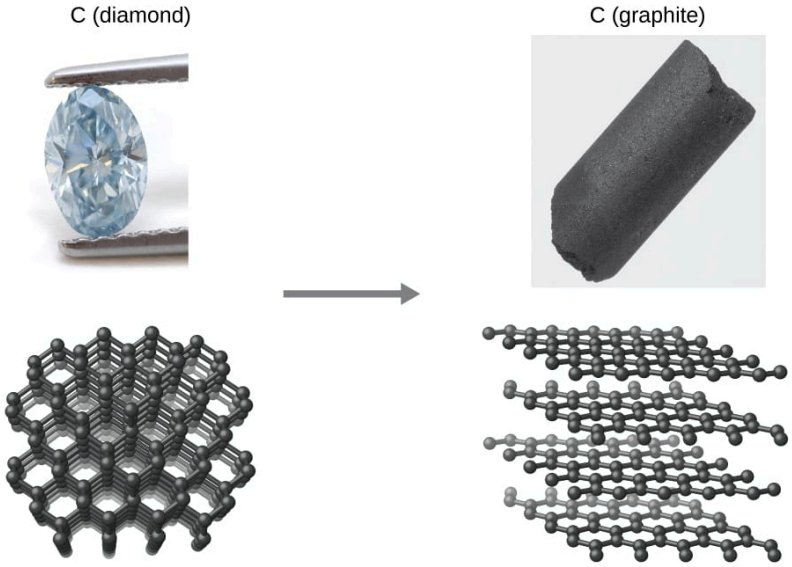


Figure 5.2.2.2: The conversion of carbon from the diamond allotrope to the graphite allotrope is spontaneous at ambient pressure, but its rate is immeasurably slow at low to moderate temperatures. This process is known as graphitization, and its rate can be increased to easily measurable values at temperatures in the 1000–2000 K range. (credit "diamond" photo: modification of work by "Fancy Diamonds"/Flickr; credit "graphite" photo: modification of work by images-of-elements.com/carbon.php)

Comparison of diamond and graphite shown in its physical form as well as its molecular arrangement respectively.

Dispersal of Matter and Energy

As we extend our discussion of thermodynamic concepts toward the objective of predicting spontaneity, consider now an isolated system consisting of two flasks connected with a closed valve. Initially there is an ideal gas on the left and a vacuum on the right (Figure 5.2.2.3). When the valve is opened, the gas spontaneously expands to fill both flasks. Recalling the definition of pressure-volume work from the chapter on thermochemistry, note that no work has been done because the pressure in a vacuum is zero.

$$w = -P\Delta V \tag{5.2.2.2}$$

$$= 0 \;\; (\mathrm{P} = 0 \text{ in a vaccum}) \tag{5.2.2.3}$$

Note as well that since the system is isolated, no heat has been exchanged with the surroundings (q = 0). The first law of thermodynamics confirms that there has been no change in the system's internal energy as a result of this process.

$$\Delta U = q + w \qquad \text{(First Law of Thermodynamics)}$$

$$= 0 + 0 = 0 \tag{5.2.2.4}$$

The spontaneity of this process is therefore not a consequence of any change in energy that accompanies the process. Instead, the movement of the gas appears to be related to the greater, more *uniform dispersal of matter* that results when the gas is allowed to expand. Initially, the system was comprised of one flask containing matter and another flask containing nothing. After the spontaneous process took place, the matter was distributed both more widely (occupying twice its original volume) and more

uniformly (present in equal amounts in each flask).

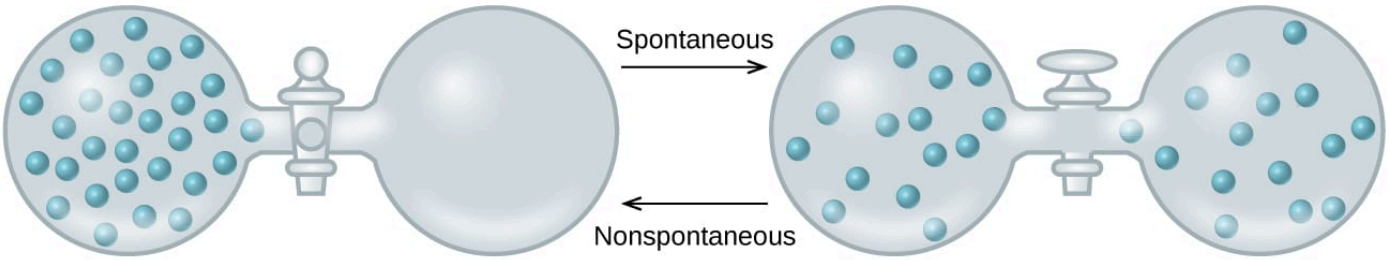


Figure 5.2.2.3: An isolated system consists of an ideal gas in one flask that is connected by a closed valve to a second flask containing a vacuum. Once the valve is opened, the gas spontaneously becomes evenly distributed between the flasks.

When the valve is closed, all of the gas molecules accumlating only in one side of the flask. The diagram with the open valve shows gas being equally distributed among the two flasks. The dispersion of the gas is labeled as spontaneous while the reverse is labeled as non spontaneous.

Now consider two objects at different temperatures: object X at temperature T_X and object Y at temperature T_Y, with $T_X > T_Y$ (Figure 5.2.2.4). When these objects come into contact, heat spontaneously flows from the hotter object (X) to the colder one (Y). This corresponds to a loss of thermal energy by X and a gain of thermal energy by Y.

$$q_X < 0 \quad \text{and} \quad q_Y = -q_X > 0 \tag{5.2.2.5}$$

From the perspective of this two-object system, there was no net gain or loss of thermal energy, rather the available thermal energy was redistributed among the two objects. This spontaneous process resulted in a *more uniform dispersal of energy*.



Figure 5.2.2.4:When two objects at different temperatures come in contact, heat spontaneously flows from the hotter to the colder object.

Two separated blocks. One is labeled X and the other labeled Y. The diagram next to it shows the two blocks in contact with one another.

As illustrated by the two processes described, an important factor in determining the spontaneity of a process is the extent to which it changes the dispersal or distribution of matter and/or energy. In each case, a spontaneous process took place that resulted in a more uniform distribution of matter or energy.

Example 5.2.2.1: Redistribution of Matter during a Spontaneous Process

Describe how matter and energy are redistributed when the following spontaneous processes take place:

a. A solid sublimes.
b. A gas condenses.
c. A drop of food coloring added to a glass of water forms a solution with uniform color.

Solution



Figure 5.2.2.5:(credit a: modification of work by Jenny Downing; credit b: modification of work by “Fuzzy Gerdes”/Flickr; credit c: modification of work by Sahar Atwa)

This figure has three photos labeled, “a,” “b,” and “c.” Photo a shows a glass with dry ice in water. There is a thick vapor coming from the top of the glass. Photo b shows water forming outside of a glass containing cold beverage. Photo c shows a sealed container that holds a red liquid.

a. *Sublimation* is the conversion of a solid (relatively high density) to a gas (much lesser density). This process yields a much greater dispersal of matter, since the molecules will occupy a much greater volume after the solid-to-gas transition. However, an input of energy from the surroundings ss required for the molecules to leave the solid phase and enter the gas phase.
b. *Condensation* is the conversion of a gas (relatively low density) to a liquid (much greater density). This process yields a much lesser dispersal of matter, since the molecules will occupy a much lesser volume after the gas-to-liquid transition. As the gas molecules move together to form the droplets of liquid, they form intermolecular forces and thus release energy to the surroundings.
c. The process in question is *dilution*. The food dye molecules initially occupy a much smaller volume (the drop of dye solution) than they occupy once the process is complete (in the full glass of water). The process therefore entails a greater dispersal of matter. The process may also yield a more uniform dispersal of matter, since the initial state of the system involves two regions of different dye concentrations (high in the drop, zero in the water), and the final state of the system contains a single dye concentration throughout. This process can occur with out a change in energy because the molecules have kinetic energy relative to the temperature of the water, and so will be constantly in motion.

Exercise 5.2.2.1

Describe how matter and energy are redistributed when you empty a canister of compressed air into a room.

Answer available at the end of this section.

Summary

Chemical and physical processes have a natural tendency to occur in one direction under certain conditions. A spontaneous process occurs without the need for a continual input of energy from some external source, while a nonspontaneous process requires such. Systems undergoing a spontaneous process may or may not experience a gain or loss of energy, but they will experience a change in the way matter and/or energy is distributed within the system. In this section we have only discussed nuclear decay, physical changes of pure substances, and macroscopic events such as water flowing downhill. In the following sections we will discuss mixtures and chemical reactions, situations in which the description of sponteneity becomes more challenging.

Glossary

nonspontaneous process
: process that requires continual input of energy from an external source

spontaneous change
: process that takes place without a continuous input of energy from an external source

Answers

Exercise 5.2.2.1

This process entails both a greater and more uniform dispersal of matter as the compressed air in the canister is permitted to expand into the lower-pressure air of the room. The process also requires an input of energy to disrupt the intermolecular forces between the closely-spaced gas molecules that are originally compressed into the container. If you were to touch the nozzle of the canister, you would notice that it is cold because the exiting molecules are taking energy away from their surroundings, and the canister is part of the surroundings.

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5.2.3: Entropy

Learning Objectives

- Define entropy
- Explain the relationship between entropy and the number of microstates
- Predict the sign of the entropy change for chemical and physical processes

In 1824, at the age of 28, Nicolas Léonard Sadi Carnot (Figure 5.2.3.2) published the results of an extensive study regarding the efficiency of steam heat engines. In a later review of Carnot's findings, Rudolf Clausius introduced a new thermodynamic property that relates the spontaneous heat flow accompanying a process to the temperature at which the process takes place. This new property was expressed as the ratio of the *reversible* heat (q_{rev}) and the kelvin temperature (T). The term reversible process refers to a process that takes place at such a slow rate that it is always at equilibrium and its direction can be changed (it can be "reversed") by an infinitesimally small change is some condition. Note that the idea of a reversible process is a formalism required to support the development of various thermodynamic concepts; no real processes are truly reversible, rather they are classified as *irreversible*.



Figure 5.2.3.1: (a) Nicholas Léonard Sadi Carnot's research into steam-powered machinery and (b) Rudolf Clausius's later study of those findings led to groundbreaking discoveries about spontaneous heat flow processes.

Similar to other thermodynamic properties, this new quantity is a state function, and so its change depends only upon the initial and final states of a system. In 1865, Clausius named this property entropy (S) and defined its change for any process as the following:

$$\Delta S = \frac{q_{\text{rev}}}{T} \tag{5.2.3.1}$$

The entropy change for a real, irreversible process is then equal to that for the theoretical reversible process that involves the same initial and final states.

Entropy and Microstates

Following the work of Carnot and Clausius, Ludwig Boltzmann developed a molecular-scale statistical model that related the entropy of a system to the number of *microstates* possible for the system. A microstate (Ω) is a specific configuration of the locations and energies of the atoms or molecules that comprise a system like the following:

$$S = k \ln \Omega \tag{5.2.3.2}$$

Here *k* is the Boltzmann constant and has a value of $1.38 \times 10^{-23}\ J/K$.

As for other state functions, the change in entropy for a process is the difference between its final (S_f) and initial (S_i) values:

$$\begin{aligned} \Delta S &= S_\mathrm{f} - S_\mathrm{i} \\ &= k \ln \Omega_\mathrm{f} - k \ln \Omega_\mathrm{i} \\ &= k \ln \frac{\Omega_\mathrm{f}}{\Omega_\mathrm{i}} \end{aligned} \tag{5.2.3.3}$$

For processes involving an increase in the number of microstates of the system, $\Omega_f > \Omega_i$, the entropy of the system increases, $\Delta S > 0$. Conversely, processes that reduce the number of microstates in the system, $\Omega_f < \Omega_i$, yield a decrease in system entropy, $\Delta S < 0$. This molecular-scale interpretation of entropy provides a link to the probability that a process will occur as illustrated in the next paragraphs.

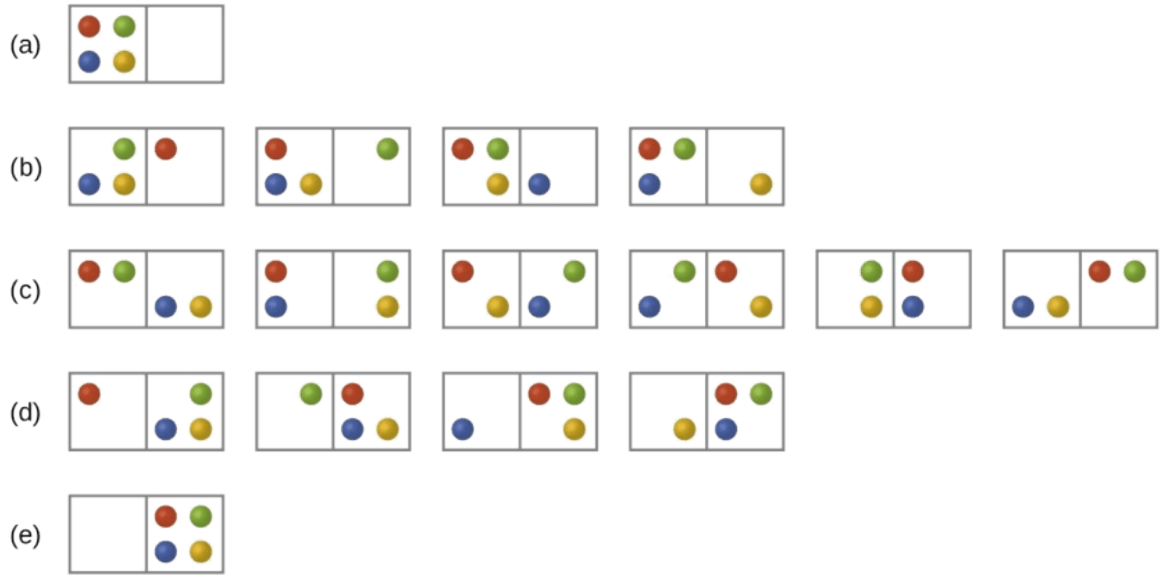


Figure 5.2.3.2: The sixteen microstates associated with placing four particles in two boxes are shown. The microstates are collected into five distributions—(a), (b), (c), (d), and (e)—based on the numbers of particles in each box.

Five rows of diagrams that look like dominoes are shown and labeled a, b, c, d, and e. Row a has one “domino” that has four dots on the left side, red, green, blue and yellow in a clockwise pattern from the top left, and no dots on the right. Row b has four “dominos,” each with three dots on the left and one dot on the right. The first shows a “domino” with green, yellow and blue on the left and red on the right. The second “domino” has yellow, blue and red on the left and green on the right. The third “domino” has red, green and yellow on the left and blue on the right while the fourth has red, green and blue on the left and yellow on the right. Row c has six “dominos”, each with two dots on either side. The first has a red and green on the left and a blue and yellow on the right. The second has a red and blue on the left and a green and yellow on the right while the third has a yellow and red on the left and a green and blue on the right. The fourth has a green and blue on the left and a red and yellow on the right. The fifth has a green and yellow on the left and a red and blue on the right. The sixth has a blue and yellow on the left and a green and red on the right. Row d has four “dominos,” each with one dot on the left and three on the right. The first “domino” has red on the left and a blue, green and yellow on the right. The second has a green on the left and a red, yellow and blue on the right. The third has a blue on the left and a red, green and yellow on the right. The fourth has a yellow on the left and a red, green and blue on the right. Row e has 1 “domino” with no dots on the left and four dots on the right that are red, green, blue and yellow.

Consider the general case of a system comprised of *N* particles distributed among *n* boxes. The number of microstates possible for such a system is n^N. For example, distributing four particles among two boxes will result in 2^4 = 16 different microstates as illustrated in Figure 5.2.3.2. Microstates with equivalent particle arrangements (not considering individual particle identities) are grouped together and are called *distributions* (sometimes called macrostates or configurations). The probability that a system will exist with its components in a given distribution is proportional to the number of microstates within the distribution. Since entropy increases logarithmically with the number of microstates, *the most probable distribution is therefore the one of greatest entropy*.

For this system, the most probable configuration is one of the six microstates associated with distribution (c) where the particles

are evenly distributed between the boxes, that is, a configuration of two particles in each box. The probability of finding the system in this configuration is

$$\frac{6}{16} = \frac{3}{8}$$

The least probable configuration of the system is one in which all four particles are in one box, corresponding to distributions (a) and (e), each with a probability of

$$\frac{1}{16}$$

The probability of finding all particles in only one box (either the left box or right box) is then

$$\left(\frac{1}{16} + \frac{1}{16}\right) = \frac{2}{16} = \frac{1}{8}$$

As you add more particles to the system, the number of possible microstates increases exponentially (2^N). A macroscopic (laboratory-sized) system would typically consist of moles of particles ($N \sim 10^{23}$), and the corresponding number of microstates would be staggeringly huge. Regardless of the number of particles in the system, however, the distributions in which roughly equal numbers of particles are found in each box are always the most probable configurations.

> The most probable distribution is therefore the one of greatest entropy.

The previous description of an ideal gas expanding into a vacuum is a macroscopic example of this particle-in-a-box model. For this system, the most probable distribution is confirmed to be the one in which the matter is most uniformly dispersed or distributed between the two flasks. The spontaneous process whereby the gas contained initially in one flask expands to fill both flasks equally therefore yields an increase in entropy for the system.

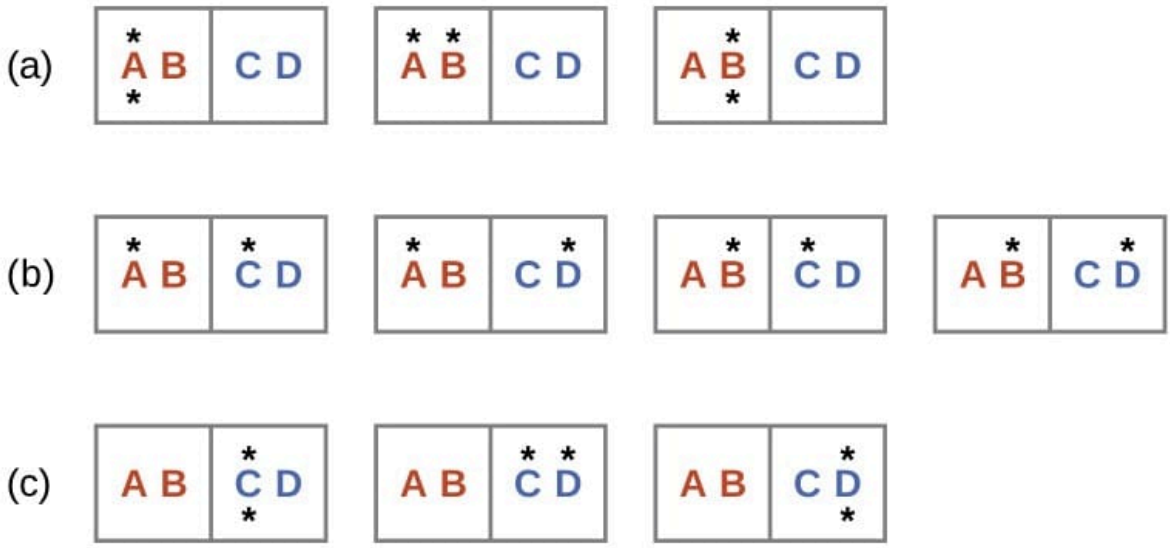


Figure 5.2.3.3: This shows a microstate model describing the flow of heat from a hot object to a cold object. (a) Before the heat flow occurs, the object comprised of particles **A** and **B** contains both units of energy and as represented by a distribution of three microstates. (b) If the heat flow results in an even dispersal of energy (one energy unit transferred), a distribution of four microstates results. (c) If both energy units are transferred, the resulting distribution has three microstates.

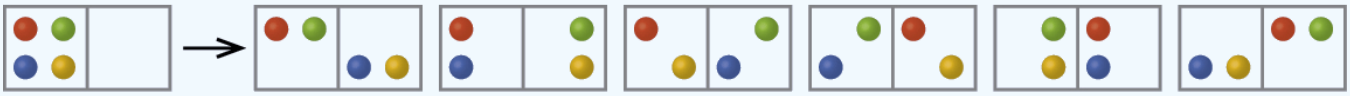
Three rows labeled a, b, and c are shown and each contains rectangles with two sides where the left side is labeled, “A,” and “B,” and the right is labeled, “C,” and “D.” Row a has three rectangles where the first has a dot above and below the letter A, the second has a dot above the A and B, and the third which has a dot above and below the letter B. Row b has four rectangles; the first has a dot above A and C, the second has a dot above A and D, the third has a dot above B and C and the fourth has a dot above B and D. Row c has three rectangles; the first has a dot above and below the letter C, the second has a dot above C and D and the third has a dot above and below the letter D.

A similar approach may be used to describe the spontaneous flow of heat. Consider a system consisting of two objects, each containing two particles, and two units of energy (represented as “*”) in Figure 5.2.3.3. The hot object is comprised of particles

A and **B** and initially contains both energy units. The cold object is comprised of particles **C** and **D**, which initially has no energy units. Distribution (a) shows the three microstates possible for the initial state of the system, with both units of energy contained within the hot object. If one of the two energy units is transferred, the result is distribution (b) consisting of four microstates. If both energy units are transferred, the result is distribution (c) consisting of three microstates. And so, we may describe this system by a total of ten microstates. The probability that the heat does not flow when the two objects are brought into contact, that is, that the system remains in distribution (a), is $\frac{3}{10}$. More likely is the flow of heat to yield one of the other two distribution, the combined probability being $\frac{7}{10}$. The most likely result is the flow of heat to yield the uniform dispersal of energy represented by distribution (b), the probability of this configuration being $\frac{4}{10}$. As for the previous example of matter dispersal, extrapolating this treatment to macroscopic collections of particles dramatically increases the probability of the uniform distribution relative to the other distributions. This supports the common observation that placing hot and cold objects in contact results in spontaneous heat flow that ultimately equalizes the objects' temperatures. And, again, this spontaneous process is also characterized by an increase in system entropy.

Example 5.2.3.1: Determination of ΔS

Consider the system shown here. What is the change in entropy for a process that converts the system from distribution (a) to (c)?



A diagram shows one rectangle with two sides that has four dots, red, green, yellow and blue written on the left side. A right-facing arrow leads to six more two-sided rectangles, each with two dots on the left and right sides. The first rectangle has a red and green dot on the left and a blue and yellow on the right, while the second shows a red and blue on the left and a green and yellow on the right. The third rectangle has a red and yellow dot on the left and a blue and green on the right, while the fourth shows a green and blue on the left and a red and yellow on the right. The fifth rectangle has a yellow and green dot on the left and a blue and red on the right, while the sixth shows a yellow and blue on the left and a green and red on the right.

Solution

We are interested in the following change:

The initial number of microstates is one, the final six:

$$\begin{aligned}\Delta S &= k \ln \frac{\Omega_c}{\Omega_a} \\ &= 1.38 \times 10^{-23}\ J/K \times \ln \frac{6}{1} \\ &= 2.47 \times 10^{-23}\ J/K\end{aligned}$$

The sign of this result is consistent with expectation; since there are more microstates possible for the final state than for the initial state, the change in entropy should be positive.

Exercise 5.2.3.1

Consider the system shown in Figure 5.2.3.3. What is the change in entropy for the process where *all* the energy is transferred from the hot object (**AB**) to the cold object (**CD**)?

Answer available at the end of this section.

Predicting the Sign of ΔS

The relationships between entropy, microstates, and matter/energy dispersal described previously allow us to make generalizations regarding the relative entropies of substances and to predict the sign of entropy changes for chemical and physical processes. Consider the phase changes illustrated in Figure 5.2.3.4. In the solid phase, the atoms or molecules are restricted to nearly fixed positions with respect to each other and are capable of only modest oscillations about these positions.

With essentially fixed locations for the system's component particles, the number of microstates is relatively small. In the liquid phase, the atoms or molecules are free to move over and around each other, though they remain in relatively close proximity to one another. This increased freedom of motion results in a greater variation in possible particle locations, so the number of microstates is correspondingly greater than for the solid. As a result, $S_{liquid} > S_{solid}$ and the process of converting a substance from solid to liquid (melting) is characterized by an increase in entropy, $\Delta S > 0$. By the same logic, the reciprocal process (freezing) exhibits a decrease in entropy, $\Delta S < 0$.

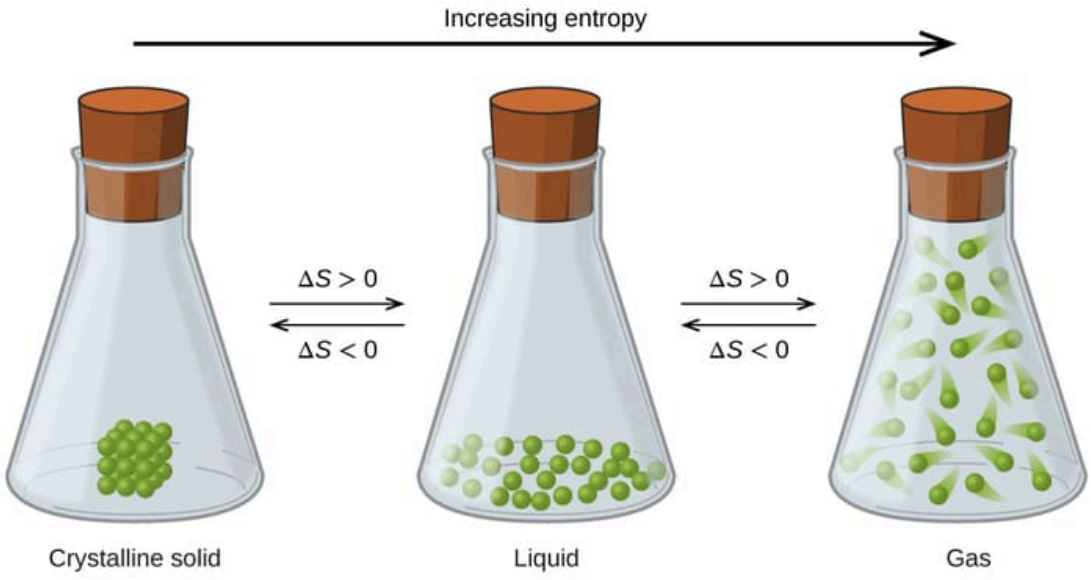


Figure 5.2.3.4: The entropy of a substance increases ($\Delta S > 0$) as it transforms from a relatively ordered solid, to a less-ordered liquid, and then to a still less-ordered gas. The entropy decreases ($\Delta S < 0$) as the substance transforms from a gas to a liquid and then to a solid.

Three stoppered flasks are shown with right and left-facing arrows in between each; the first is labeled above as, "delta S greater than 0," and below as, "delta S less than 0," while the second is labeled above as, "delta S greater than 0," and below as, "delta S less than 0." A long, right-facing arrow is drawn above all the flasks and labeled, "Increasing entropy." The left flask contains twenty-seven particles arranged in a cube in the bottom of the flask and is labeled, "Crystalline solid," below. The middle flask contains twenty-seven particles dispersed randomly in the bottom of the flask and is labeled, "Liquid," below. The right flask contains twenty-seven particles dispersed inside of the flask and moving rapidly and is labeled, "Gas," below.

Now consider the vapor or gas phase. The atoms or molecules occupy a *much* greater volume than in the liquid phase; therefore each atom or molecule can be found in many more locations than in the liquid (or solid) phase. Consequently, for any substance, $S_{gas} > S_{liquid} > S_{solid}$, and the processes of vaporization and sublimation likewise involve increases in entropy, $\Delta S > 0$. Likewise, the reciprocal phase transitions, condensation and deposition, involve decreases in entropy, $\Delta S < 0$.

According to kinetic-molecular theory, the temperature of a substance is proportional to the average kinetic energy of its particles. Raising the temperature of a substance will result in more extensive vibrations of the particles in solids and more rapid translations of the particles in liquids and gases. At higher temperatures, the distribution of kinetic energies among the atoms or molecules of the substance is also broader (more dispersed) than at lower temperatures. Thus, the entropy for any substance increases with temperature (Figure 5.2.3.5).

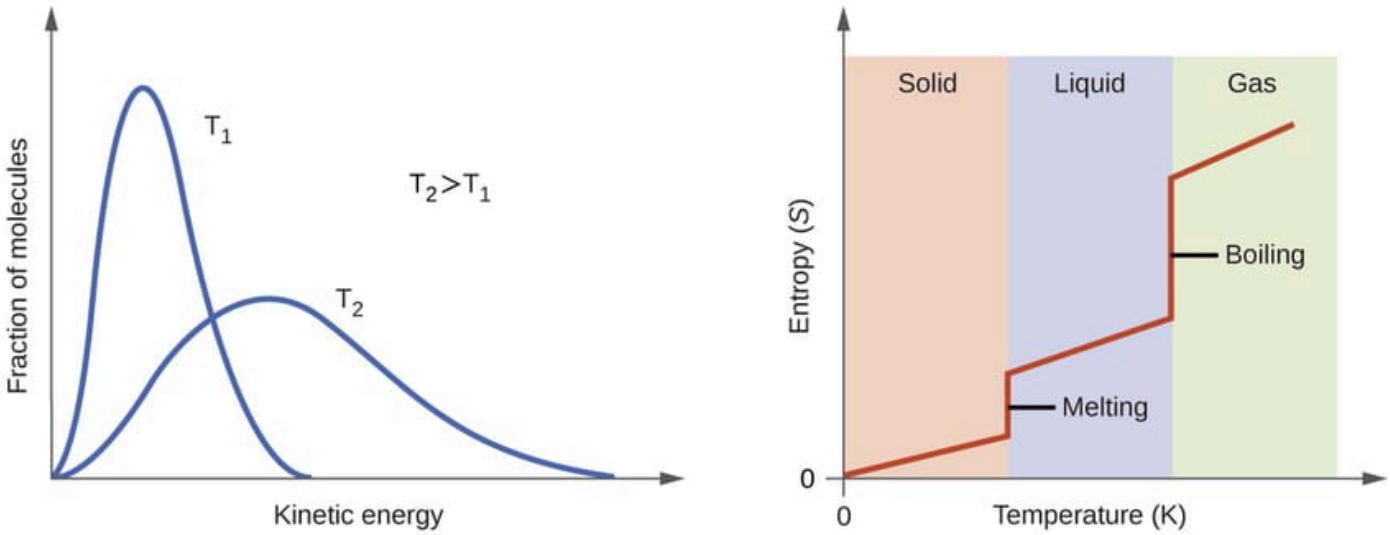


Figure 5.2.3.5: Entropy increases as the temperature of a substance is raised, which corresponds to the greater spread of kinetic energies. When a substance melts or vaporizes, it experiences a significant increase in entropy.

Two graphs are shown. The y-axis of the left graph is labeled, “Fraction of molecules,” while the x-axis is labeled, “Velocity, v (m / s),” and has values of 0 through 1,500 along the axis with increments of 500. Four lines are plotted on this graph. The first, labeled, “100 K,” peaks around 200 m / s while the second, labeled, “200 K,” peaks near 300 m / s and is slightly lower on the y-axis than the first. The third line, labeled, “500 K,” peaks around 550 m / s and is lower than the first two on the y-axis. The fourth line, labeled, “1000 K,” peaks around 750 m / s and is the lowest of the four on the y-axis. Each line get increasingly broad. The second graph has a y-axis labeled, “Entropy, S,” with an upward-facing arrow and an x-axis labeled, “Temperature (K),” and a right-facing arrow. The graph has three equally spaced columns in the background, labeled, “Solid,” “Liquid,” and, “Gas,” from left to right. A line extends slightly upward through the first column in a slight upward direction, then goes straight up in the transition between the first two columns. In then progresses in a slight upward direction through the second column, then goes up dramatically between the second and third columns, then continues in a slight upward direction once more. The first vertical region of this line is labeled, “Melting,” and the second is labeled, “Boiling.”

The entropy of a substance is influenced by structure of the particles (atoms or molecules) that comprise the substance. With regard to atomic substances, heavier atoms possess greater entropy at a given temperature than lighter atoms, which is a consequence of the relation between a particle’s mass and the spacing of quantized translational energy levels (which is a topic beyond the scope of our treatment). For molecules, greater numbers of atoms (regardless of their masses) increase the ways in which the molecules can vibrate and thus the number of possible microstates and the system entropy.

Finally, variations in the types of particles affects the entropy of a system. Compared to a pure substance, in which all particles are identical, the entropy of a mixture of two or more different particle types is greater. This is because of the additional orientations and interactions that are possible in a system comprised of nonidentical components. For example, when a solid dissolves in a liquid, the particles of the solid experience both a greater freedom of motion and additional interactions with the solvent particles. This corresponds to a more uniform dispersal of matter and energy and a greater number of microstates. The process of dissolution therefore involves an increase in entropy, $\Delta S > 0$.

Considering the various factors that affect entropy allows us to make informed predictions of the sign of ΔS for various chemical and physical processes as illustrated in Example .

Example 5.2.3.2: Predicting the Sign of ΔS

Predict the sign of the entropy change for the following processes. Indicate the reason for each of your predictions.

a. One mole liquid water at room temperature $\longrightarrow$ one mole liquid water at 50 °C
b. $\mathrm{Ag^+}(aq) + \mathrm{Cl^-}(aq) \longrightarrow \mathrm{AgCl}(s)$
c. $\mathrm{C_6H_6}(l) + \frac{15}{2}\mathrm{O_2}(g) \longrightarrow 6\,\mathrm{CO_2}(g) + 3\,\mathrm{H_2O}(l)$
d. $\mathrm{NH_3}(s) \longrightarrow \mathrm{NH_3}(l)$

Solution

a. positive, temperature increases
b. negative, reduction in the number of ions (particles) in solution, decreased dispersal of matter
c. negative, net decrease in the amount of gaseous species
d. positive, phase transition from solid to liquid, net increase in dispersal of matter

Exercise 5.2.3.2

Predict the sign of the enthalpy change for the following processes. Give a reason for your prediction.

a. $\mathrm{NaNO_3}(s) \longrightarrow \mathrm{Na^+}(aq) + \mathrm{NO_3^-}(aq)$
b. the freezing of liquid water
c. $\mathrm{CO_2}(s) \longrightarrow \mathrm{CO_2}(g)$
d. $\mathrm{CaCO}(s) \longrightarrow \mathrm{CaO}(s) + \mathrm{CO_2}(g)$

Answer a available at the end of this section.

Summary

Entropy (\(S\)) is a state function that can be related to the number of microstates for a system (the number of ways the system can be arranged) and to the ratio of reversible heat to kelvin temperature. It may be interpreted as a measure of the dispersal or distribution of matter and/or energy in a system, and it is often described as representing the “disorder” of the system. For a given substance, $S_{solid} < S_{liquid} \ll S_{gas}$ in a given physical state at a given temperature, entropy is typically greater for heavier atoms or more complex molecules. Entropy increases when a system is heated and when solutions form. Using these guidelines, the sign of entropy changes for some chemical reactions may be reliably predicted.

Key Equations

- $\Delta S = \frac{q_{\mathrm{rev}}}{T}$
- $S = k \ln W$
- $\Delta S = k \ln \frac{W_{\mathrm{f}}}{W_{\mathrm{i}}}$

Glossary

entropy (S)
state function that is a measure of the matter and/or energy dispersal within a system, determined by the number of system microstates often described as a measure of the disorder of the system

microstate (*W*)
possible configuration or arrangement of matter and energy within a system

reversible process
process that takes place so slowly as to be capable of reversing direction in response to an infinitesimally small change in conditions; hypothetical construct that can only be approximated by real processes removed

Answers

Exercise 5.2.3.1

0 J/K

Exercise 5.2.3.2

Positive; The solid dissolves to give an increase of mobile ions in solution.
Negative; The liquid becomes a more ordered solid.
Positive; The relatively ordered solid becomes a gas
Positive; There is a net production of one mole of gas.

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5.2.4: Gibbs Energy

Learning Objectives

- Define Gibbs free energy, and describe its relation to spontaneity
- Calculate the standard free energy change for a process using standard free energies of formation for its reactants and products
- Calculate standard free energy change for a process using senthalpies of formation and the entropies for its reactants and products
- Explain how temperature affects the spontaneity of some processes
- Relate standard free energy changes to equilibrium constants

One of the challenges of using the second law of thermodynamics to determine if a chemical reaction is spontaneous is that we must determine the entropy change for the system *and* the entropy change for the surroundings. A second challenge when working with a chemical reaction is that we need to take into account the mixing of the substances, an issue that does not occur when observing the phase change if a pure substance. An alternative approach involving a new thermodynamic property defined in terms of system properties only was introduced in the late nineteenth century by American mathematician Josiah Willard Gibbs. This new property is called the Gibbs free energy (G) (or simply the *free energy*), and it is defined in terms of a system's enthalpy and entropy as the following:

$$G = H - TS$$

Free energy is a state function, and at constant temperature and pressure, the standard free energy change (ΔG°) may be expressed as the following:

$$\Delta G^{\circ}_{\text{sys}} = \Delta H^{\circ}_{\text{sys}} - T\Delta S^{\circ}_{\text{sys}}$$

(For simplicity's sake, the subscript "sys" will be omitted henceforth.) We can understand the relationship between this system property and the spontaneity of a process by recalling the previously derived second law expression:

$$\Delta S_{\text{univ}} = \Delta S + \frac{q_{\text{surr}}}{T}$$

The first law requires that $q_{surr} = -q_{sys}$, and at constant pressure $q_{sys} = \Delta H$, and so this expression may be rewritten as the following:

$$\Delta S_{\text{univ}} = \Delta S - \frac{\Delta H}{T}$$

ΔH is the enthalpy change of the system. Multiplying both sides of this equation by –T, and rearranging yields the following:

$$-T\Delta S_{\text{univ}} = \Delta H - T\Delta S$$

Comparing this equation to the previous one for free energy change shows the following relation:

$$\Delta G = -T\Delta S_{\text{univ}} \tag{5.2.4.1}$$

The free energy change is therefore a reliable indicator of the spontaneity of a process, being directly related to the previously identified spontaneity indicator, ΔS_{univ}. Table 5.2.4.1 summarizes the relation between the spontaneity of a process and the arithmetic signs of these indicators.

Table 5.2.4.1: Relation between Process Spontaneity and Signs of Thermodynamic Properties

$\Delta S_{univ} > 0$	ΔG < 0	moves spontaneously in the forward direction, as written, to reach equilibrium

$\Delta S_{univ} < 0$	ΔG > 0	nonspontaneous in the forward direction, as written, but moves spontaneously in the reverse direction, as written, to reach equilibrium
$\Delta S_{univ} = 0$	ΔG = 0	reversible (at equilibrium)

Calculating Free Energy Change

Free energy is a state function, so its value depends only on the conditions of the initial and final states of the system that have undergone some change. A convenient and common approach to the calculation of free energy changes for physical changes and chemical reactions is by use of widely available compilations of standard state thermodynamic data. One method involves the use of standard enthalpies and entropies to compute standard free energy changes according to the following relation as demonstrated in Example 5.2.4.1.

$$\Delta G°= \Delta H°-T\Delta S° \tag{5.2.4.2}$$

It is important to understand that for phase changes, ΔG^{o} tells you if the phase change is spontaneous or not; will it happen, or not happen. For chemical reactions, ΔG^{o} tells you the **extent** of a reaction. In other words, ΔG^{o} for a reaction tells you how much product will be present at equilibrium. A reaction with ΔG^{o} < 0 is considered **product-favored at equilibrium**; there will be more products than reactants when the reaction reaches equilibrium. A reaction with ΔG^{o} > 0 is considered **reactant-favored at equilibrium**; there will be more reactants than products when the reaction reaches equilibrium.

Example 5.2.4.1: Evaluation of ΔG° for a Phase Change of a Pure Substance

Use standard enthalpy and entropy data from Tables T1 or T2 to calculate the standard free energy change for the vaporization of water at room temperature (298 K). What does the computed value for ΔG° say about the spontaneity of this physical change for a pure substance?

Solution

The process of interest is the following:

$$\mathrm{H_2O}(l) \longrightarrow \mathrm{H_2O}(g) \tag{5.2.4.3}$$

The standard change in free energy may be calculated using the following equation:

$$\Delta G^{\circ}_{298} = \Delta H°-T\Delta S° \tag{5.2.4.4}$$

From Tables T1 or T2, here are the data:

Data from Tables T1 or T2

Substance	$\Delta H^{\circ}_{f}(k\,\mathrm{J/mol})$	$S^{\circ}_{298}(\mathrm{J/K{\cdot}mol})$
$H_2O(l)$	–286.83	70.0
$H_2O(g)$	–241.82	188.8

Combining at 298 K:

$$\begin{aligned}\Delta H^\circ = \Delta H^\circ_{298} &= \Delta H^\circ_f(\mathrm{H_2O}(g)) - \Delta H^\circ_f(\mathrm{H_2O}(l)) \\ &= [-241.82\ kJ - (-285.83)]\ kJ/mol \\ &= 44.01\ kJ/mol \\ \Delta S^\circ = \Delta S^\circ_{298} &= S^\circ_{298}(\mathrm{H_2O}(g)) - S^\circ_{298}(\mathrm{H_2O}(l)) \\ &= 188.8\ J/mol \cdot K - 70.0\ J/K \\ &= 118.8\ J/mol \cdot K\end{aligned}$$

then use Equation 5.2.4.2:

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

Converting everything into kJ and combining at 298 K:

$$\begin{aligned}\Delta G^\circ_{298} &= \Delta H^\circ - T\Delta S^\circ \\ &= 44.01\ kJ/mol - (298\ K \times 118.8\ J/mol \cdot K) \times \frac{1\ kJ}{1000\ J}\end{aligned}$$

$$44.01\ \mathrm{kJ/mol} - 35.4\ \mathrm{kJ/mol} = 8.6\ \mathrm{kJ/mol}$$

At 298 K (25 °C) $\Delta G^\circ_{298} > 0$, and so boiling is nonspontaneous (not spontaneous) at 298 K.

Exercise 5.2.4.1: Evaluation of ΔG° for a Chemical Reaction

Use standard enthalpy and entropy data from Tables T1 or T2 to calculate the standard free energy change for the reaction shown here (298 K). What does the computed value for ΔG° say about the extent of this reaction at 298 K?

$$\mathrm{C_2H_6}(g) \longrightarrow \mathrm{H_2}(g) + \mathrm{C_2H_4}(g)$$

Answer available at the end of this section.

Free energy changes may also use the standard free energy of formation (ΔG°_f), for each of the reactants and products involved in the reaction. The standard free energy of formation is the free energy change that accompanies the formation of one mole of a substance from its elements in their standard states. Similar to the standard enthalpies of formation, (ΔG°_f) is by definition zero for elemental substances under standard state conditions. The approach to computing the free energy change for a reaction using this approach is the same as that demonstrated previously for enthalpy and entropy changes. For the reaction

$$m\mathrm{A} + n\mathrm{B} \longrightarrow x\mathrm{C} + y\mathrm{D},$$

the standard free energy change at room temperature may be calculated as

$$\Delta G^\circ_{298} = \Delta G^\circ \tag{5.2.4.5}$$

$$= \sum \nu \Delta G^\circ_{298}(\text{products}) - \sum \nu \Delta G^\circ_{298}(\text{reactants}) \tag{5.2.4.6}$$

$$= [x\Delta G^\circ_f(\mathrm{C}) + y\Delta G^\circ_f(\mathrm{D})] - [m\Delta G^\circ_f(\mathrm{A}) + n\Delta G^\circ_f(\mathrm{B})]. \tag{5.2.4.7}$$

Example 5.2.4.2: Calculation of ΔG°_{298}

Consider the decomposition of yellow mercury(II) oxide.

$$\mathrm{HgO}(s,\ \text{yellow}) \longrightarrow \mathrm{Hg}(l) + \tfrac{1}{2}\,\mathrm{O_2}\,(\mathrm{g})$$

Calculate the standard free energy change at room temperature, ΔG°_{298}, using:

a. standard free energies of formation and
b. standard enthalpies of formation and standard entropies.

Do the results indicate the reaction to be product-favored or reactant-favored at equilibrium?

Solution

The required data are available in Tables T1 or T2 and are shown here.

Required data for Tables T1 or T2

Compound	ΔG_f° (kJ/mol)	ΔH_f° (kJ/mol)	S_{298}° (J/K·mol)
HgO (s, yellow)	−58.43	−90.46	71.13
Hg(*l*)	0	0	75.9
O_2(*g*)	0	0	205.2

(a) Using free energies of formation:

$$\begin{aligned}\Delta G_{298}^\circ &= \sum \nu G S_{298}^\circ(\text{products}) - \sum \nu \Delta G_{298}^\circ(\text{reactants}) \\ &= \left[1\Delta G_{298}^\circ \text{Hg}(l) + \frac{1}{2}\Delta G_{298}^\circ \text{O}_2(g)\right] - 1\Delta G_{298}^\circ \text{HgO}(s,\text{ yellow}) \\ &= \left[1\text{ mol}(0\text{ kJ/mol}) + \frac{1}{2}\text{mol}(0\text{ kJ/mol})\right] - 1\text{ mol}(-58.43\text{ kJ/mol}) = 58.43\text{ kJ/mol}\end{aligned}$$

(b) Using enthalpies and entropies of formation:

$$\begin{aligned}\Delta H_{298}^\circ &= \sum \nu \Delta H_{298}^\circ(\text{products}) - \sum \nu \Delta H_{298}^\circ(\text{reactants}) \\ &= \left[1\Delta H_{298}^\circ \text{Hg}(l) + \frac{1}{2}\Delta H_{298}^\circ \text{O}_2(g)\right] - 1\Delta H_{298}^\circ \text{HgO}(s,\text{ yellow}) \\ &= [1\text{ mol}(0\text{ kJ/mol}) + \frac{1}{2}\text{mol}(0\text{ kJ/mol})] - 1\text{ mol}(-90.46\text{ kJ/mol}) = 90.46\text{ kJ/mol} \\ \Delta S_{298}^\circ &= \sum \nu \Delta S_{298}^\circ(\text{products}) - \sum \nu \Delta S_{298}^\circ(\text{reactants}) \\ &= \left[1\Delta S_{298}^\circ \text{Hg}(l) + \frac{1}{2}\Delta S_{298}^\circ \text{O}_2(g)\right] - 1\Delta S_{298}^\circ \text{HgO}(s,\text{ yellow}) \\ &= \left[1\text{ mol}(75.9\text{ J/mol K}) + \frac{1}{2}\text{mol}(205.2\text{ J/mol K})\right] - 1\text{ mol}(71.13\text{ J/mol K}) = 107.4\text{ J/mol K}\end{aligned}$$

then we can use Equation \ref7} directly:

$$\begin{aligned}\Delta G° &= \Delta H° - T\Delta S° \\ &= 90.46\text{ kJ} - 298.15\text{ K} \times 107.4\text{ J/K} \cdot \text{mol} \times \frac{1\text{ kJ}}{1000\text{ J}} \\ &= (90.46 - 32.01)\text{ kJ/mol} = 58.45\text{ kJ/mol}\end{aligned}$$

Both ways to calculate the standard free energy change at 25 °C give the same numerical value (to three significant figures), and both predict that the process is reactant-favored at equilibrium at room temperature.

Exercise 5.2.4.2

Calculate ΔG° using (a) free energies of formation and (b) enthalpies of formation and entropies (Tables T1 or T2). Do the results indicate the reaction to be product-favored or reactant-favored at equilibrium at 25 °C?

$$\text{C}_2\text{H}_4(g) \longrightarrow \text{H}_2(g) + \text{C}_2\text{H}_2(g)$$

Answer available at the end of this section.

Temperature Dependence of Spontaneity and Extent of Reaction

As was previously demonstrated in this chapter's section on entropy, the spontaneity of a process may depend upon the temperature of the system. Phase transitions, for example, will proceed spontaneously in one direction or the other depending upon the temperature of the substance in question. In a similar, but not identical fashion, some chemical reactions can switch from being product-favored at equilibrium, to being reactant-favored at equilibrium, depending on the temperature.

Note

The numerical value of ΔG^{o} is always dependent on the temperature. In this section we are determining whether or not the **sign** of ΔG^{o} is dependent on the temperature.

To illustrate this concept, the equation relating free energy change to the enthalpy and entropy changes for the process is considered:

$$\Delta G^{o} = \Delta H^{o} - T\Delta S^{o}$$

The extent of a process, as reflected in the arithmetic sign of its standard free energy change, is then determined by the signs of the enthalpy and entropy changes and, in some cases, the absolute temperature. Since T is the absolute (Kelvin) temperature, it can only have positive values. Four possibilities therefore exist with regard to the signs of the enthalpy and entropy changes:

1. **Both Δ*H*° and Δ*S*° are positive.** This condition describes an endothermic process that involves an increase in system entropy. In this case, Δ*G*° will be negative if the magnitude of the *T*Δ*S*° term is greater than Δ*H*°. If the *T*Δ*S*° term is less than Δ*H*°, the free energy change will be positive. Such a process is *product-favored at equilibrium at high temperatures and reactant-favored at equilibrium at low temperatures*.
2. **Both Δ*H*° and Δ*S*° are negative.** This condition describes an exothermic process that involves a decrease in system entropy. In this case, Δ*G*° will be negative if the magnitude of the *T*Δ*S*° term is less than Δ*H*°. If the *T*Δ*S*° term's magnitude is greater than Δ*H*°, the free energy change will be positive. Such a process is *product-favored at equilibrium at low temperatures* and *reactant-favored at equilibrium at high temperatures*.
3. **Δ*H*° is positive and Δ*S*° is negative.** This condition describes an endothermic process that involves a decrease in system entropy. In this case, Δ*G*° will be positive regardless of the temperature. Such a process is *reactant-favored at equilibrium at all temperatures*.
4. **Δ*H*° is negative and Δ*S*° is positive.** This condition describes an exothermic process that involves an increase in system entropy. In this case, Δ*G*° will be negative regardless of the temperature. Such a process is *product-favored at equilibrium at all temperatures*.

These four scenarios are summarized in Table 5.2.4.1

Table 5.2.4.1

Sign of ΔH^{o}	Sign of ΔS^{o}	Sign of ΔG^{o}	Temperature Dependence of ΔG^{o}
-	+	-	The sign of ΔG^{o} does not depend on the temperature.The reaction is product-favored at equilibrium at all temperatures.
+	-	+	The sign of ΔG^{o} does not depend on the temperature.The reaction is reactant-favored at equilibrium at all temperatures.
-	-	- or +	The sign of ΔG^{o} **does** depend on the temperature. The reaction will be product-favored at equilibrium at lower temperatures.
+	+	- or +	The sign of ΔG^{o} **does** depend on the temperature. The reaction will be product-favored at equilibrium at lower temperatures.

Example 5.2.4.3: Predicting the Temperature Dependence of Spontaneity

The incomplete combustion of carbon is described by the following equation:

$$2\,\mathrm{C}(s)+\mathrm{O}_2(g) \longrightarrow 2\,\mathrm{CO}(g)$$

Does the sign of ΔG° of this process depend upon temperature?

Solution

Combustion processes are exothermic ($\Delta H^{\circ} < 0$). This particular reaction involves an increase in entropy due to the accompanying increase in the amount of gaseous species (net gain of one mole of gas, $\Delta S^{\circ} > 0$). The reaction is therefore product-favored at equilibrium ($\Delta G^{\circ} < 0$) at all temperatures.

Exercise 5.2.4.3

Popular chemical hand warmers generate heat by the air-oxidation of iron:

$$4\,\mathrm{Fe}(s)+3\,\mathrm{O}_2(g) \longrightarrow 2\,\mathrm{Fe}_2\mathrm{O}_3(s)$$

Does the sign of ΔG^{o} of this process depend upon temperature?

Answer available at the end of this section.

When considering the conclusions drawn regarding the temperature dependence of the sign of $\Delta G°$, it is important to keep in mind what the terms “high” and “low” mean. Since these terms are adjectives, the temperatures in question are deemed high or low relative to some reference temperature. A process that is reactant-favored at equilibrium at one temperature but product-favored at equilibrium at another temperature will necessarily undergo a change in “extent” (as reflected by its $\Delta G°$) as temperature varies. This is clearly illustrated by a graphical presentation of the free energy change equation, in which $\Delta G°$ is plotted on the *y* axis versus *T* on the *x* axis:

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$$

$$y = b + mx$$

Such a plot is shown in Figure 5.2.4.2. A process whose enthalpy and entropy changes are of the same arithmetic sign will exhibit a temperature-dependence for the sign of $\Delta G°$ as depicted by the two yellow lines in the plot. Each line crosses from one spontaneity domain (positive or negative $\Delta G°$) to the other at a temperature that is characteristic of the process in question. This temperature is represented by the *x*-intercept of the line, that is, the value of *T* for which $\Delta G°$ is zero:

$$\Delta G^{\circ} = 0 = \Delta H^{\circ} - T\Delta S^{\circ}$$

$$T = \frac{\Delta H^{\circ}}{\Delta S^{\circ}}$$

Thus, saying a process is product-favored at equilibrium at “high” or “low” temperatures means the temperature is above or below, respectively, that temperature at which $\Delta G°$ for the process is zero.

Note

In this discussion, we have used two different descriptions for the meaning of the sign of $\Delta G°$. You should be aware of the meaning of each description.

a) **Extent of Reaction:** This description is used to predict the ratio of the product and reactant concentrations at equilibrium. In this description, we use the thermodynamic term $\Delta G°$ to tell us the same information as the equilibrium constant, K. When $\Delta G° < 0$, $K > 1$, and the reaction will be product-favored at equilibrium. When $\Delta G° > 0$, $K < 1$, and the reaction is

reactant-favored at equilibrium. When $\Delta G^\circ = 0$, K =1, and the reaction will have roughly equal amounts of products and reactants at equilibrium. In all cases, the reaction will form a mixture of products and reactants at equilibrium. We use the sign and magnitude of ΔG° to tell us how much product will be made if the reaction is allowed to reach equilibrium.

b) **Spontaneity:** This description is much more complicated because it involves two different interpretations of how a reaction at standard state occurs. One interpretation involves the hypothetical process in which the reaction proceeds from a starting point of pure reactants to a finishing point of pure products, with all substances isolated in their own containers under standard state conditions. In the second, more realistic interpretation, the reaction starts with all reactants and all products in their standard state in one container. We then allow this specific mixture to react an infinitesimally small amount so that we can obtain a rate of change in free energy with respect to the extent of reaction when all reactants and products are mixed and (essentially) in their standard states. Although each interpretation describes a different reaction scenario, the value of the difference in free energy and the value of the rate of change in free energy are the same number. If $\Delta G^\circ < 0$, we say that the reaction is spontaneous, meaning that the reaction would proceed in the forward direction, as written, to form pure products in their standard state. If $\Delta G^\circ > 0$, we say that the reaction is nonspontaneous, meaning that the reaction would proceed in the reverse direction, as written, to form pure reactants in their standard state. If $\Delta G^\circ = 0$, we say that the neither the reactants nor the products are favored to be formed.

A detailed treatment of the meaning of ΔG° can be found in the paper, "Free Energy versus Extent of Reaction" by Richard S. Treptow, Journal of Chemical Education, **1996**, Volume 73 (1), 51-54.

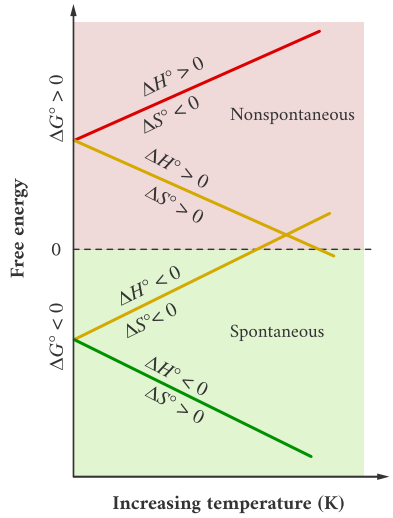


Figure 5.2.4.2: These plots show the variation in ΔG° with temperature for the four possible combinations of arithmetic sign for ΔH° and ΔS°. Note that in this graph of ΔG°, "spontaneous" is synonymous with "product-favored at equilibrium", and "nonspontaneous" is synonymous with "reactant-favored at equilibrium".

Example 5.2.4.4: Equilibrium Temperature for a Phase Transition

As defined in the chapter on liquids and solids, the boiling point of a liquid is the temperature at which its solid and liquid phases are in equilibrium (that is, when vaporization and condensation occur at equal rates). Use the information in Tables T1 or T2 to estimate the boiling point of water.

Solution

The process of interest is the following phase change:

$$\mathrm{H_2O}(l) \longrightarrow \mathrm{H_2O}(g)$$

When this process is at equilibrium, $\Delta G = 0$, so the following is true:

$$0 = \Delta H° - T\Delta S° \qquad \text{or} \qquad T = \frac{\Delta H°}{\Delta S°}$$

Using the standard thermodynamic data from Tables T1 or T2,

$$\begin{aligned}\Delta H° &= \Delta H_f^\circ(\mathrm{H_2O}(g)) - \Delta H_f^\circ(\mathrm{H_2O}(l)) \\ &= -241.82\ \mathrm{kJ/mol} - (-285.83\ \mathrm{kJ/mol}) = 44.01\ \mathrm{kJ/mol}\end{aligned}$$

$$\begin{aligned}\Delta S° &= \Delta S_{298}^\circ(\mathrm{H_2O}(g)) - \Delta S_{298}^\circ(\mathrm{H_2O}(l)) \\ &= 188.8\ \mathrm{J/K \cdot mol} - 70.0\ \mathrm{J/K \cdot mol} = 118.8\ \mathrm{J/K \cdot mol}\end{aligned}$$

$$T = \frac{\Delta H°}{\Delta S°} = \frac{44.01 \times 10^3\ \mathrm{J/mol}}{118.8\ \mathrm{J/K \cdot mol}} = 370.5\ \mathrm{K} = 97.3\ °\mathrm{C}$$

The accepted value for water's normal boiling point is 373.2 K (100.0 °C), and so this calculation is in reasonable agreement. Note that the values for enthalpy and entropy changes data used were derived from standard data at 298 K (Tables T1 or T2.). If desired, you could obtain more accurate results by using enthalpy and entropy changes determined at (or at least closer to) the actual boiling point.

Exercise 5.2.4.4

Use the information in Tables T1 or T2 to estimate the boiling point of CS_2.

Answer available at the end of this section.

Free Energy and Equilibrium

The free energy change for a process may be viewed as a measure of its driving force. A negative value for ΔG represents a finite driving force for the process in the forward direction, while a positive value represents a driving force for the process in the reverse direction. When ΔG is zero, the forward and reverse driving forces are equal, and so the process occurs in both directions at the same rate (the system is at equilibrium).

In the chapter on equilibrium the *reaction quotient*, Q, was introduced as a convenient measure of the status of an equilibrium system. Recall that Q is the numerical value of the mass action expression for the system, and that you may use its value to identify the direction in which a reaction will proceed in order to achieve equilibrium. When Q is lesser than the equilibrium constant, *K*, the reaction will proceed in the forward direction until equilibrium is reached and $Q = K$. Conversely, if $Q > K$, the process will proceed in the reverse direction until equilibrium is achieved.

The free energy change for a process taking place with reactants and products present under nonstandard conditions, ΔG, is related to the standard free energy change, $\Delta G°$, according to this equation:

$$\Delta G = \Delta G° + RT \ln Q \tag{5.2.4.8}$$

R is the gas constant (8.314 J/K mol), *T* is the kelvin or absolute temperature, and Q is the reaction quotient. We may use this equation to predict the spontaneity for a process under any given set of conditions as illustrated in Example 5.2.4.1.

Example 5.2.4.5: Calculating ΔG under Nonstandard Conditions

What is the free energy change for the process shown here under the specified conditions?

T = 25 °C, $P_{N_2} = 0.870\ \mathrm{atm}$, $P_{H_2} = 0.250\ \mathrm{atm}$, and $P_{NH_3} = 12.9\ \mathrm{atm}$

$$2\,\mathrm{NH_3}(g) \longrightarrow 3\,\mathrm{H_2}(g) + \mathrm{N_2}(g) \qquad \Delta G° = 33.0\ \mathrm{kJ/mol}$$

Solution

Equation 5.2.4.8 relates free energy change to standard free energy change and reaction quotient and may be used directly:

$$\begin{aligned}\Delta G &= \Delta G^\circ + RT\ln Q \\ &= 33.0\ \frac{\text{kJ}}{\text{mol}} + \left(8.314\ \frac{\text{J}}{\text{mol K}} \times 298\ \text{K} \times \ln\frac{(0.250^3)\times 0.870}{12.9^2}\right) \\ &= 9680\ \frac{\text{J}}{\text{mol}}\ \text{or}\ 9.68\ \text{kJ/mol}\end{aligned}$$

Since the computed value for ΔG is positive, the reaction is nonspontaneous under these conditions. The reaction will proceed in the reverse direction to reach equilibrium.

Exercise 5.2.4.5

Calculate the free energy change for this same reaction at 875 °C in a 5.00 L mixture containing 0.100 mol of each gas. Is the reaction spontaneous under these conditions?

Answer available at the end of this section.

For a system at equilibrium, $Q = K$ and $\Delta G = 0$, and the Equation 5.2.4.8 may be written as

$$\underbrace{0 = \Delta G^\circ + RT\ln K}_{\text{at equilibrium}}$$

$$\Delta G^\circ = -RT\ln K \tag{5.2.4.9}$$

or alternatively

$$K = e^{-\frac{\Delta G^\circ}{RT}} \tag{5.2.4.10}$$

This form of the equation provides a useful link between these two essential thermodynamic properties, and it can be used to derive equilibrium constants from standard free energy changes and vice versa. The relations between standard free energy changes and equilibrium constants are summarized in Table 5.2.4.1.

Table 5.2.4.1: Relations between Standard Free Energy Changes and Equilibrium Constants

K	ΔG°	Comments
< 1	> 0	Reactants are more abundant at equilibrium.
= 1	= 0	Reactants and products are equally abundant at equilibrium.
> 1	< 0	Products are more abundant at equilibrium.

Example 5.2.4.6: Equilibrium Constant using Standard Free Energy Change

Given that the standard free energies of formation of $Ag^+(aq)$, $Cl^-(aq)$, and AgCl(s) are 77.1 kJ/mol, –131.2 kJ/mol, and –109.8 kJ/mol, respectively, calculate the solubility product, K_{sp}, for AgCl.

Solution

The reaction of interest is the following:

$$\text{AgCl}(s) \rightleftharpoons \text{Ag}^+(aq) + \text{Cl}^-(aq) \quad K_{\text{sp}} = [\text{Ag}^+][\text{Cl}^-]$$

The standard free energy change for this reaction is first computed using standard free energies of formation for its reactants and products:

$$\begin{aligned}\Delta G^\circ = \Delta G^\circ_{298} &= [\Delta G^\circ_f(Ag^+(aq)) + \Delta G^\circ_f(Cl^-(aq))] - [\Delta G^\circ_f(AgCl(s))] \\ &= [77.1\ kJ/mol - 131.2\ kJ/mol] - [-109.8\ kJ/mol] \\ &= 55.7\ kJ/mol\end{aligned}$$

The equilibrium constant for the reaction may then be derived from its standard free energy change via Equation 5.2.4.10:

$$\begin{aligned}K_{sp} = e^{-\frac{\Delta G^\circ}{RT}} &= \exp\left(-\frac{\Delta G^\circ}{RT}\right) \\ &= \exp\left(-\frac{55.7 \times 10^3\ \text{J/mol}}{8.314\ \text{J/mol}\cdot\text{K} \times 298.15\ \text{K}}\right) \\ &= \exp(-22.470) = e^{-22.470} = 1.74 \times 10^{-10}\end{aligned}$$

Exercise 5.2.4.6: dissociation of dinitrogen tetroxide

Use the thermodynamic data provided in Tables T1 or T2 to calculate the equilibrium constant for the dissociation of dinitrogen tetroxide at 25 °C.

$$NO_{2(g)} \rightleftharpoons N_2O_{4(g)}$$

Answer available at the end of this section.

To further illustrate the relation between these two essential thermodynamic concepts, consider the observation that reactions spontaneously proceed in a direction that ultimately establishes equilibrium. As may be shown by plotting the free energy change versus the extent of the reaction (for example, as reflected in the value of *Q*), equilibrium is established when the system's free energy is minimized (Figure 5.2.4.3). If a system is present with reactants and products present in nonequilibrium amounts ($Q \neq K$), the reaction will proceed spontaneously in the direction necessary to establish equilibrium.

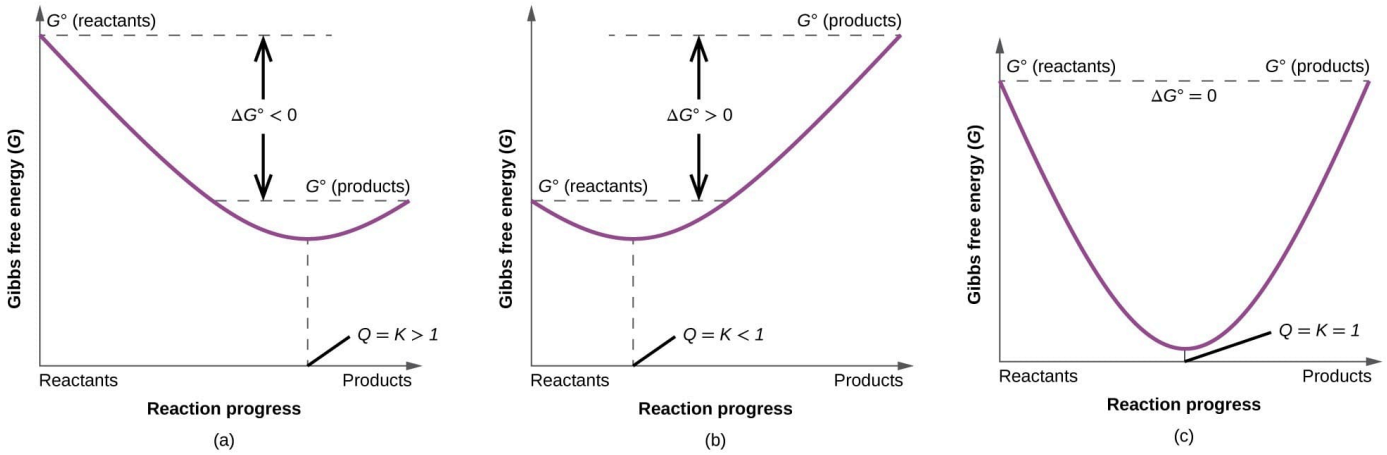


Figure 5.2.4.3: These plots show the free energy versus reaction progress for systems whose standard free changes are (a) negative, (b) positive, and (c) zero. Nonequilibrium systems will proceed spontaneously in whatever direction is necessary to minimize free energy and establish equilibrium. Note that reactions with K equal to exactly 1.000 are rare.

Summary

Gibbs free energy (*G*) is a state function defined with regard to system quantities only and may be used to predict the spontaneity of a process. A negative value for Δ*G* indicates that the process will proceed in the forward direction to reach equilibrium; a positive Δ*G* indicates that the process will proceed in the reverse direction to reach equilibrium ; and a Δ*G* of zero indicates that the system is at equilibrium. A negative value for Δ*G°* means that the reaction is product-favored at equilibrium. A positive value for Δ*G°* means that the reaction is reactant-favored at equilibrium. If Δ*G°* equals 0 (a rare occurrence), the reaction has roughly equal amounts of reactants and products at equilibrium.A number of approaches to the computation of free energy changes are

possible.

Key Equations

- $\Delta G = \Delta H - T\Delta S$
- $\Delta G = \Delta G° + RT \ln Q$
- $\Delta G° = -RT \ln K$

Glossary

Gibbs free energy change (*G*)
thermodynamic property defined in terms of system enthalpy and entropy; all spontaneous processes involve a decrease in *G*

standard free energy change (ΔG°)
change in free energy for a process occurring under standard conditions (1 bar pressure for gases, 1 M concentration for solutions)

standard free energy of formation (ΔG_f°)
change in free energy accompanying the formation of one mole of substance from its elements in their standard states

Answers

Exercise 5.2.4.1**: Evaluation of ΔG° for a Chemical Reaction**
$\Delta G_{298}^\circ = 102.0\ \text{kJ/mol}$; the reaction is reactant-favored at equilibrium at 25 °C. There will be more $C_2H_6(g)$ than $H_2(g)$ and $C_2H_4(g)$ at equilibrium

Exercise 5.2.4.2
141.5 kJ/mol, reactant-favored at equilibrium

Exercise 5.2.4.3
Δ*H*° and Δ*S*° are both negative; the reaction is product-favored at equilibrium at low temperatures.

Exercise 5.2.4.4
313 K (accepted value 319 K).

Exercise 5.2.4.5
Δ*G* = −47 kJ; yes, the reaction proceeds in the forward direction, as written, to reach equilibrium.

Exercise 5.2.4.6**: dissociation of dinitrogen tetroxide**
K = 6.9

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5.2: CHAPTER 6 - INORGANIC THERMODYNAMICS

5.2.1: Enthalpy

5.2.2: Spontaneity

5.2.3: Entropy

5.2.4: Gibbs Energy

5.2.5: Lattice Energy

5.2.6: The Born-Lande' equation

5.2.7: Lattice energies and solubility

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5.2.5: Lattice Energy

Discussion Questions

- How is lattice energy estimated using Born-Haber cycle?
- How is lattice energy related to crystal structure?

The Lattice energy, U, is the amount of energy required to separate a mole of the solid (s) into a gas (g) of its ions.

$$\mathrm{M}_a\ \mathrm{L}_b\,(\mathrm{s}) \ \rightarrow a\,\mathrm{M}^{b+}\,(\mathrm{g}) + b\,\mathrm{X}^{a-}\,(\mathrm{g}) \tag{5.2.5.1}$$

This quantity cannot be experimentally determined directly, but it can be estimated using a Hess Law approach in the form of *Born-Haber cycle*. It can also be calculated from the electrostatic consideration of its crystal structure. As defined in Equation 5.2.5.1, the lattice energy is positive, because energy is always required to separate the ions. For the reverse process of Equation 5.2.5.1:

$$a\,\mathrm{M}^{b+}\,(\mathrm{g}) + b\,\mathrm{X}^{a-}\,(\mathrm{g}) \ \rightarrow \mathrm{M}_a\mathrm{L}_b\,(\mathrm{s})$$

the energy released is called **energy of crystallization** (E_{cryst}). Therefore,

$$U_{lattice} = -E_{cryst}$$

Values of lattice energies for various solids have been given in literature, especially for some common solids. Some are given here.

Table 5.2.5.1: Comparison of Lattice Energies (U in 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

The following trends are obvious at a glance of the data in Table 5.2.5.1:

- 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.

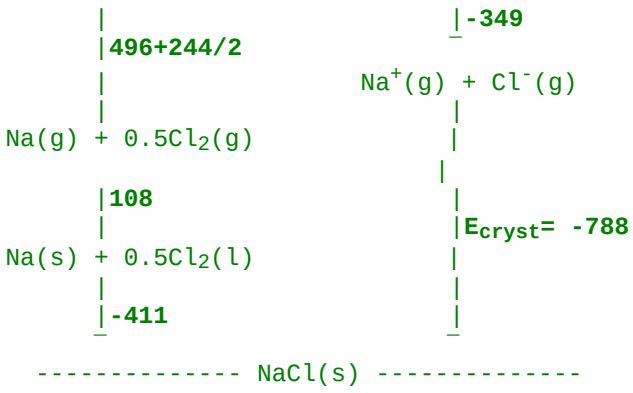
How is lattice energy estimated using Born-Haber cycle?

Estimating lattice energy using the Born-Haber cycle has been discussed in Ionic Solids. For a quick review, the following is an example that illustrate the estimate of the energy of crystallization of NaCl.

Hsub of Na = 108 kJ/mol (Heat of sublimation)
D of Cl2 = 244 (Bond dissociation energy)
IP of Na(g) = 496 (Ionization potential or energy)
EA of Cl(g) = -349 (Electron affinity of Cl)
Hf of NaCl = -411 (Enthalpy of formation)

The Born-Haber cycle to evaluate $E_{lattice}$ is shown below:

```
----------Na+ + Cl(g)--------
                            |
```



E_{cryst} = -411-(108+496+244/2)-(-349) kJ/mol
= -788 kJ/mol.

Discussion
The value calculated for *U* depends on the data used. Data from various sources differ slightly, and so is the result. The lattice energies for NaCl most often quoted in other texts is about 765 kJ/mol.

Compare with the method shown below

Na(s) + 0.5 Cl_2(l) ® NaCl(s)	- 411	H_f
Na(g) ® Na(s)	- 108	-H_{sub}
Na^+(g) + e ® Na(g)	- 496	-*IP*
Cl(g) ® 0.5 Cl_2(g)	- 0.5 * 244	-0.5*D
Cl^-(g) ® Cl(g) + 2 e	349	-*EA*
Add all the above equations leading to		
Na^+(g) + Cl^-(g) ® NaCl(s)	-788 kJ/mol = E_{cryst}	

Lattice Energy is Related to Crystal Structure

There are many other factors to be considered such as covalent character and electron-electron interactions in ionic solids. But for simplicity, let us consider the ionic solids as a collection of positive and negative ions. In this simple view, appropriate number of cations and anions come together to form a solid. The positive ions experience both attraction and repulson from ions of opposite charge and ions of the same charge.

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 6 Cl^- ions at a distance 1*r*, 12 Na^+ ions at a distance 2*r*, 8 Cl^- at 3*r*, 6 Na^+ at 4*r*, 24 Na^+ at 5*r*, and so on. Thus, the energy due to one ion is

$$E = \frac{Z^2 e^2}{4\pi\epsilon_o r} M \tag{5.2.5.2}$$

The Madelung constant, M, is a poorly converging series of interaction energies:

$$M = \frac{6}{1} - \frac{12}{2} + \frac{8}{3} - \frac{6}{4} + \frac{24}{5} \ldots \tag{5.2.5.3}$$

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).

The above discussion is valid only for the sodium chloride (also called rock salt) structure type. This is a geometrical factor, depending on the arrangement of ions in the solid. The Madelung constant depends on the structure type, and its values for several structural types are given in Table 6.13.1.

A is the number of anions coordinated to cation and *C* is the numbers of cations coordinated to anion.

Table 5.2.5.2: 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.				

Madelung constants for a few more types of crystal structures are available from the Handbook Menu. There are other factors to consider for the evaluation of energy of crystallization, and the treatment by *M. Born* led to the formula for the evaluation of crystallization energy E_{cryst}, for a mole of **crystalline solid**.

$$E_{cryst} = \frac{NZ^2e^2}{4\pi\epsilon_o r}\left(1 - \frac{1}{n}\right) \tag{5.2.5.4}$$

where *N* is the Avogadro's number (6.022x10^{-23}), and *n* is a number related to the electronic configurations of the ions involved. The *n* values and the electronic configurations (e.c.) of the corresponding inert gases are given below:

n =	5	7	9	10	12
e.c.	He	Ne	Ar	Kr	Xe

The following values of *n* have been suggested for some common solids:

n =	5.9	8.0	8.7	9.1	9.5
e.c.	LiF	LiCl	LiBr	NaCl	NaBr

Example 5.2.5.1

Estimate the energy of crystallization for NaCl.

Solution

Using the values giving in the discussion above, the estimation is given by Equation 5.2.5.4:

$$E_c ryst = \frac{(6.022 \times 10^{23}/mol(1.6022 \times 10^{-19})^2(1.747558)}{4\pi\,(8.854 \times 10^{-12}C^2/m)(282 \times 10^{-12}\ m} \left(1 - \frac{1}{9.1}\right)$$
$$= -766kJ/mol$$

Discussion

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-Haber cycle to evaluate other chemical properties, for example the electron affinity, which is really difficult to determine directly by experiment.

Exercise 5.2.5.1

Which one of the following has the largest lattice energy? LiF, NaF, CaF_2, AlF_3

Answer available at the end of this section.

Exercise 5.2.5.2

Which one of the following has the largest lattice energy? LiCl, NaCl, $CaCl_2$, Al_2O_3

Answer available at the end of this section.

Exercise 5.2.5.3

Lime, CaO, is know to have the same structure as NaCl and the edge length of the unit cell for CaO is 481 pm. Thus, Ca-O distance is 241 pm. Evaluate the energy of crystallization, E_{cryst} for CaO.

Answer available at the end of this section.

Exercise 5.2.5.4

Assume the interionic distance for $NaCl_2$ to be the same as those of NaCl (r = 282 pm), and assume the structure to be of the fluorite type (M = 2.512). Evaluate the energy of crystallization, E_{cryst} .

Answer available at the end of this section.

Contributors and Attributions

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Answers

Exercise 5.2.5.1

Skill: Explain the trend of lattice energy.

Exercise 5.2.5.2

Corrundum Al_2O_3 has some covalent character in the solid as well as the higher charge of the ions.

Exercise 5.2.5.3

Energy of crystallization is -3527 kJ/mol

Skill: Evaluate the lattice energy and know what values are needed.

Exercise 5.2.5.4

-515 kJ/mol

Discussion: This number has not been checked. If you get a different value, please let me know.

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5.2.6: The Born-Lande' equation

The Born-Landé equation is a concept originally formulated in 1918 by the scientists Born and Landé and is used to calculate the lattice energy (measure of the strength of bonds) of a compound. This expression takes into account both the Born interactions as well as the Coulomb attractions.

Introduction

Due to its high simplicity and ease, the Born-Landé equation is commonly used by chemists when solving for lattice energy. This equation proposed by Max Born and Alfred Landé states that lattice energy can be derived from ionic lattice based on electrostatic potential and the potential energy due to repulsion. 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:

$$\Delta U = -\frac{N_A M \left|Z^+\right| \left|Z^-\right| e^2}{4\pi\epsilon_o r} \tag{5.2.6.1}$$

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:

$$\Delta U = \frac{N_A B}{r^n} \tag{5.2.6.2}$$

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 to form:

$$\Delta U(0K) = \frac{N_A M \left|Z^+\right| \left|Z^-\right| e^2}{4\pi\epsilon_o r_o}\left(1 - \frac{1}{n}\right) \tag{5.2.6.3}$$

with

- r_0 is the closest ion distance

Calculate Lattice Energy

Lattice energy, based on the equation from above, is dependent on multiple factors. We see that the charge of ions is proportional to the increase in lattice energy. In addition, as ions come into closer contact, lattice energy also increases.

Example 5.2.6.1

Which compound has the greatest lattice energy?

- AlF_3
- NACl
- LiF
- $CaCl_2$

Solution

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.

Example 5.2.6.2

What is the lattice energy of NaCl? (Hint: you must look up the values for the constants for this compound)

Solution

-756 kJ/mol (again, this value is found in a table of constants)

Example 5.2.6.3

Calculate the lattice energy of NaCl.

Solution

$$Lattice\ Energy\ of\ NaCl = -\frac{\frac{6.022\,x\,10^{23}}{mole}\left(1.6022^{-19}\right)\times 1.747}{4\pi \times 8.85\,x\,10^{-12}\frac{c^2}{m}\times 282\,x\,10^{-12}m}\left(1-\frac{1}{9}\right) \approx -756\ \frac{kJ}{mol}$$

References

1. Johnson, D. A. *Metals and Chemical Change*. Cambridge: Royal Society of Chemistry, 2002.
2. Cotton, F. Albert, and F. Albert Cotton. *Advanced Inorganic Chemistry*. New York: Wiley, 1999.

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5.2.7: Lattice energies and solubility

9.10: Lattice energies and solubility

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6: CHEM 2101 TOPIC 6 - ACIDS, BASES, AND IONS IN AQUEOUS MEDIA

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6.1: ACIDS, BASES AND IONS IN AQUEOUS SOLUTION



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6.1.1: Introduction

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.

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

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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6.1.1A: Acid-Base Theories and Concepts

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.

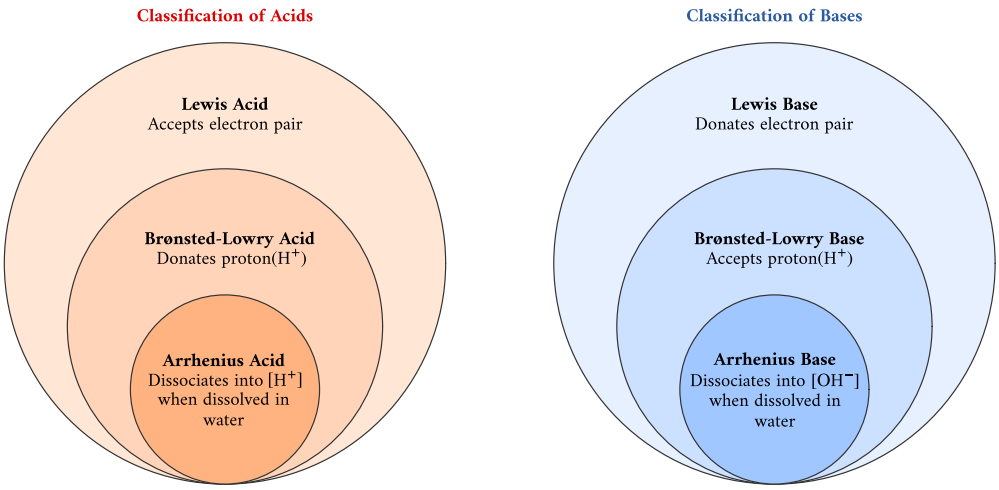


Figure 6.1.1A.1: Hierarchal definitions of acids and bases via the three primary theories. These theories are designed to be "superset" of the previous classification. (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

Arrhenius Definition of Acids and Bases

The Swedish chemist Svante Arrhenius attributed the properties of acidity to hydrogen ions ($\mathrm{H^+}$) in 1884. An Arrhenius acid is a substance that, when added to water, increases the concentration of $\mathrm{H^+}$ ions in the water. Note that chemists often write $\mathrm{H^+(aq)}$ 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, $\mathrm{H_3O^+}$. 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 ($\mathrm{OH^-}$) ions:

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

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

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

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 $\mathrm{H_2O}$, 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 $\mathrm{H^+}$, this should really be reserved for H (protium) not D (deuterium) or T (tritium). The more general term, hydron covers all isotopes of hydrogen.

An Arrhenius base, on the other hand, is a substance which increases the concentration of hydroxide ions when dissolved in water, hence decreasing the concentration of hydronium ions.

Upshot

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.

Conversely, 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:

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

With an acid, HA, the equation can be written symbolically as:

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

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

Brønsted-Lowry Definition of 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 ($\mathrm{CH_3COOH}$):

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

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

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

Upshot

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

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

- donate a proton.
- accept a proton.

Lewis Definition of 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.

Upshot

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

Other Acid-Base Definitions

Lux-Flood acid-base definition

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 acid-base definition

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.

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6.1.2: PROPERTIES OF WATER

Water covers 71% of the Earth's surface and is vital for all known forms of life. On Earth, 96.5% of the planet's water is found in seas and oceans, 1.7% in groundwater, 1.7% in glaciers and the ice caps of Antarctica and Greenland, a small fraction in other large water bodies, and 0.001% in the air as vapour, clouds (formed from solid and liquid water particles suspended in air), and precipitation.

Only 2.5% of the Earth's water is freshwater, and 98.8% of that water is in ice and groundwater. Less than 0.3% of all freshwater is in rivers, lakes, and the atmosphere, and an even smaller amount of the Earth's freshwater (0.003%) is contained within biological bodies and manufactured products.

The major chemical and physical properties of water are:

- Water is a liquid at standard temperature and pressure. It is tasteless and odourless. The intrinsic colour of water and ice is a very slight blue hue, although both appear colourless in small quantities. Water vapour is essentially invisible as a gas.
- Water is the only substance occurring naturally in all three phases as solid, liquid, and gas on the Earth's surface
- Water is transparent in the visible electromagnetic spectrum. Thus aquatic plants can live in water because sunlight can reach them. Infrared light is strongly absorbed by the hydrogen-oxygen or OH bonds.
- Since the water molecule is not linear and the oxygen atom has a higher electronegativity than hydrogen atoms, the oxygen atom carries a partial negative charge, whereas the hydrogen atoms have partial positive charges. As a result, water is a polar molecule with an electrical dipole moment.
- Water can form an unusually large number of intermolecular hydrogen bonds (four) for a molecule of its size. These factors lead to strong attractive forces between molecules of water, giving rise to water's high surface tension and capillary forces. The capillary action refers to the tendency of water to move up a narrow tube against the force of gravity. This property is relied upon by all vascular plants, such as trees.
- The boiling point of water (like all other liquids) is dependent on the barometric pressure. For example, on the top of Mount Everest water boils at 68 °C, compared to 100 °C at sea level at a similar latitude (since latitude modifies atmospheric pressure slightly). Conversely, water deep in the ocean near geothermal vents can reach temperatures of hundreds of degrees and remain liquid.
- Water has a high specific heat capacity, 4181.3 J kg^{-1} K^{-1}, as well as a high heat of vaporization (40.65 kJ mol^{-1}), both result from the extensive hydrogen bonding between its molecules. These two unusual properties allow water to moderate Earth's climate by buffering large fluctuations in temperature.
- Solid ice has a density of 917 kg m^{-3}. The maximum density of liquid water occurs at 3.98 °C where it is 1000 kg m^{-3}.
- Elements that are more electropositive than hydrogen such as lithium, sodium, calcium, potassium and caesium displace hydrogen from water, forming hydroxides. Since hydrogen is a flammable gas, when given off it is dangerous and the reaction of water with the more electropositive of these elements can be violently explosive so they are often stored in oil.

Most known pure substances display simple behaviour when they are cooled, they shrink. Liquids contract as they are cooled because the molecules move slower and they are less able to overcome the attractive intermolecular forces drawing them closer to each other. Once the freezing temperature is reached, the substances solidify, causing them to contract even more because crystalline solids are usually tightly packed.

Water however water has the anomalous property of becoming **less dense when it is cooled to its solid form, ice**.

When liquid water is cooled, it initially contracts as expected, until a temperature of 3.98 °C is reached (~4 °C). After that, it expands slightly until it reaches the freezing point, and then when it freezes, it expands by approximately 9%.

Just above the freezing point, the water molecules begin to locally arrange into ice-like structures with an extended hydrogen bonded network. This creates some "openness" in the liquid water, accounting for the decrease in its density. This is in opposition to the usual tendency for cooling to increase the density. At 3.98 °C these opposing tendencies cancel out, producing the density maximum.

Since water expands to occupy a 9% greater volume in the form of ice and is less dense, it floats on liquid water, as in icebergs. Fortunately this happens, since in colder climates where water is susceptible to freezing, if it all turned solid during the winter, it would kill all the life within it.

The extended structure of the water molecule in liquid and solid form seen in the models below provides the explanation for the variation of density with temperature.



- Topic hierarchy

6.1.2A: Structure and Hydrogen Bonding

6.1.2B: The Self Ionization of Water

6.1.2C: Water as a Brønstead Acid or Base

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6.1.2A: Structure and Hydrogen Bonding

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6.1.2B: The Self Ionization of Water

Solvated H^+ ions

The hydron (a completely free or "naked" hydrogen atomic nucleus) is far too reactive to exist in isolation and readily hydrates in aqueous solution. The simplest hydrated form of the hydrogen cation, the hydronium (hydroxonium) ion H_3O^+ (aq), is a key object of Arrhenius' definition of acid. Other "simple" hydrated forms include the Zundel cation $H_5O_2^+$ which is formed from a hydron and two water molecules, and the Eigen cation $H_9O_4^+$, formed from a hydronium ion and three water molecules. The hydron itself is crucial in the more general Brønsted-Lowry acid-base theory, which extends the concept of acid-base chemistry beyond aqueous solutions. Both of these complexes represent ideal structures in a more general hydrogen bonded network defect. A freezing-point depression study determined that the mean hydration ion in cold water is on average approximately $H_3O^+(H_2O)_6$: where each hydronium ion is solvated by 6 water molecules. Some hydration structures are quite large: the $H_3O^+.20H_2O$ magic ion number structure (called magic because of its increased stability with respect to hydration structures involving a comparable number of water molecules).

Structure from Lancaster site

In 1806 Theodor Grotthuss proposed a theory of water conductivity. He envisioned the electrolytic reaction as a sort of "bucket line" where each oxygen atom simultaneously passes and receives a single hydrogen atom. It was an astonishing theory to propose at the time, since the water molecule was thought to be OH not H_2O and the existence of ions was not fully understood. The theory became known as the Grotthuss mechanism. The transport mechanism is now thought to involve the inter-conversion between the Eigen and Zundel solvation structures, Eigen to Zundel to Eigen (E-Z-E).

Water

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6.1.2C: Water as a Brønstead Acid or Base

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6.1.3: DEFINITIONS AND UNITS IN AQUEOUS SOLUTION

- Topic hierarchy

6.1.3A: Molarity and Molality

6.1.3B: Standard State

6.1.3C: Activity

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6.1.4: Some Bronstead Acids and Bases

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6.1.5: The Energetics of Acid Dissociation in Aqueous Solution

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6.1.5B: H_2S, H_2Se, and H_2Te

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6.1.7: AQUATED CATIONS - FORMATION AND ACIDIC PROPERTIES

- Topic hierarchy

6.1.7A: Water as a Lewis Base

6.1.7B: Aquated Cations as Bronstead Acids

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6.1.8: Amphoteric Oxides and Hydroxides

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6.1.8A: Amphoteric Behavior

Oxides and Hydroxides

An early classification of substances arose from the differences observed in their solubility in acidic and basic solutions. This led to the classification of oxides and hydroxides as being either *acidic* or *basic*. Acidic oxides or hydroxides either reacted with water to produce an acidic solution or were soluble in aqueous base. Basic oxides and hydroxides either reacted with water to produce a basic solution or readily dissolved in aqueous acids. The diagram below shows there is strong correlation between the acidic or basic character of oxides (E_xO_y) and the position of the element, E, in the periodic table.

Oxides of metallic elements are generally basic oxides, and oxides of nonmetallic elements acidic oxides. Take for example, the reactions with water of calcium oxide, a metallic oxide, and carbon dioxide, a nonmetallic oxide:

$CaO(s) + H_2O(l) \rightarrow Ca(OH)_2$
$CO_2(g) + H_2O(l) \rightarrow H_2CO_3(aq)$ Calcium oxide reacts with water to produce a basic solution of calcium hydroxide, whereas carbon dioxide reacts with water to produce a solution of carbonic acid.
classification of oxides

There is a gradual transition from basic oxides to acidic oxides from the lower left to the upper right in the periodic table.

Basicity of the oxides increase with increasing atomic number down a group:
$BeO < MgO < CaO < SrO < BaO$ Note as well that acidity increases with increasing oxidation state of the element:
$MnO < Mn_2O_3 < MnO_2 < Mn_2O_7$
in keeping with the increase in covalency. Oxides of intermediate character, called *amphoteric oxides*, are located along the diagonal line between the two extremes. Amphoteric species are molecules or ions that can react as an acid as well as a base. The word has Greek origins, *amphoteroi* (άμφότεροι) meaning "both". Many metals (such as copper, zinc, tin, lead, aluminium, and beryllium) form amphoteric oxides or hydroxides. Amphoterism depends on the oxidation state of the oxide.

For example, zinc oxide (ZnO) reacts with both acids and with bases: In acid: $ZnO + 2H^+ \rightarrow Zn^{2+} + H_2O$
In base: $ZnO + 2OH^- + H_2O \rightarrow [Zn(OH)_4]^{2-}$

This reactivity can be used to separate different cations, such as zinc(II), which dissolves in base, from manganese(II), which does not dissolve in base.

Aluminium hydroxide is another amphoteric species:

As a base (neutralizing an acid): $Al(OH)_3 + 3HCl \rightarrow AlCl_3 + 3H_2O$
As an acid (neutralizing a base): $Al(OH)_3 + NaOH \rightarrow Na[Al(OH)_4]$

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6.1.9: Solubilities of Ionic Salts

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6.1.9B: Sparingly Soluble Salts and Solubility Products

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6.1.9C: The Energetics of the Dissolution of an Ionic Salt - $\Delta_{sol}G^{\circ}$

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6.1.9D: The Energetics of the Dissolution of an Ionic Salt - Hydration of Ions

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6.1.9E: Soubilities - Some Concluding Remarks

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6.1.10: Common-Ion Effect

Learning Objectives

- Recognize common ions from various salts, acids, and bases.
- Calculate concentrations involving common ions.
- Calculate ion concentrations involving chemical equilibrium.

The common ion effect is used to describe the effect on an equilibrium when one or more species in the reaction is shared with another reaction. This results in a shifting of the equilibrium properties.

Introduction

The solubility products K_{sp}'s are equilibrium constants in heterogeneous equilibria (i.e., between two different phases). If several salts are present in a system, they all ionize in the solution. If the salts contain a common cation or anion, these salts contribute to the concentration of the common ion. Contributions from all salts must be included in the calculation of concentration of the common ion. For example, a solution containing sodium chloride and potassium chloride will have the following relationship:

$$[\mathrm{Na^+}] + [\mathrm{K^+}] = [\mathrm{Cl^-}]$$

Consideration of *charge balance* or *mass balance* or both leads to the same conclusion.

Common Ions

When NaCl and KCl are dissolved in the same solution, the $\mathrm{Cl^-}$ ions are *common* to both salts. In a system containing NaCl and KCl, the $\mathrm{Cl^-}$ ions are common ions.

$$\mathrm{NaCl} \rightleftharpoons \mathrm{Na^+} + \mathrm{Cl^-}$$
$$\mathrm{KCl} \rightleftharpoons \mathrm{K^+} + \mathrm{Cl^-}$$
$$\mathrm{CaCl_2} \rightleftharpoons \mathrm{Ca^{2+}} + 2\,\mathrm{Cl^-}$$
$$\mathrm{AlCl_3} \rightleftharpoons \mathrm{Al^{3+}} + 3\,\mathrm{Cl^-}$$
$$\mathrm{AgCl} \rightleftharpoons \mathrm{Ag^+} + \mathrm{Cl^-}$$

For example, when AgCl is dissolved into a solution already containing NaCl (actually $\mathrm{Na^+}$ and $\mathrm{Cl^-}$ ions), the $\mathrm{Cl^-}$ ions come from the ionization of both AgCl and NaCl. Thus, $[\mathrm{Cl^-}]$ differs from $[\mathrm{Ag^+}]$. The following examples show how the concentration of the common ion is calculated.

Example 6.1.10.1

What are $[\mathrm{Na^+}]$, $[\mathrm{Cl^-}]$, $[\mathrm{Ca^{2+}}]$, and $[\mathrm{H^+}]$ in a solution containing 0.10 M each of NaCl, $\mathrm{CaCl_2}$, and HCl?

Solution

Due to the conservation of ions, we have

Extra close brace or missing open brace

but

$$\begin{aligned}[\mathrm{Cl^-}] &= 0.10\,(\text{due to } \mathrm{NaCl}) \\ &+ 0.20\,(\text{due to } \mathrm{CaCl_2}) \\ &+ 0.10\,(\text{due to } \mathrm{HCl}) \\ &= 0.40\,\mathrm{M}\end{aligned}$$

Exercise 6.1.10.1

John poured 10.0 mL of 0.10 M NaCl, 10.0 mL of 0.10 M KOH, and 5.0 mL of 0.20 M HCl solutions together and then he made the total volume to be 100.0 mL. What is $[\mathrm{Cl^-}]$ in the final solution?

Answer available at the end of this section.

Le Chatelier's Principle states that if an equilibrium becomes unbalanced, the reaction will shift to restore the balance. If a common ion is added to a weak acid or weak base equilibrium, then the equilibrium will shift towards the reactants, in this case the weak acid or base.

Example 6.1.10.2

Consider the lead(II) ion concentration in this *saturated* solution of $\mathrm{PbCl_2}$. The balanced reaction is

$$\mathrm{PbCl_2\,(s) \rightleftharpoons Pb^{2+}\,(aq) + 2\,Cl^-\,(aq)} \tag{6.1.10.1}$$

Defining s as the concentration of dissolved lead(II) chloride, then:

$$[\blacksquare] = s$$

$$[\mathrm{Cl^-}] = 2s$$

These values can be substituted into the solubility product expression, which can be solved for s:

$$\begin{aligned}K_{sp} &= [\blacksquare][\mathrm{Cl^-}^2] \\ &= s \times (2s)^2 \\ 1.7 \times 10^{-5} &= 4s^3 \\ s^3 &= \frac{1.7 \times 10^{-5}}{4} \\ &= 4.25 \times 10^{-6} \\ s &= \sqrt[3]{4.25 \times 10^{-6}} \\ &= 1.62 \times 10^{-2}\ mol\ dm^{-3}\end{aligned}$$

The concentration of lead(II) ions in the solution is 1.62 x 10^{-2} M. Consider what happens if sodium chloride is added to this saturated solution. Sodium chloride shares an ion with lead(II) chloride. The chloride ion is **common** to both of them; this is the origin of the term "common ion effect".

Look at the original equilibrium expression in Equation 6.1.10.1. What happens to that equilibrium if extra chloride ions are added? According to *Le* Chatelier, the position of equilibrium will shift to counter the change, in this case, by removing the chloride ions by making extra solid lead(II) chloride.

Of course, the concentration of lead(II) ions in the solution is so small that only a tiny proportion of the extra chloride ions can be converted into solid lead(II) chloride. The lead(II) chloride becomes even *less soluble*, and the concentration of lead(II) ions in the solution *decreases*. This type of response occurs with any sparingly soluble substance: it is less soluble in a solution which contains any ion which it has in common. This is the common ion effect.

A Simple Example

If an attempt is made to dissolve some lead(II) chloride in some 0.100 M sodium chloride solution instead of in water, what is the equilibrium concentration of the lead(II) ions this time? As before, define s to be the concentration of the lead(II) ions.

$$[\mathrm{Pb}^{2+}] = s$$

The calculations are different from before. This time the concentration of the chloride ions is governed by the concentration of the sodium chloride solution. The number of ions coming from the lead(II) chloride is going to be tiny compared with the 0.100 M coming from the sodium chloride solution.

In calculations like this, it can be assumed that the concentration of the common ion is entirely due to the other solution. This simplifies the calculation.

So we assume:

$$[\mathrm{Cl}^{-}\ ] = 0.100\ M$$

The rest of the mathematics looks like this:

$$\begin{aligned} K_{sp} &= [\blacksquare][\mathrm{Cl}^{-2}] \\ &= s \times (0.100)^2 \\ 1.7 \times 10^{-5} &= s \times 0.00100 \end{aligned}$$

therefore:

$$\begin{aligned} s &= \frac{1.7 \times 10^{-5}}{0.0100} \\ &= 1.7 \times 10^{-3}\ \mathrm{M} \end{aligned}$$

Finally, compare that value with the simple saturated solution:

Original solution:

$$[\mathrm{Pb}^{2+}] = 0.0162\ M$$

Solution in 0.100 M NaCl solution:

$$[\mathrm{Pb}^{2+}] = 0.0017\ M$$

The concentration of the lead(II) ions has decreased by a factor of about 10. If more concentrated solutions of sodium chloride are used, the solubility decreases further.

> Adding a common ion to a system at equilibrium affects the equilibrium composition, but **not** the ionization constant.

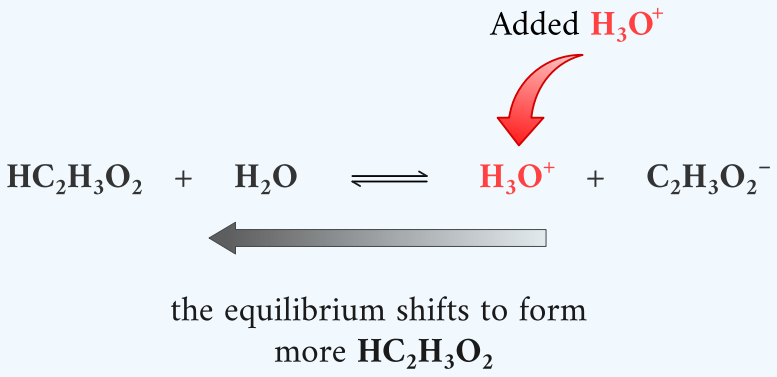
Common Ion Effect with Weak Acids and Bases

Adding a common ion prevents the weak acid or weak base from ionizing as much as it would without the added common ion. The common ion effect suppresses the ionization of a weak acid by adding more of an ion that is a product of this equilibrium.

Example 6.1.10.3A

The common ion effect of $\mathrm{H_3O^+}$ on the ionization of acetic acid

When a strong acid supplies the common ion H_3O^+
the equilibrium shifts to form more $HC_2H_3O_2$.



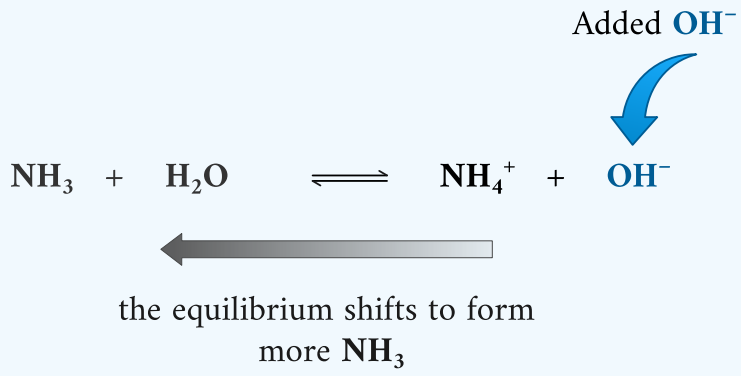
The common ion effect can be conceptualized as an applied Le Chatelier effect. Adding products will shift the equilibrium to more favor the reactants. (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

The common ion effect suppresses the ionization of a weak base by adding more of an ion that is a product of this equilibrium.

Example 6.1.10.3B

Consider the common ion effect of OH^- on the ionization of ammonia

When a strong base supplies the common ion OH^-
the equilibrium shifts to form more NH_3.



The common ion effect can be conceptualized as an applied Le Chatelier effect. Adding products will shift the equilibrium to more favor the reactants. (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

Adding the common ion of hydroxide shifts the reaction towards the left to decrease the stress (in accordance with Le Chatelier's Principle), forming more reactants. This decreases the reaction quotient, because the reaction is being pushed towards the left to reach equilibrium. The equilibrium constant, $K_b = 1.8 \times 10^{-5}$, does not change. The reaction is put out of balance, or equilibrium.

$$Q_a = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

At first, when more hydroxide is added, the quotient is greater than the equilibrium constant. The reaction then shifts right, causing the denominator to increase, decreasing the reaction quotient and pulling towards equilibrium and causing Q to decrease towards K.

Common Ion Effect on Solubility

Adding a common ion decreases solubility, as the reaction shifts toward the left to relieve the stress of the excess product. Adding a common ion to a dissociation reaction causes the equilibrium to shift left, toward the reactants, causing precipitation.

Example 6.1.10.4

Consider the reaction:

$$\mathrm{PbCl_2\,(s) \rightleftharpoons Pb^{2+}\,(aq) + 2\,Cl^-\,(aq)}$$

What happens to the solubility of $\mathrm{PbCl_2\,(s)}$ when 0.1 M NaCl is added?

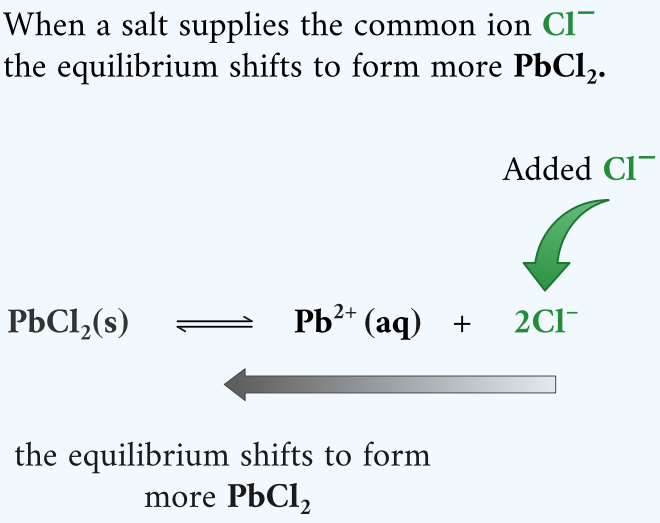
Solution

$$K_{sp} = 1.7 \times 10^{-5}$$

$$Q_{sp} = 1.8 \times 10^{-5}$$

Identify the common ion: $\mathrm{Cl^-}$

Notice: $Q_{sp} > K_{sp}$ The addition of NaCl has caused the reaction to shift out of equilibrium because there are more dissociated ions. Typically, solving for the molarities requires the assumption that the solubility of $\mathrm{PbCl_2\,(s)}$ is equivalent to the concentration of $\mathrm{Pb^{2+}}$ produced because they are in a 1:1 ratio.



The common ion effect can be conceptualized as an applied Le Chatelier effect. Adding products will shift the equilibrium to more favor the reactants. (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

Because K_{sp} for the reaction is 1.7×10^{-5}, the overall reaction would be

$$(s)(2s)^2 = 1.7 \times 10^{-5}.$$

Solving the equation for s gives $s = 1.62 \times 10^{-2}\ \mathrm{M}$. The coefficient on Cl^- is 2, so it is assumed that twice as much Cl^- is produced as Pb^{2+}, hence the '2s.' The solubility equilibrium constant can be used to solve for the molarities of the ions at equilibrium.

The molarity of Cl^- added would be 0.1 M because Na^+ and Cl^- are in a 1:1 ratio in the ionic salt, NaCl. Therefore, the overall molarity of Cl^- would be $2s + 0.1$, with $2s$ referring to the contribution of the chloride ion from the dissociation of lead chloride.

$$\begin{aligned} Q_{sp} &= [\blacksquare][\mathrm{Cl}^{-2}] \\ &= 1.8 \times 10^{-5} \\ &= (s)(2s + 0.1)^2 \\ s &= [Pb^{2+}] \\ &= 1.8 \times 10^{-3} M \\ 2s &= [\mathrm{Cl}^-] \\ &\approx 0.1 M \end{aligned}$$

Notice that the molarity of Pb^{2+} is lower when NaCl is added. The equilibrium constant remains the same because of the increased concentration of the chloride ion. To simplify the reaction, it can be assumed that $[\mathrm{Cl}^-]$ is approximately 0.1 M since the formation of the chloride ion from the dissociation of lead chloride is so small. The reaction quotient for $\mathrm{PbCl_2\,(s)}$ is greater than the equilibrium constant because of the added Cl^-. This therefore shift the reaction left towards equilibrium, causing precipitation and lowering the current solubility of the reaction. Overall, the solubility of the reaction decreases with the added sodium chloride.

References

1. 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.

Answers

Exercise 6.1.10.1

$$[\mathrm{Cl}^-] = \frac{0.1\ \mathrm{M} \times 10\ \mathrm{mL} + 0.2\ \mathrm{M} \times 5.0\ \mathrm{mL}}{100.0\ \mathrm{mL}} = 0.020\ \mathrm{M}$$

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6.1.11: COORDINATION COMPLEXES - AN INTRODUCTION



- Topic hierarchy

6.1.11A: Definitions and Terminology

6.1.11B: Investigating Coordination Complex Formation

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6.1.12: Stability Constants of Coordination Complexes

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6.1.13: Factors Affecting the Stabilities of Complexes Containing Only Monodentate Ligands

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6.1.13A: Ionic Size and Charge

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6.1.13B: Hard and Soft Metal Centers and Ligands

Hard and Soft Acids and Bases, Pearson's HSAB

This theory proposes that ***soft acids react faster and form stronger bonds with soft bases, whereas hard acids react faster and form stronger bonds with hard bases***, all other factors being equal. The classification in the original work was largely based on equilibrium constants for the reaction of two Lewis bases competing for a Lewis acid.

Hard acids and hard bases tend to have the following characteristics:

- small atomic/ionic radius
- high oxidation state
- low polarizability
- high electronegativity (bases)

Examples of **hard acids** are: H^+, light alkali ions (Li through K are considered to have small ionic radii), Ti^{4+}, Cr^{3+}, Cr^{6+}, BF_3. Examples of **hard bases** are: OH^-, F^-, Cl^-, NH_3, CH_3COO^-, CO_3^{2-}. The affinity of hard acids and hard bases for each other is mainly **ionic** in nature.

Soft acids and soft bases tend to have the following characteristics:

- large atomic/ionic radius
- low or zero oxidation state bonding
- high polarizability
- low electronegativity

Examples of **soft acids** are: CH_3Hg^+, Pt^{2+}, Pd^{2+}, Ag^+, Au^+, Hg^{2+}, Hg_2^{2+}, Cd^{2+}, BH_3. Examples of **soft bases** are: H^-, R_3P, SCN^-, I^-. The affinity of soft acids and bases for each other is mainly **covalent** in nature.

HSAB acids HSAB bases
HSAB acids and bases This provides a qualitative approach to looking at the reactions of metal ions with various ligands since, from the diagram above, it is expected that whereas Al(III) and Ti(III) would prefer to react with O-species over S-species, the reverse would be predicted for Hg(II).

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6.2: ACID-BASE AND DONOR-ACCEPTOR CHEMISTRY

6.2.1: Acid-Base Models as Organizing Concepts

6.2.2: Arrhenius Concept

6.2.3: Brønsted-Lowry Concept

6.2.3.1: Brønsted-Lowry Concept

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6.2.3.11: Non-nucleophilic Brønsted-Lowry Superbases

6.2.4: Lewis Concept and Frontier Orbitals

6.2.4.1: The frontier orbital approach considers Lewis acid-base reactions in terms of the donation of electrons from the base's highest occupied orbital into the acid's lowest unoccupied orbital.

6.2.4.2: All other things being equal, electron withdrawing groups tend to make Lewis acids stronger and bases weaker while electron donating groups tend to make Lewis bases stronger and acids weaker

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6.2.4.8: Frustrated Lewis pair chemistry uses Lewis acid and base sites within a molecule that are sterically restricted from forming an adduct with each other.

6.2.5: Intermolecular Forces

6.2.5.1: Host-Guest Chemistry and π-π Stacking Interactions

6.2.5.2: Hydrogen bonds may be considered as a special type of Lewis acid-base interaction in which a Lewis acid hydrogen ion is shared between Lewis bases

6.2.6: Hard and Soft Acids and Bases

6.2.6.1: Quantitative Measures of Hardness, Softness, and Acid-Base Interactions from a Hard Soft Acid-Base Principle Perspective Involve Orbital Energies and/or Apportioning Acid-Base Bonding in Terms of Electrostatic and Covalent Factors

6.2.6.2: 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

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6.2.1: Acid-Base Models as Organizing 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

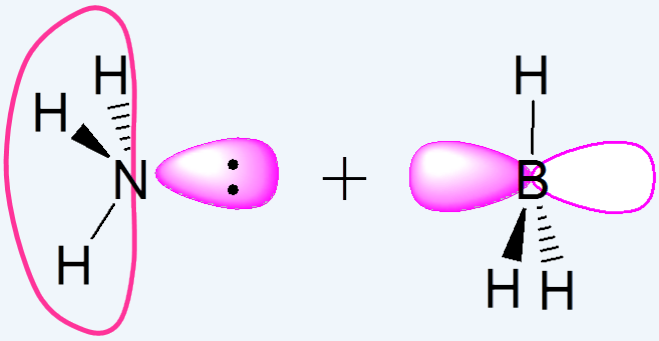
The concept of acids and bases is often associated with the movement of hydrogen ions from one molecule or ion to another. However, a host of acid-base concepts have been developed to help chemists organize and make sense of a wide range of reactions (Table 6.1).

Table 6.1. Summary of major acid-base models.

Definition	Theoretical paradigm and notable features.	Acid	Base	Illustrative sam
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^+	$\underset{acid}{HCl} + \underset{base}{NH_3} \rightarrow \underset{conj.\ acid}{NH_4^+} + \underset{conj.\ base}{Cl^-}$ $\underset{acid}{HOAc} + \underset{base}{NH_3} \rightarrow \underset{conj.\ acid}{NH_4^+} + \underset{conj.\ base}{OAc^-}$ $\underset{amphoteric}{2\ H_2O} \rightarrow \underset{conj.\ acid}{H_3O^+} + \underset{conj.\ base}{OH^-}$

Definition	Theoretical paradigm and notable features.	Acid	Base	Illustrative sam
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	$\underset{acid}{SbF_5} + \underset{base}{BrF_3} \rightarrow \underset{conj.\ base}{SbF_6^-} + \underset{conj.\ acid}{BrF_2^+}$ $\underset{amphoteric}{2\ BrF_3} \rightarrow \underset{conj.\ acid}{BrF_2^+} + \underset{conj.\ base}{BrF_4^-}$

Definition	Theoretical paradigm and notable features.	Acid	Base	Illustrative sam
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 integrates with molecular orbital descriptions of chemical reactivity in Frontier orbital theory.	Accepts an electron pair	Donates an electron pair	$:\underset{base}{NH_3} + \underset{acid}{BF_3} \rightarrow H_3N + BF_3$
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	$:\underset{base}{NH_3} + \underset{acid}{BH_3} \rightarrow \underset{adduct}{H_3N-BH_3}$ $\underset{acid}{Fe^{2+}} + \underset{base}{Zn^0} \rightarrow Fe^0 + Zn^{2+}$

Definition	Theoretical paradigm and notable features.	Acid	Base	Illustrative sam
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

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.

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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6.2.2: 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:

$$\mathrm{HA\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + A^-\,(aq)} \tag{6.2.2.1}$$

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 pK_a values for selected weak acids are given in Table $6.2.2.1$.

Table $6.2.2.1$: 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 $\mathrm{H_3O^+}$ in aqueous solution, Arrhenius bases decrease $\mathrm{H_3O^+}$. 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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6.2.3: BRØNSTED-LOWRY CONCEPT

6.2.3.1: Brønsted-Lowry Concept

6.2.3.2: Rules of Thumb for thinking about the relationship between Molecular Structure and Brønsted Acidity and Basicity*

6.2.3.3: The acid-base behavior of binary element hydrides is determined primarily by the element's electronegativity and secondarily by the element-hydrogen bond strength

6.2.3.4: Brønsted-Lowry Superacids and the Hammett Acidity Function

6.2.3.5: Thermodynamics of Solution-Phase Brønsted Acidity and Basicity

6.2.3.6: Thermodynamics of Gas Phase Brønsted Acidity and Basicity

6.2.3.7: The Acidity of an Oxoacid is Determined by the Electronegativity and Oxidation State of the Oxoacid's Central Atom*

6.2.3.8: High Charge-to-Size Ratio Metal Ions Act as Brønsted Acids in Water

6.2.3.9: The Solvent System Acid Base Concept

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

6.2.3.11: Non-nucleophilic Brønsted-Lowry Superbases

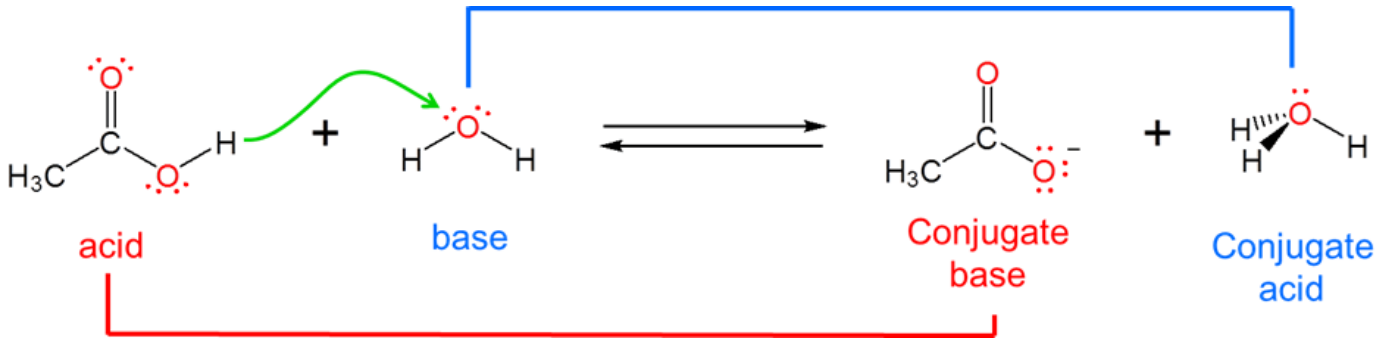
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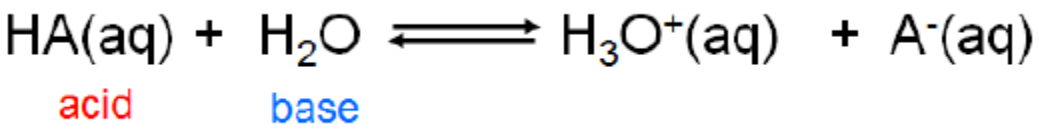
6.2.3.1: Brønsted-Lowry Concept

The Brønsted-Lowry acid-base concept

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.

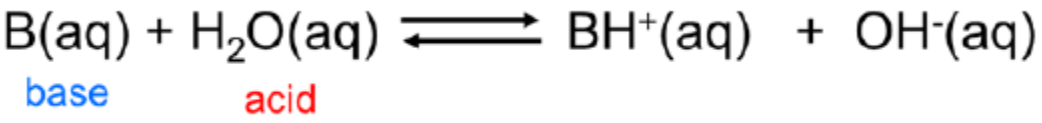


Because the Brønsted-Lowry concept is concerned with H^+ ion transfer rather than the creation of a particular chemical species, it is able to handle a diverse array of acid-base concepts. In fact, from the viewpoint of the Brønsted-Lowry concept, Arrhenius acids and bases are just a special case involving 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^+:



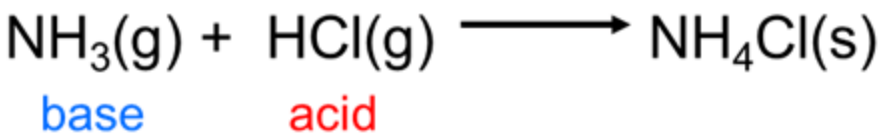
(6.2.3.1.1)

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.

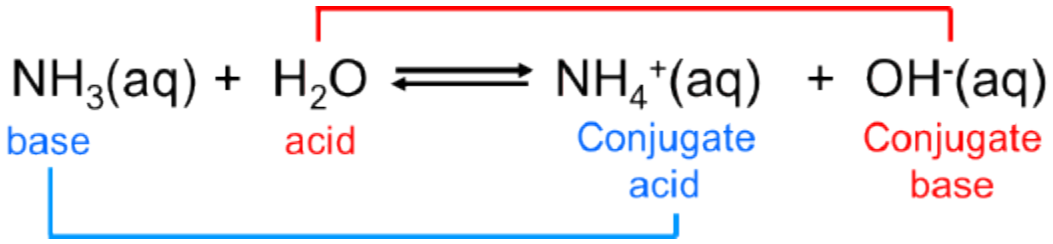
Becasue the Brønsted-Lowry concept can handle any sort of hydrogen ion transfer it readily accommodates many reactions that Arrhenius theory cannot, including those that take place outside of water, such as the reaction between gaseous hydrochloric acid and ammonia:



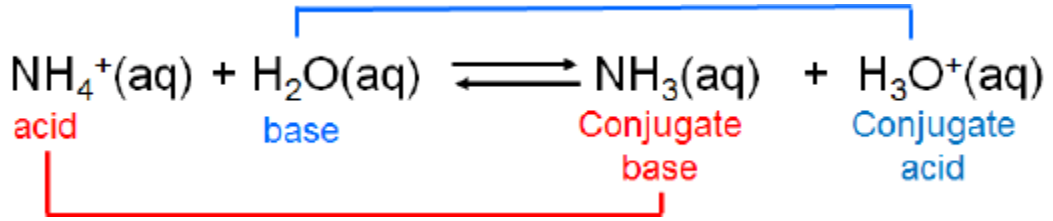
The classification of acids as strong or weak usually refers to their ability to donate or abstract hydrogen ions to or from water to give H_3O^+ and OH^-, respectively, *i.e.,* their Arrhenius acidity and basicity. However, acids and bases may be classified as strong and weak under the Brønsted-Lowry 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:

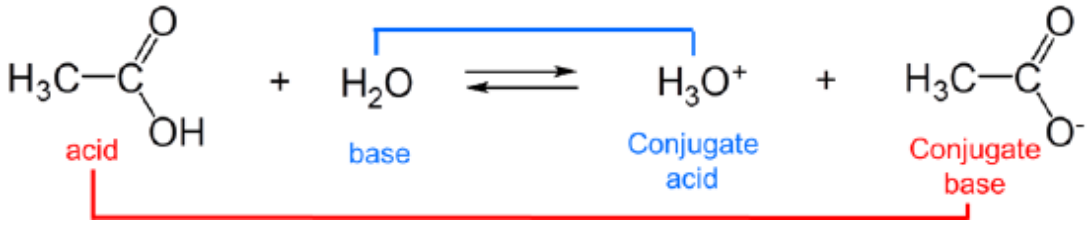


The ammonium ion is itself a weak acid that can undergo dissociation:

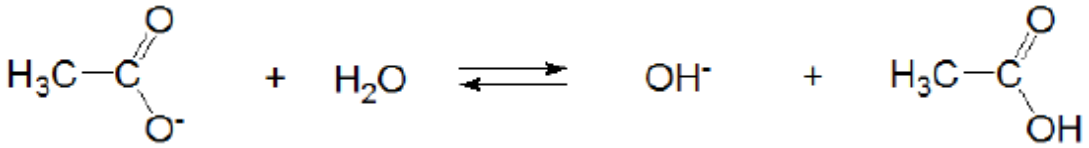


In this case ammonia and ammonium ion are acid-base conjugates. In general acids and bases that differ by a *single ionizable hydrogen ion* are said to be conjugates of one another.

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:



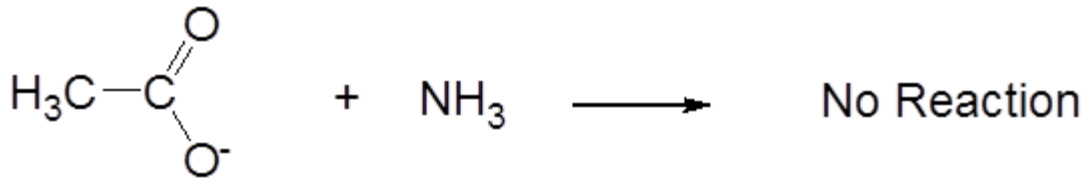
and acetic acid's conjugate base, acetate, acts as a weak Brønsted base.



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



while its conjugate base, acetate, is neutral.

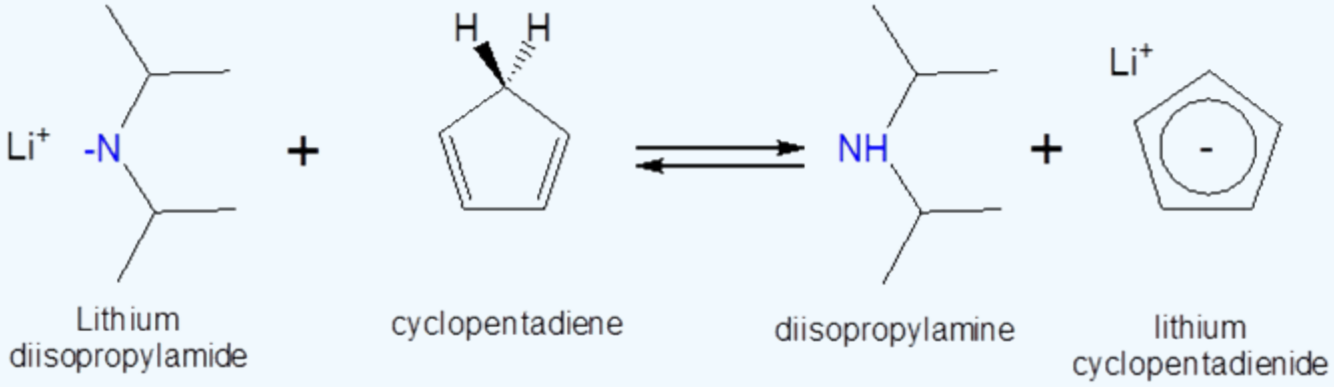


The reciprocal relationship between the strengths of acids and their conjugate bases has several consequences:

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.

Example 6.2.3.1.1

Can a solution of lithium diisopropylamide in heptane be used to form lithium cyclopentadienide? The pK_a of cyclopentadiene and diisopropylamine are ~15 and 40, respectively, and the proposed reaction is as follows:



Solution: available at the end of this section.

Answers

Example 6.2.3.1.1

Since cyclopentadiene is a stronger acid than diisopropylamine (the stronger the acid the lower the pK_a) the equilibrium will favor protonation of the diisopropylamine by cyclopentadiene. Consequently addition of a heptane solution of lithium diisopropylamide to monomeric cyclopentadiene should give lithium cyclopentadienide.

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6.2.3.2: Rules of Thumb for thinking about the relationship between Molecular Structure and 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 main factors should be considered when thinking about the relationship between molecular structure and Brønsted acidity and basicity

Some simple factors that it can be helpful to consider when thinking about the strength of a given acid or base are:

1. Bond strength effects

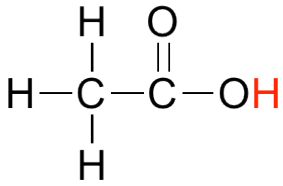
The weaker the bond to the ionizable hydrogen, the stronger the acid. Strongly bonded hydrogen ions are difficult to remove, weakly bonded ones much less so.

2. Inductive effects

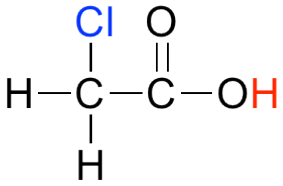
Inductive effects involve the donation or withdrawal of electrons from an atom by a group connected to it through bonds. **Electron donating groups** increase the electron density while **electron withdrawing groups** decrease it. Atoms or groups that withdraw electron density away from a center increase 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:

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

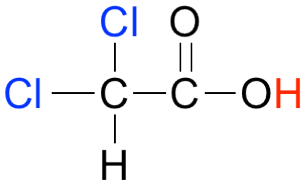
- When a bond to hydrogen is more polarized away from the H (more like $^{-\delta}E-H^{\delta+}$) it is easier to cleave off the hydrogen ion from that E-H bond. This may be seen from how the pK_a values of acetic acid and its mono-, di-, and tri-chlorinated derivatives decreases with the extent of chlorination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



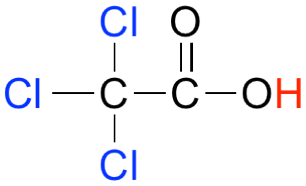
$pK_a = 4.8$



$pK_a = 2.8$



$pK_a = 1.3$



$pK_a = 0.64$

- 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

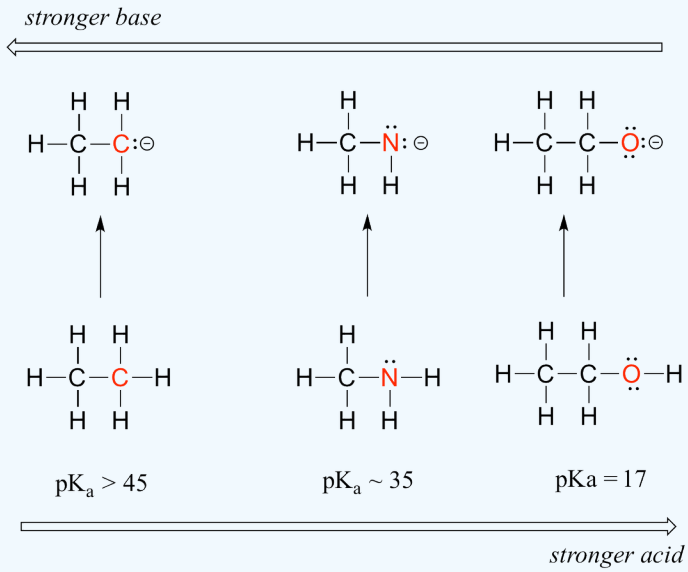
The more stable the acid's conjugate base, the stronger the Brønsted acid. All reactions are in theory reversible, and so when considering the propensity of an acid to donate hydrogen ions, it can be helpful to look at the reverse of hydrogen ion donation, namely, protonation of the acid's conjugate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

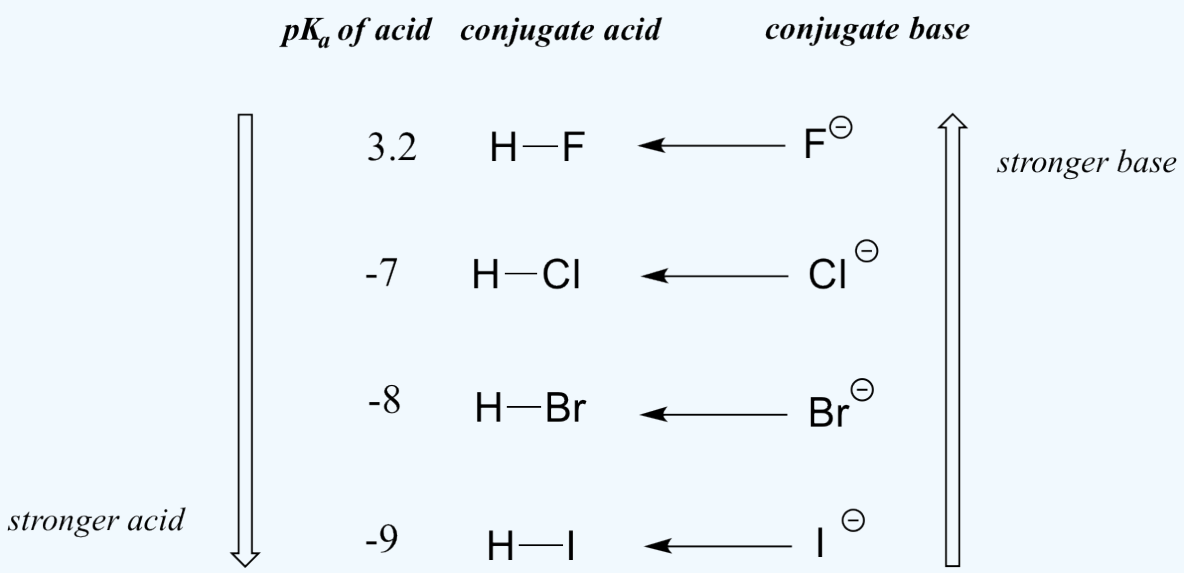
4. Size effects on Bond Strength and Charge Delocalization

There are two classes of size effects to be considered:

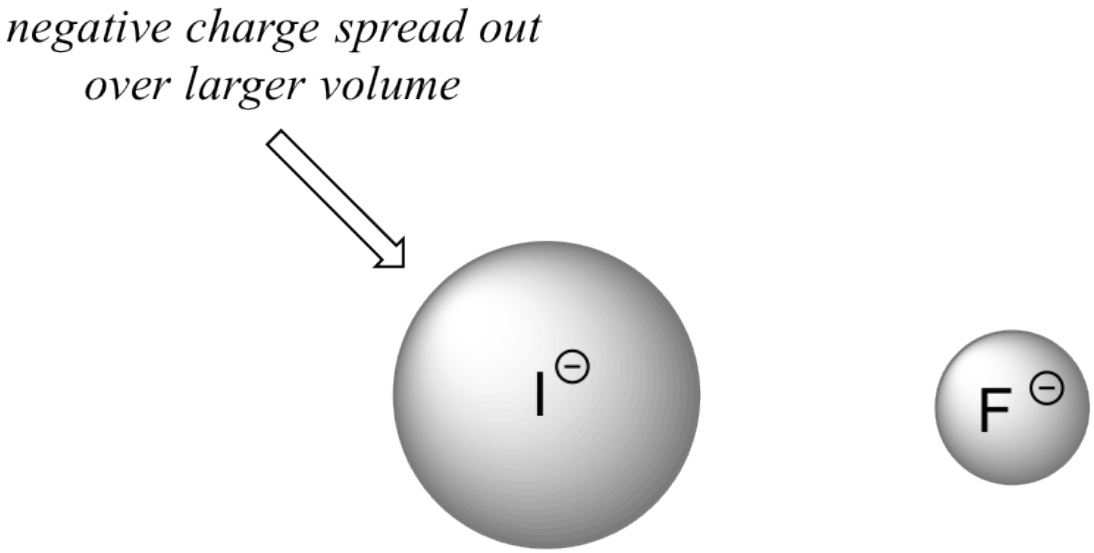
a. The larger the atom to which a H is bound in an E-H bond, the weaker the bond and the stronger the acid.
b. Increased charge delocalization with increasing size. Electrostatic charges, whether positive or negative, are more stable when they are 'spread out' over a larger area. The greater the volume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

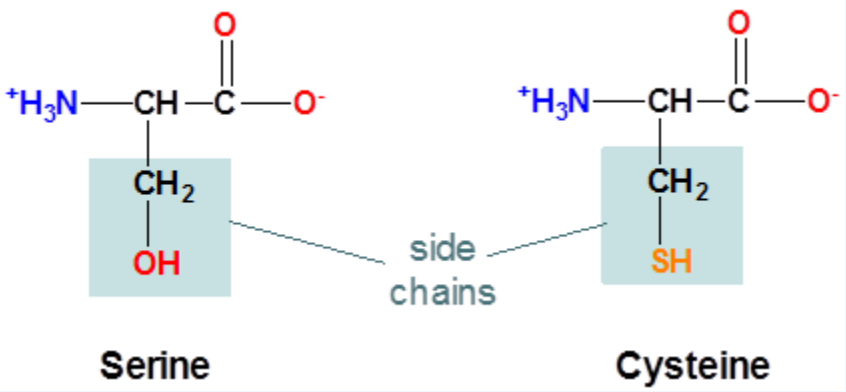


The increase in the acidity of the hydrogen halides down a group suggests that size effects are more important than inductive effects. In the case of the hydrogen halides, because fluorine is the most electronegative halogen element, we might expect fluoride to also be the least basic halogen ion. But 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.

Exercise

The structure of the amino acids serine and cysteine are shown below. Which do you expect will have the more acidic side chain?



Answer available at the end of this section.

Contributors and Attributions

Stephen M. Contakes (Westmont College),

* 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_base/7.3%3A_Structural_effects_on_acidity_and_basicity

Answers

Exercise

Cysteine, since the cysteine side chain possesses an ionizable S-H bond while serine's side chain possesses an ionizable O-H bond. Since S is larger than O, cysteine's S-H bond will be weaker than serine's O-H bond, and the cysteine side chain's thiolate conjugate base more stable than the serine side chain's alkoxide conjugate base. In fact, the side chain pK_a of cysteine is 8.3 while serine is considered to be nonionizable under physiological conditions.

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6.2.3.3: The acid-base behavior of binary element hydrides is determined primarily by the element's electronegativity and secondarily by the element-hydrogen bond strength

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 6.2.3.3.1. As can be seen from the constants in Figure 6.2.3.3.2, the ability of the hydrides to transfer a hydrogen to water increases across a period and down a group.

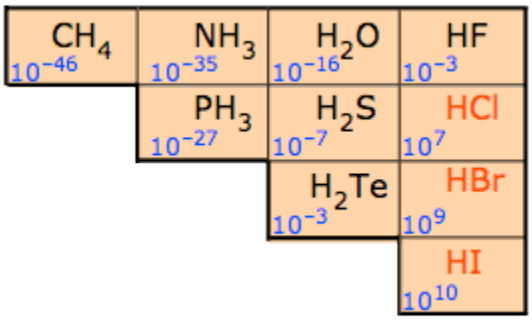


Figure 6.2.3.3.1: The acid ionization constants of nonmetal hydrides increase across a period and down a group. (CC BY-NC 3.0; Stephen Lower via Chem1)

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

1. Foing 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 difficult to break. Remember, the weaker the bond, the stronger the acid strength. This is further illustrated in Table 6.2.3.3.1, where the weakest bond has produced the strongest acid.

Table 6.2.3.3.1 *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}

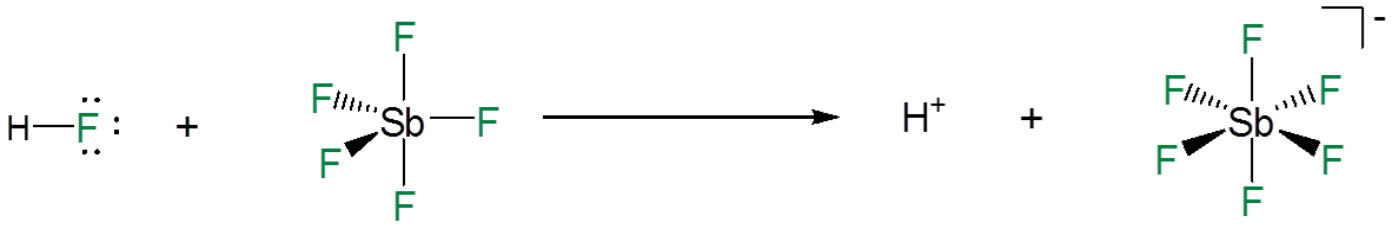
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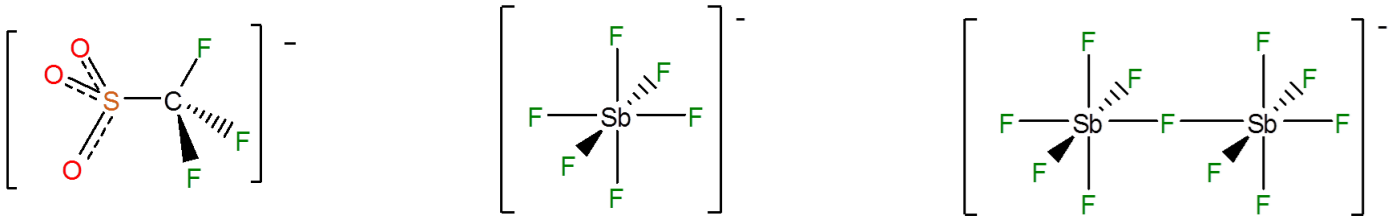
6.2.3.4: Brønsted-Lowry Superacids and the Hammett Acidity Function

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

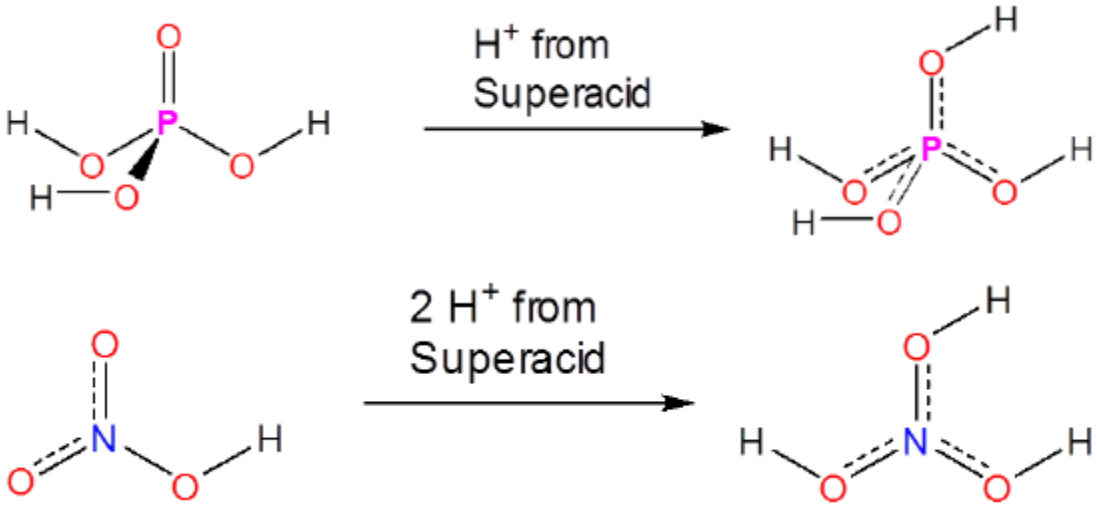
Superacids are able to dissociate completely because when they do so they give an extremely stable anion in which the residual negative charge is distributed among multiple electronegative atoms. For example, in mixtures of HF and antimony pentaflouride the dissociation of a hydrogen ion from the HF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

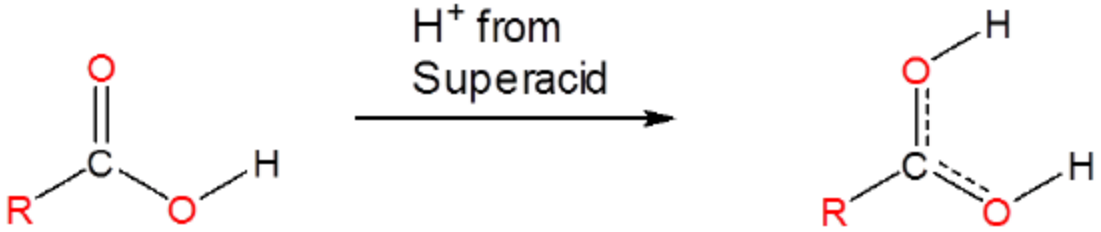


This gives extremely stable anions like $\mathrm{SbF_6^-}$ and $\mathrm{Sb_2F_{11}^-}$, in which a single negative charge is delocalized among many electronegative groups and atoms; of these, CF_3 and F are particularly common.



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:





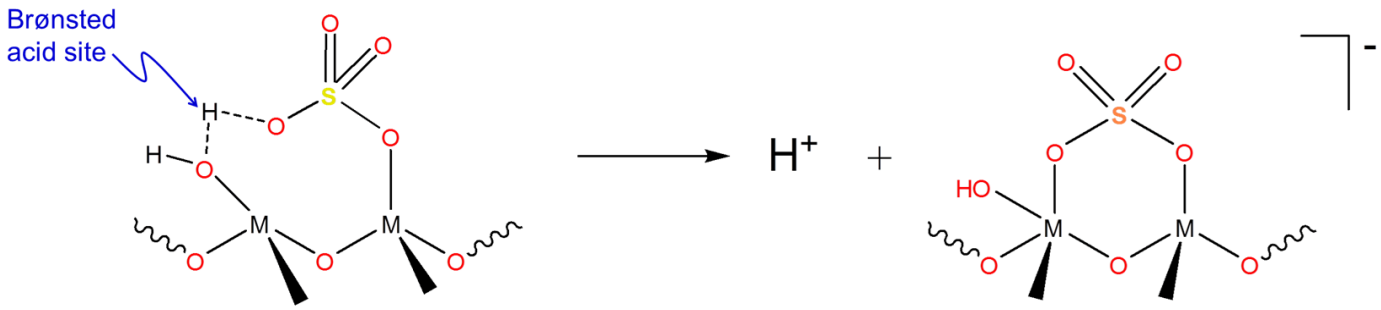
However, superacids also protonate many species that are not usually considered to have acid base properties. Even alkanes can be protonated and, in fact, superacids are used to generate carbocations in a variety of synthetic applications. They do this by protonating alkanes to give unstable species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

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

which subsequently decomposes to give an ordinary carbocation

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

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:

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

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

where $\mathrm{A_{H^+}}$ is the activity of $\mathrm{H^+}$, 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:

$$\mathrm{H^+ + B \rightleftharpoons BH^+}$$

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

$$\mathrm{BH^+ \rightleftharpoons B + H^+}$$

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

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

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

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

which can be rearranged to give

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

or

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

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 $\mathrm{BH^+}$ towards $\mathrm{BH^+}$. 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 $\mathrm{BH^+}$ 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 $6.2.3.4.1$.

As can be seen from table $6.2.3.4.1$, 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 $6.2.3.4.1$: 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, $\mathrm{H_2SO_4}$	-12
Perchloric Acid, $\mathrm{HClO_4}$	-13.0
Triflic acid (triflouromethanesulfonic acid), $\mathrm{CF_3SO_3H}$	-14.6
Flourosulfonic acid, $\mathrm{FSO_3H}$	-15.6
Magic Acid, $\mathrm{F_5Sb{-}{-}{-}FSO_3H}$	-24 to -21[a]
Fluoroantimonic acid, $\mathrm{SbF_5{-}{-}{-}FH}$	-24 to -21[a,b]

References

1. Gillespie, R. J.; T. E. Peel, T. E.; Robinson, E.A. *J. Am. Chem. Soc.* 1971, *93(20)*, 5083-5087.
2. Gillespie, R. J.; T. E. Peel, T. E. *J. Am. Chem. Soc.*, 1973, 95(16), 5173-5178.3.
3. Olah, George A. *Superacid chemistry, 2nd ed.* Hoboken, N.J.: Wiley. 2009.

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6.2.3.5: Thermodynamics of Solution-Phase Brønsted Acidity and Basicity

The behavior of Brønsted-Lowry acids and bases in solution is heavily influenced by solvation

This is particularly true in aqueous systems in which the energies and entropies of hydration can be quite significant. Consider the enthalpy and entropy changes for the dissociation of a number of acids in dilute aqueous solution at 25°C as given in Table 6.2.3.5.1.

Table 6.2.3.5.1: Thermochemical parameters for acid dissociation of selected inorganic acids.[1,2]

Acid	ΔS° (J/mol-K)	$-T \times \Delta S^\circ$ (kJ/mol)	ΔH° (kJ/mol)	ΔG° (kJ/mol)	K_a (calcd. from ΔG°)
HF	-102	30	-16	14	6.8×10^{-4}
HCl	-35	10	-57	-47	10^{8}
HBr	-13	4	-65	-61	10^{10}
HI	11	-3	-62	-65	10^{11}
HClO	-95.4	28.4	13.9	42.3	4×10^{-8}
$HClO_2$	-86.6	25.8	-14.6	11.2	1.1×10^{-2}
$H_3PO_4 \rightarrow H^+ + H_2PO_4^-$	-66.9	20.0	-7.9	12.1	7.9×10^{-3}
$CH_3CO_2H \rightarrow H^+ + CH_3CO_2^-$	-92.4	27.5	-0.4	27.1	1.8×10^{-5}

As can be seen from the data in Table 6.2.3.5.1, the major driving force for dissociation of inorganic acids is the enthalpy of dissociation, which is exothermic for all of the acids listed except very weakly acidic $HClO$. In contrast, the entropy term usually disfavors dissociation since it is negative for all acids except weakly polar HI (for which it contributes little to the overall free energy of dissociation). The situation is exactly reversed in the case of acetic acid, CH_3CO_2H, for which the enthalphly of dissociation is small and the entropy is the dominant contributor to the free energy.

Further insight into the factors which govern Brønsted acid strength in aqueous solution may be gained by examining the relative contributions of heterolytic H-A bond breaking and hydration to the enthalpy of dissociation. This is done using the thermodynamic cycle depicted in Figure 6.2.3.5.1.

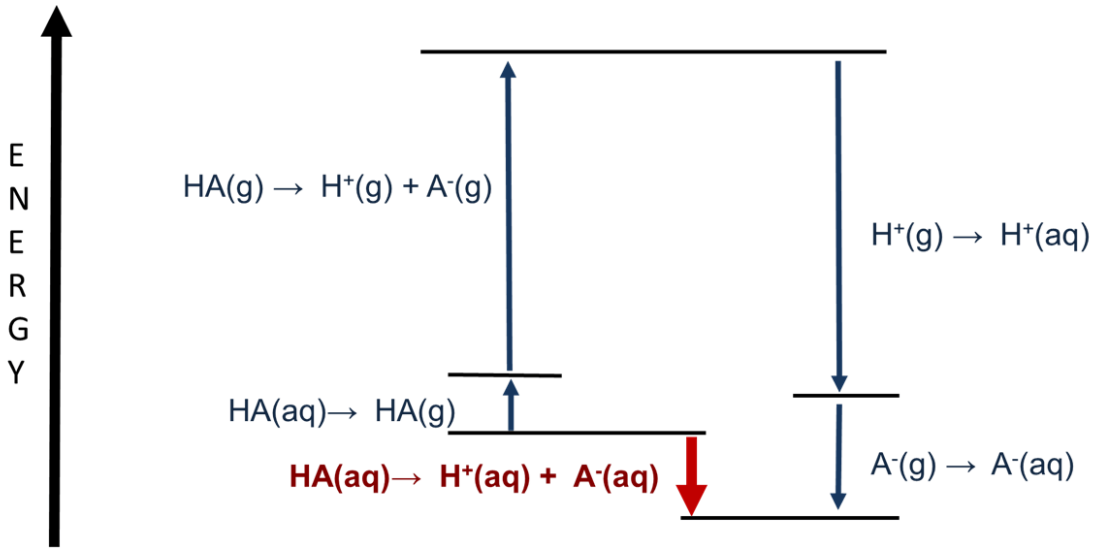


Figure 6.2.3.5.1: Thermodynamic cycle showing the contributions of gas phase bond dissociation and solvation to the enthalpy of acid dissociation. This scheme is more than just a way to think about the relative importance of the various contributions ot the acid dissociation enthalpy, though. Since weak acid ionization is incomplete it can be difficult to determine the enthalpy of ionization for weak acids directly. In these cases it can be easier to determine the gas phase bond dissociation energy (proton affinity) and solvation energies and then calculate the acid ionization enthalpy using Hess' Law.

As can be seen from Figure 6.2.3.5.1, while most of the process involves solvation energies, the heterolytic bond dissociation enthalpy is also a major factor in determining the acid dissociation enthalpy. The heterolytic bond dissociation energy step is a gas phase Brønsted acid base reaction:

$$\mathrm{HA\,(g) \longrightarrow H^+\,(g) + A^-\,(g)}$$

Consequently it will be important to consider gas phase acidity before examining the thermodynamics of acid ionization further.

References

1. The data for inorganic acids is compiled from or calculated from data compiled in Dasent, W. E. Inorganic Energetics: An Introduction, 2nd ed. Cambridge University Press, 1982, pp. 168-170.
2. The data for acetic acid is calculated from the data given in Meissler, G.L.; Fischer, P.J.; Tarr, D.A. Inorganic Chemistry, 5th ed. Pearson, 2014, pg. 175.

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6.2.3.6: Thermodynamics of Gas Phase Brønsted Acidity and Basicity

Proton Affinity and Gas Phase Acidity/Basicity Describe Thermodynamic Aspects of Hydrogen Ion Transfer

Defining acidity in terms of hydrogen ion donation and acceptance within the Brønsted-Lowry acid base concept allows for the understanding of acidity and basicity in a variety of liquid, solid, and gaseous media. The latter are particularly important for understanding the thermodynamics of hydrogen ion donation and acceptance since the energies of gas phase species are uninfluenced by solvation factors. These reactions are perhaps best thought of in terms of the association of a hydrogen ion and a base, B.

Formally the gas phase **proton affinity (PA)** of B is defined as the negative of the enthalpy change for the its association with hydrogen:

$$\mathrm{H^+\,(g) + B\,(g) \rightleftharpoons BH^+\,(g)} \tag{6.2.3.6.1}$$

where ΔH_{rxn} is the Proton Affinity of B.

However, it is simpler to think about the PA in terms of the reverse reaction of Equation 6.2.3.6.1, which describes the dissociation of $\mathrm{BH^+}$:

$$\mathrm{BH^+\,(g) \rightleftharpoons H^+\,(g) + B\,(g)}$$

where ΔH_{rxn} is the PA of B and is also the **heterolytic bond dissociation enthalpy,** from which it can be seen that the proton affinity is just the enthalpy for heterolytic cleavage of the $\mathrm{H{-}B}$ bond.

The **absolute or gas phase basicity (GB)** of B is the negative of the Gibb's free energy change for the same reaction:

$$\mathrm{H^+\,(g) + B\,(g) \rightleftharpoons BH^+\,(g)}$$

where $\Delta\ G_{rxn}$ is the negative of the Absolute or Gas phase basicity of B.

Again, it is simpler to think about the GB of B as the free energy change upon heterolytic dissociation of the $\mathrm{B{-}H}$ bond in $\mathrm{BH^+}$:

$$\mathrm{BH^+\,(g) \rightleftharpoons H^+\,(g) + B\,(g)}$$

where ΔG_{rxn} is the Absolute or Gas phase basicity of B and is also the **free energy for heterolytic bond dissociation**.

Because both PA and GB values correspond to heterolytic bond dissociation, more positive values of the PA and GB correspond to higher thermodynamic affinity between B and $\mathrm{H^+}$.

Note that the **gas phase acidity (GA)** is a very similar quantity to the gas phase basicity, being defined for an acid of formula HA as the Gibb's free energy change for:[††]

$$\mathrm{HA\,(g) \rightleftharpoons H^+\,(g) + A^-\,(g)}$$

where ΔG_{rxn} is the Absolute or Gas phase acidity of HA.

Since $\mathrm{A^-}$ and B are just both convenient shorthand notations for a Brønsted base gas phase acidity and gas phase basicity, both refer to ionization of a gas phase acid. The quantities only differ in that gas phase acidities correspond to ionization of a neutral acid, HA, while gas phase basicities correspond to ionization of a monocationic base, $\mathrm{BH^+}$. For many purposes this difference may be ignored.

Gas phase proton affinities and acidities/basicities have been determined for a large number of species and are available through

the NIST chemistry webbook. Selected values are given in Table 6.2.3.6.1. As can be seen from the data in Table 6.2.3.6.1, typical proton affinity and gas phase acidity values fall between 600 and 1750 kJ/mol, with proton affinities being slightly larger by 20-50 kJ/mol.

Table 6.2.3.6.1: Gas phase proton affinity and acidity values for selected species. Data are taken from the NIST Chemistry Webbook. When more than one value is available, the number presented below represents the average of those reported (after rejection of outliers at the 90% confidence interval using a G-test).

Base	Proton Affinity (kJ/mol)	Gas Phase Acidity (kJ/mol)
hexafluorobenzene C_6F_6	648	
H_2O	691	
benzene	750	
NH_3	854	819
aniline	882	851
pyridine	930	898
triethylamine	982	951
ClO_4^-	1238	1201
ClO_3^-	1310	1284
I^-	1313	1293
Br^-	1349	1328
NO_3^-	1368	1330
Cl^-	1390	1367
NO_2^-	1424	1396
ClO_2^-	1488	1461
$anilide^-$	1537	1506
F^-	1555	1524
CH_3O^-	1573	1570
O^-	1601	1576
$H:^-$	1675	1649
$NH_2:^-$	1686	1656
$FCH_2:^-$	1734	1676
$CH_3CH_2:^-$	1758	1723

Proton Affinity and Gas Phase Acidity/Basicity Data are Consistent with Expected Acidity Trends but also Illuminate the Role of Solvation and Dissociation Entropy in Solution Phase Acid-Base Behavior

Two lessons may be derived from gas phase acidity and proton affinity data:

1. The gas phase proton affinities and acidities of neutral and anionic bases are large, positive, and strongly disfavor acid ionization. As shown in Figure 6.3.3.1, acid ionization is driven by the high solvation energy of the hydrogen ion ($\Delta H^o = -1091$ $\mathrm{kJ/mol}$) with smaller contributions from solvation of the acid's conjugate base.
2. Trends in gas phase proton affinities and acidities indicate the importance of solvation for acid-base behavior in solution. As can be seen from the data in Table 6.2.3.6.1, water is a very weak base in the gas phase. In fact, water's proton affinity

is even lower than the proton affinity of the conjugate bases of most strong acids. This means that transfer of hydrogen ion from most strong acids to water is endothermic in the gas phase. For instance, for

$$\mathrm{HCl\,(g) + H_2O\,(g) \longrightarrow H_3O^+\,(g) + Cl^-\,(g)} \qquad \Delta H = +699 kJ/mol$$

In other words, based on the thermodynamics of hydrogen ion transfer in the gas phase, most strong Brønsted acids should not act as Brønsted acids towards water. Nevertheless they do act as strong acids. This means that the solvation energy terms in the thermodynamic cycle of Figure 6.3.3.1 (possibly assisted by entropic effects) are driving hydrogen ion transfer in solution.

This is confirmed by the values for the proton affinities and hydration energies for the hydrohalic acids given in Table 6.2.3.6.2 . For these acids the solvation energies for the hydrogen ion (-1130 kJ/mol) and anions (*e.g.,* for Cl^-, -363 kJ/mol) are much larger than the hydration energies of the neutral acids and contribute towards an overall exothermic enthalpy of acid dissociation in water.

Table 6.2.3.6.2 Contribution of heterolytic bond dissociation and hydration (hyd) energies to the enthalpy of dissociation for the hydrohalic acids.1

Acid	Proton Affinity (PA) $H-A(g) \rightarrow H^+(g) + A^-(g)$ (kJ/mol)	ΔH_{hyd} *for* HX $HX(aq) \rightarrow HX(g)$ (kJ/mol)	$\Delta\ H_{hyd}$ *for* H^+ $H^+(g) \rightarrow H^+(aq)$ (kJ/mol)	$\Delta\ H_{hyd}$ *for* X^- $X^-(g) \rightarrow X^-(aq)$ (kJ/mol)	Total (acid dissociation enthalpy) $H-A(aq) \rightarrow H^+(aq) + A^-(aq)$ (kJ/mol)
HF	+1555	+48	-1091	-524	-12
HCl	+1390	+18	-1091	-378	-61
HBr	+1349	+21	-1091	-348	-69
HI	+1313	+23	-1091	-308	-63

Although solvation plays a crucial role in determining a substance's acid-base behavior in solution, an acid's strength cannot be predicted from solvation energies alone. This is because it is difficult to predict the relative importance of the large proton affinity and conjugate base hydration enthalpy terms (and to a lesser extent the acid hydration enthalpy) in a given case. This is also illustrated by the data in Table 6.2.3.6.2. The hydrohalic acid bond dissociation energy and halide hydration enthalpy both decrease in magnitude by approximately the same amount on going from HCl to HI, so that the acid dissociation enthalpies remain approximately constant. While proton affinities and hydration enthalpies often change in tandem, it is not always the case that they change by similar magnitudes. This may be seen by comparing the data shown for HF with those for the other hydrohalic acids in Table 6.2.3.6.2. In the case of HF, the 165 kJ/mol increase in proton affinity between HCl and HF is not compensated for by the -146 kJ/mol decrease in hydration energy on going from Cl^- to F^- (due to fluorine's ability to form hydrogen bonds), leading HF to exhibit an anomalously small ionization enthalpy.

How Gas phase acidity values are measured

Gas phase acidities can be conveniently determined thermochemically relative to a standard by measuring the relative affinity of a hydrogen ion for two bases, B_1 & B_2, by using mass spectrometry to follow the equilibrium of the hydrogen ion transfer reaction:

$$HB_1^+ + B_2 \rightarrow B_1 + HB_2^+$$

The free energy change of this reaction may be found from the relative populations of HB_1^+ and HB_2^+ using mass spectrometry:

$$\Delta G = \frac{[B_1][HB_2^+]}{[HB_1^+][B_2]}$$

and the enthalpies and entropies of reaction from the temperature dependence of the free energies (since $\Delta G = \Delta H - T \times \Delta S$.

Gas phase acidity values determined from hydrogen ion transfer equilibrium values are called relative acidities. In contrast, absolute acidities are those which can be traced back to the standard forms of the elements at standard temperature and pressure. Absolute acidities can be found from relative ones as long as the absolute acidity of at least one of the bases is known. Fortunately, the absolute affinities of a number of gas phase acidity standards have been determined thermochemically. For instance, the gas phase proton affinity of H-A corresponds to the sum of the following processes:

$$H - A(g) \rightleftharpoons H(g) + A(g) \qquad \Delta H = Bond\ Dissociation\ Energy\ of\ HA,\ BDE_{HA}$$

$$H(g) \rightleftharpoons H^+(g) + e^-(g) \qquad \Delta H = Ionization\ Energy\ of\ H,\ IE_H$$

$$A(g) + e^-(g) \rightleftharpoons A^-(g) \qquad \Delta H = Electron\ Affinity\ of\ A^-,\ IE_A$$

$$HA(g) \rightleftharpoons H^+(g) + A^-(g) \qquad \Delta H_{rxn} = Proton\ affinity\ of\ A^-$$

so that

$$Proton\ Affinity\ of\ A^- = DeltaH_{rxn} = BDE_{HA} + IE_H - EA_A$$

For a more detailed explanation of how gas phase acidities are found see the gas phase ion thermochemistry page at the NIST chemistry webbook.

References

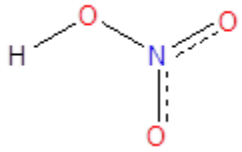
1. Proton affinities are taken from the NIST NIST Chemistry Webbook. Hydration enthalpies are from Dasent, W. E. *Inorganic Energetics: An Introduction*, 2nd ed. Cambridge University Press, 1982, pp. 168-170.

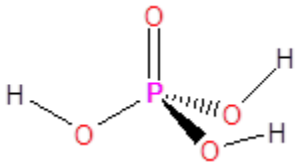
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6.2.3.7: The Acidity of an Oxoacid is Determined by the Electronegativity and Oxidation State of the Oxoacid's Central Atom*

Oxyacids (also known as **oxoacids**) are compounds of the general formula $\mathrm{H}_n\mathrm{EO}_m$, 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 ($\mathrm{HNO_3}$) and phosphoric acid, ($\mathrm{H_3PO_4}$).





The acidity of oxyacids follows three trends:

Trend 1: In a homologous series the acidity increases with the electronegativity of the central atom

Elements in the same group frequently form oxyacids of the same general formula. For example, chlorine, bromine, and iodine all form oxyacids of formula HOE: hypochlorous, hypobromous and hypoiodous acids. In the case of these homologous oxyacids, the acidity is largely determined by the electronegativity of the central element. Central atoms that are better able to inductively pull electron density towards themselves make the oxygen-hydrogen bond that is to be ionized more polar and stabilize the conjugate base, OE^-. Thus the acid strength in such homologous series increases with the electronegativity of the central atom. This may be seen from the data for the hypohalous acids in Table $6.2.3.7.1$, in which the acid strength increases with the electronegativity of the halogen so that the order of acidity is:

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

and the order of basicity is:

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

Table $6.2.3.7.1$: Relationship of central atom's electronegativity to acid ionization constant in the hypohalous acids.

HOX	Electronegativity of X	K_a
HOCl	3.0	4.0×10^{-8}
HOBr	2.8	2.8×10^{-9}
HOI	2.5	3.2×10^{-11}

Note that the influence of central atom electronegativity on the strength of oxyacids is exactly the opposite to that observed for the binary hydrides in Table $6.2.3.7.5$, for which the acidity increased down a group, giving the order of acidity:

$$\mathrm{HI} > \mathrm{HBr} > \mathrm{HCl} \gg \mathrm{HF}$$

The reason for this is that in the hydrogen halides, the bond to be broken (H-E bond) decreased in strength down the group, while in oxyacids the bond to be broken is always an O-H bond and so varies much less in strength with the electronegativity of the central atom.

Trend 2: For oxoacids of a given central atom the acidity increases with the central element's oxidation state or, in other words, the number of oxygens bound to the central atom.

Here we are looking at the trend for acids in which there are variable numbers of oxygen bound to a given central atom. An examples is the perchloric (ClO_4^-), chloric (ClO_3^-), chlorous (ClO_2^-), and hypochlous (ClO^-) acid series. In such a series, the greater the number of oxygens, the stronger the acid. This can be explained in several ways. From the viewpoint of the acid itself the key factor is again the inductive effect, in this case involving the ability of the oxygens attached to the central atom to pull on electron density across the OH bond. This is seen from the charge density diagram for the chlorine oxoacids shown in Figure 6.2.3.7.1, in which the partial positive charge on the acidic hydrogen increases with the number of oxygens present.

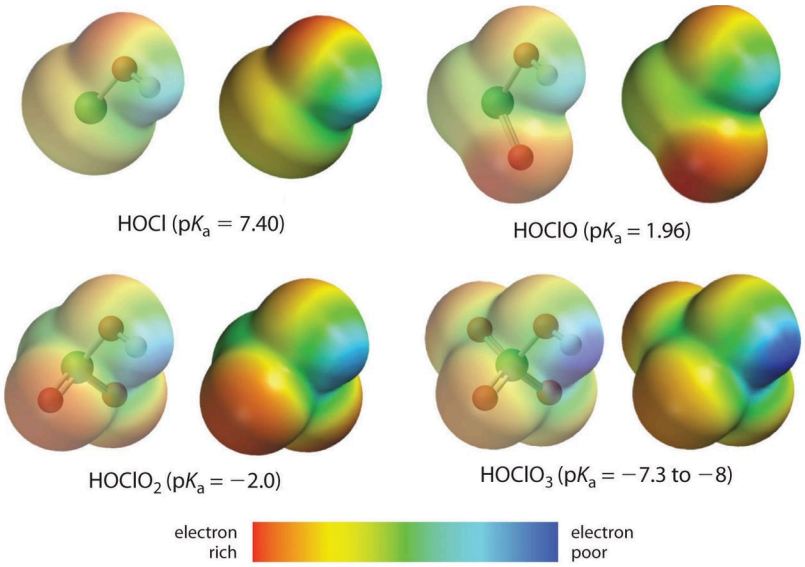


Figure 6.2.3.7.1: Increasing the number of oxygens increases K_a, as evidenced by the decreased electron density on the acidic hydrogen (which is most blue in $HClO_4$). Note, $K_a = 10^{-pK_a}$, and so the larger the pK_a, the smaller the K_a. (CC BY-SA-NC; anonymous)

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 oxyanion. That the stability of the conjugate base increases with the number of oxygens may be seen from the charge distribution diagrams and Lewis bonding models for the chlorine oxyanions shown in figure 6.2.3.7.2. As the negative charge is spread over more oxygen atoms it becomes increasingly diffuse.

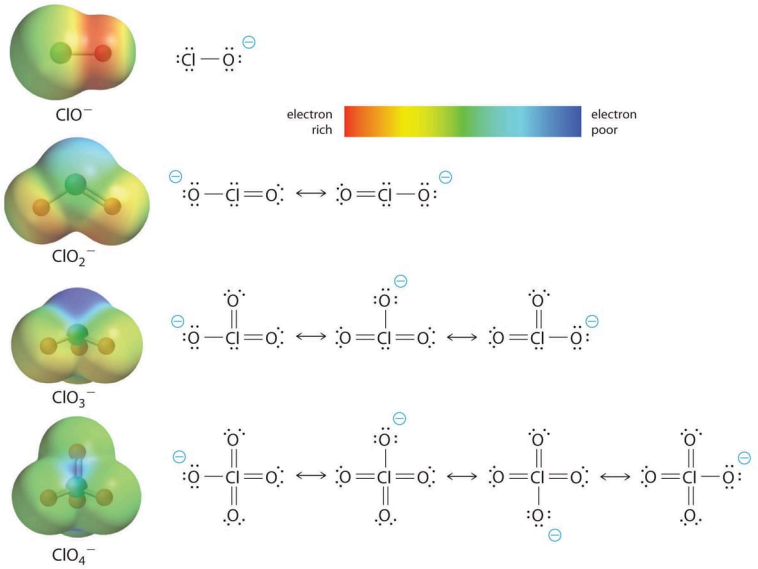


Figure 6.2.3.7.2: Increased diffusion of charge in chlorine oxyanions with increasing number of oxygens. The larger the ion the more dispersed the charge and thus the less the charge density, making the perchlorate the most stable anion in the series. Even the simplistic treatment of bonding depicted in the resonance structures correctly shows an increased dispersion of the charge density. (CC BY-SA-NC 3.0; anonymous)

Exercise 6.2.3.7.1

Sulfur and selenium both forms oxoacids of formula $\mathrm{H_2EO_3}$, 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 available at the end of this section.

Trend 3: 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
$$pK_a = 8 - 5 \times p \qquad (6.2.3.7.1)$$
2. As an oxoaxid undergoes successive ionizations the pK_a increases by five each time (i.e., K_a decreases 10,000-fold).

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 6.2.3.7.2: 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 available at the end of this section.

Answers

Exercise 6.2.3.7.1

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

Exercise 6.2.3.7.2**: How well do Pauling's rules for oxoacids work?**

For phosphoric acid, Pauling's rules (Equation 6.2.3.7.1) predict the pK_a values quite well:

- 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.
- $H_2PO_4^-$:

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

  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.

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

- 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.

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.

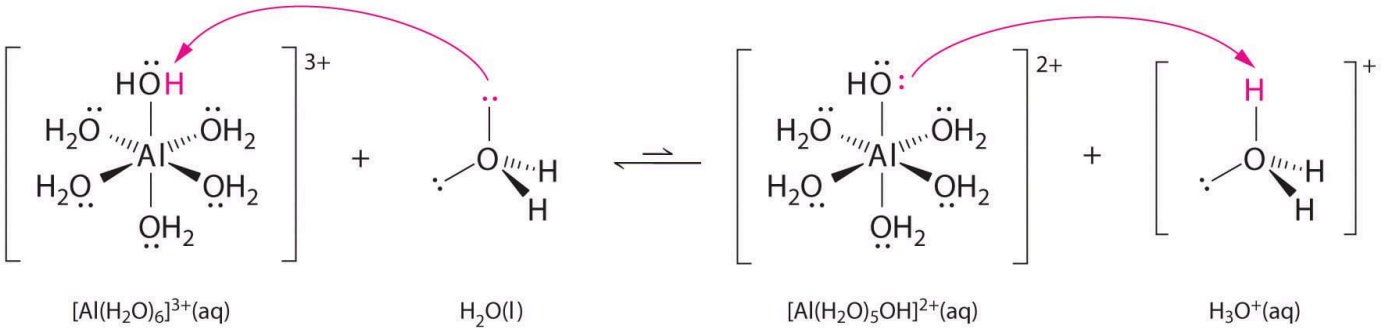
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6.2.3.8: High Charge-to-Size Ratio Metal Ions Act as Brønsted Acids in Water

Metal Ions 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 6.2.3.8.5*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 6.2.3.8.1.

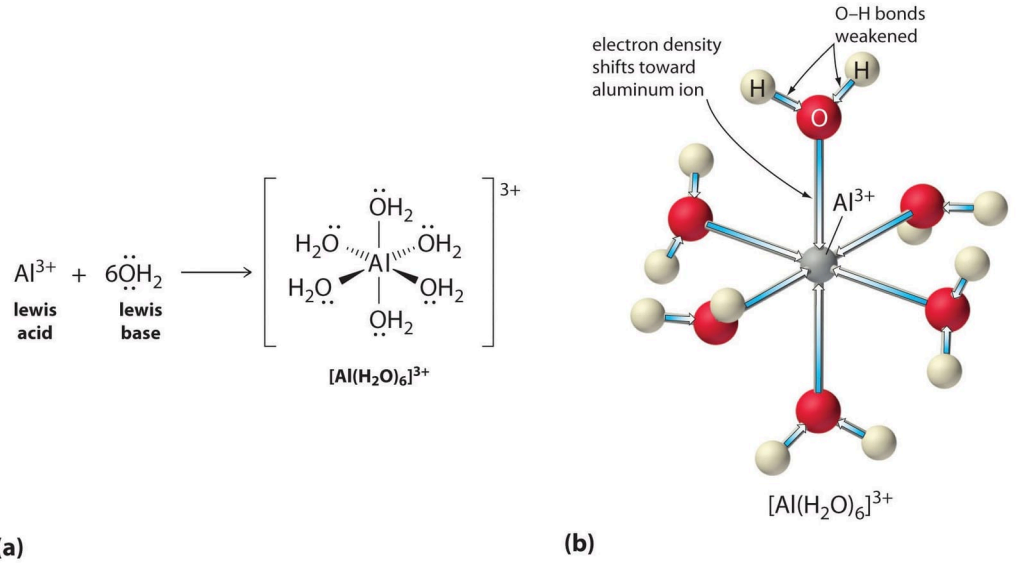


Figure 6.2.3.8.1: Effect of a Metal Ion on the Acidity of Water (a) Reaction of the metal ion Al^{3+} with water to form the hydrated metal ion is an example of a Lewis acid–base reaction. (b) The positive charge on the aluminum ion attracts electron density from the oxygen atoms, which shifts electron 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)

The acidity of a given metal ion largely depends on its charge to size ratio and electronegativity, although in some cases hardness and ligand field effects also play a role.

The magnitude of this effect depends on the following factors, of which the first two are generally considered the most important (Figure 6.2.3.8.2):

The charge on the metal ion

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^{+}) of the same radius.

The radius of the metal ion

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.

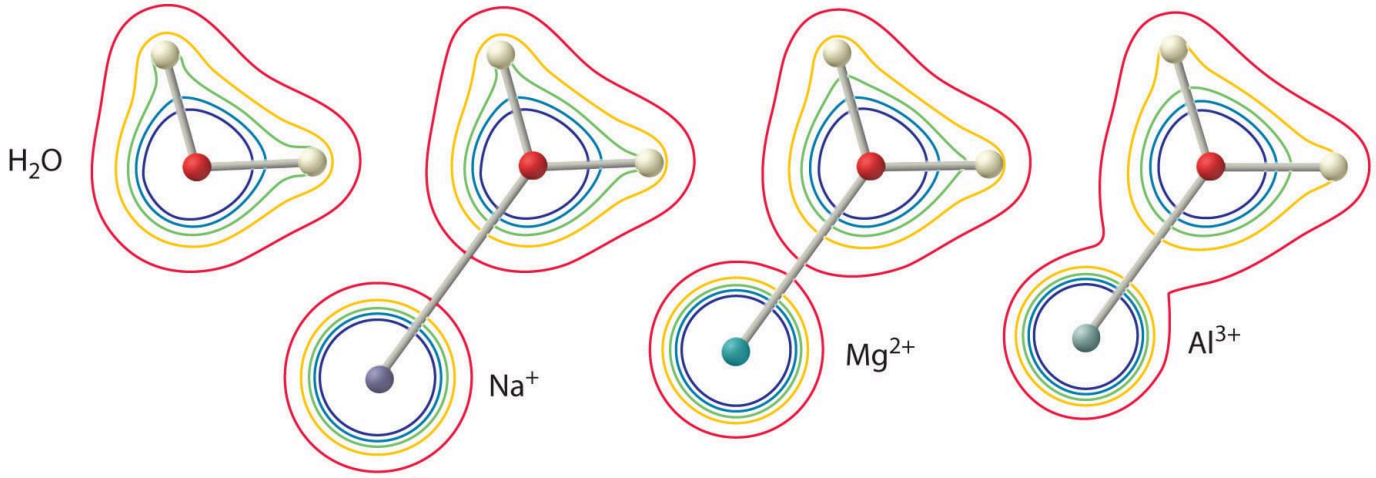


Figure 6.2.3.8.2: The effect of the charge and radius of a metal ion on the acidity of a coordinated water molecule. The contours show the electron density on the O atoms and the H atoms in both a free water molecule (left) and water molecules coordinated to Na^{+}, Mg^{2+}, and Al^{3+} ions. These contour 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 first two of these factors explain 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:

$$[\mathrm{Al(H_2O)_6}]^{3+}\,(\mathrm{aq}) \rightleftharpoons [\mathrm{Al(H_2O)_5(OH)}]^{2+}\,(\mathrm{aq}) + \mathrm{H}^{+}\,(\mathrm{aq}) \tag{6.2.3.8.1}$$

The $[\mathrm{Al(H_2O)_6}]^{3+}$ 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]

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

where Z is the charge on the metal ion and r its radius. As can be seen from figure 6.2.3.8.3, 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.

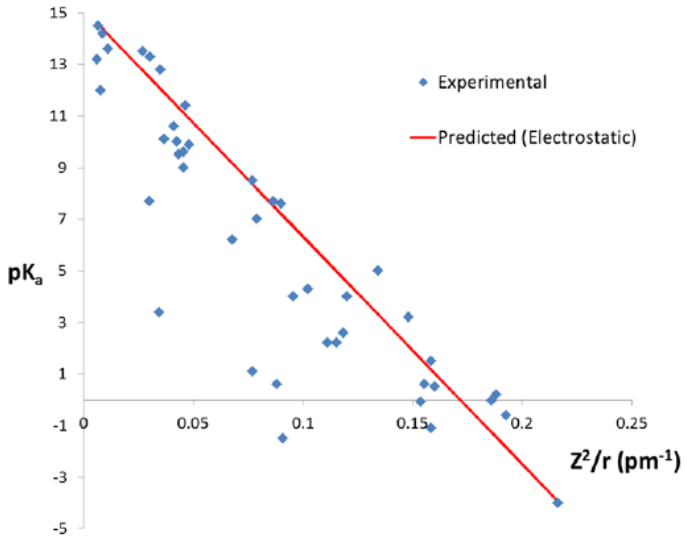


Figure 6.2.3.8.3: The pK_a of metal ions (♦) as a function of $\frac{Z^2}{r}$ for 43 metal ions. Drawn using radii listed in reference 1.

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:

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:

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

where r is the ion radius in pm and χ is its Pauling electronegativity. As can be seen from figure 6.2.3.8.4, the electronegativity term accounts for some of the deviations in metal ion acidity predicted from charge and size effects alone.

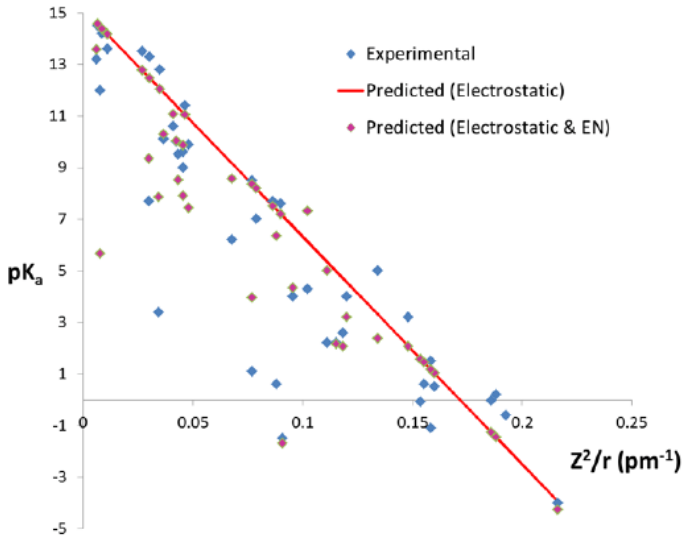


Figure 6.2.3.8.4: Comparison between the experimental pK_a values (♦) for 43 metal ions and those predicted empirically accounting for size and charge effects (-) and accounting for size, charge, and electronegativity effects (♦). Drawn using radii listed in reference 1.

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 6.2.3.8.1. The greater than expected acidity of softer cations is thought to reflect the importance of covalent contributions to the metal-water bond.

Table 6.2.3.8.1: 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

Ligand field effects

Ligand field effects involve bonding and antibonding interactions between the *d* orbitals on a transition metal and ligand orbitals. The importance of ligand field interactions on cation acidity is not well established, but ligand field interactions might influence the acidity of a hydrated metal in two cases: (a) when the ligand field stabilization of the aqua complex (metal with H_2O or OH^- bound) is greater or less than that in its conjugate base and (b) in complexes which undergo Jahn-Teller distortions that alter the metal's ability to polarize the OH bond.

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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6.2.3.9: The Solvent System Acid Base Concept

The proton-centered nature of Arrhenius and Brønsted-Lowry definitions of acids and bases limits the utility of the acid-base formalism to reactions in protic solvents. A more generalizable theory is the **solvent-system** acid/base definition, which can be used to describe acid/base chemistry in non-protic solutions.

The solvent system acid-base concept generalizes the Arrhenius acid-base concept

Remember that the Brønsted-Lowry concept seeks to generalize Arrhenius acidity in ways that allow all hydrogen ion transfers to be thought of as acid-base reactions.

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

Like the Brønsted-Lowry acid-base concept, the solvent system acid-base concept is a way to generalize the Arrhenius acid-base concept by focusing on cations and anions generated in any solvent that autoionizes. These include Brønsted-Lowry type autoionizations:

$$\mathrm{2\,NH_3\,(l) \rightleftharpoons {NH_4}^+ + {NH_2}^-}$$
$$\mathrm{2\,H_2SO_4\,(l) \rightleftharpoons {H_3SO_4}^+ + {HSO_4}^-}$$

However, the solvent system definition also allows for autoionizations that involve the transfer of an ion other than hydrogen. For example,

$$\mathrm{2\,SeOCl_2\,(l) \rightleftharpoons SeOCl^+ + {SeOCl_3}^-}$$
$$\mathrm{2\,BrF_3\,(l) \rightleftharpoons {BrF_2}^+ + {BrF_4}^-}$$

However, the solvent system concept does not define acidity in terms of ion transfer. Rather, like the Arrhenius concept, it defines acids and bases in terms of the impact those acids and bases have on the concentrations of cations and anions in solution (Figure 6.2.3.9.1).

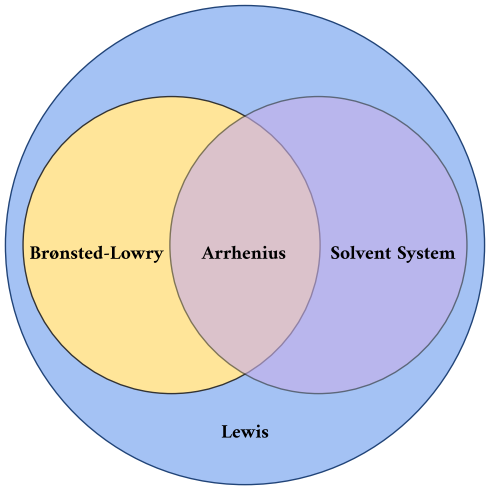


Figure 6.2.3.9.1: Venn diagram showing the hierarchical relationship between the major acid-base definitions. (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

Definition: Solvent System Definitions of Acids and Bases

This means that under the solvent system definition:

- an acid is the solvent cation or any substance that increases the concentration of the solvent cations normally produced by solvent autoionization.
- a base is the solvent anion or any substance that increases the concentration of the solvent anions normally produced by solvent autoionization.

Note that in the solvent system concept, salts of the solvent cation are acids and salts of the solvent anion are bases. For instance, if a salt of $\mathrm{BrF_4^-}$ such as sodium tetrafluorobromate ($\mathrm{NaBrF_4}$) is added to $\mathrm{BrF_3\,(l)}$, the concentration of $\mathrm{BrF_4^-}$ increases.

The Solvent System Concept

The solvent system definition collapses to the Arrhenius definition for Brønsted acids in water. For instance, HCl is an acid in water since it increases the concentration of $\mathrm{H_3O}$ when it dissociates:

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

The solvent system broadens the Arrhenius definition by allowing for similar reactions in a variety of solvents. For instance, HCl also acts as an acid in liquid ammonia since it gives an $\mathrm{NH_4^+}$ ion on dissociation.

$$\underset{acid}{\mathrm{HCl}} + \mathrm{NH_3\,(l) \rightarrow NH_4^+ + Cl^-}$$

Antimony pentafluoride acts as an acid in liquid $\mathrm{BrF_3}$ since it abstracts a fluoride to give $\mathrm{BrF_2^+}$.

$$\underset{acid}{\mathrm{SbF_5}} + \mathrm{BrF_3\,(l) \rightleftharpoons SbF_6^- + BrF_2^+}$$

In contrast, the fluoride ion of potassium fluoride acts as a base, since it adds to $\mathrm{BrF_3}$ to give $\mathrm{BrF_4^-}$.

$$\underset{base}{\mathrm{KF}} + \mathrm{BrF_3\,(l) \rightleftharpoons K^+ + BrF_4^-}$$

The solvent system definition also allows for acid-base neutralization reactions. An example would be the reaction between KF and $\mathrm{SbF_5}$ in $\mathrm{BrF_3}$.

$$\underset{base}{\mathrm{KF}} + \underset{acid}{\mathrm{SbF_5}} \rightarrow \mathrm{KSbF_6}$$

although in this case it may be easier to see what is happening by writing the complete ionic form of the neutralization reaction equation.

$$\mathrm{K^+ + \underset{base}{F^-} + \underset{acid}{SbF_5} \rightarrow KSbF_6}$$

The solvent system concept allows for successive ionizations just as the Brønsted-Lowry system does. Acids like sulfuric acid can be described well under the Arrhenius, Brønsted-Lowry, and solvent system definitions.

$$\mathrm{2\,H_2SO_4 \rightleftharpoons H_3SO_4^+ + HSO_4^-}$$
$$\mathrm{HSO_4^- + H_2SO_4 \rightleftharpoons H_3SO_4^+ + SO_4^{2-}}$$

The solvent system definition also describes the autoionization of nonprotic solvents like thionyl chloride, $\mathrm{SOCl_2}$:

$$\mathrm{SOCl_2\,(l) \rightleftharpoons SOCl^+ + SOCl_3^-}$$
$$\mathrm{SOCl^+ + SOCl_2\,(l) \rightleftharpoons SO^{2+} + SOCl_3^-}$$

Successive equilibria are often useful in applying the solvent system to neutralization reactions, as may be seen in Example 6.2.3.9.1.

Example 6.2.3.9.1

The reaction between sodium sulfite, Na_2SO_3, and thionyl chloride, $SOCl_2$, is a neutralization reaction according to the solvent system acid-base concept.

$$Na_2SO_3\,(s) + SOCl_2\,(l) \longrightarrow 2\,NaCl\,(s) + 2\,SO_2\,(g)$$

Write out the relevant equilibria and use them to explain the reaction in acid-base terms.

Solution

In the reaction shown the Na^+ just acts as a counterion. Consequently the reaction that should be considered is

$$2\,{SO_3}^{2-} + SOCl_2 \longrightarrow 2\,Cl^- + 2\,SO_2$$

A good place to start is to consider each of the species involved under the solvent-system acid-base concept by seeing if it is possible to write out ionization (or autoionization) reactions for them.

For ${SO_3}^{2-}$ these are

$$2\,{SO_3}^{2-} \rightleftharpoons \underset{acid}{SO_2} + \underset{base}{{SO_4}^{4-}}$$

$$\underset{acid}{SO_2} + 2\,\underset{base}{{SO_3}^{2-}} \rightleftharpoons \underset{acid}{\blacksquare} + \underset{base}{{SO_4}^{4-}}$$

These equations reveal that

- ${SO_3}^{2-}$ and SO_2 are amphoteric since they can act as either an acid or a base
- ${SO_4}^{4-}$ acts only as a base since it is the solvent anion
- SO^{2+} acts only as an acid since it is the solvent cation

Since ${SO_3}^{2-}$ is amphoteric, this does not resolve the issue of whether it is acting as an acid or a base. However, notice that the product of the reaction between ${SO_3}^{2-}$ and $SOCl_2$ is SO_2. This means that ${SO_3}^{2-}$ is acting as if it is following the pathway:

$$2\,{SO_3}^{2-} \rightleftharpoons SO_2 + {SO_4}^{4-}$$

The ionizations of $SOCl_2$ were already given in the main text but are also reproduced here for convenience:

$$SOCl_2\,(l) \rightleftharpoons SOCl^+ + {SOCl_3}^-$$

$$SOCl^+ + SOCl_2\,(l) \rightleftharpoons \blacksquare + {SOCl_3}^-$$

We could write an expression involving ionization of $2\,SO^{2+}$ to S^{4+} and SO_2 but that is unnecessary for solving the present problem.

The equations we have written reveal that

- $SOCl_2$ and $SOCl^+$ are amphoteric since they can act as either an acid or a base
- ${SOCl_3}^-$ acts only as a base since it is the solvent anion
- SO^{2+} acts only as an acid since it is the solvent cation

Again, since $SOCl_2$ is amphoteric this does not resolve the issue of whether it is acting as an acid or a base. However, notice that the product of the reaction between ${SO_3}^{2-}$ and $SOCl_2$ is SO_2. The only species in a reaction pathway involving $SOCl_2$ that can react to form SO_2 is SO^{2+}. This means that $SOCl_2$ is acting as if it is following the pathway:

$$2\,SOCl_2\,(l) \rightleftharpoons SOCl^+ + {SOCl_3}^-$$

$$SOCl^+ + SOCl_2\,(l) \rightleftharpoons SO^{2+} + {SOCl_3}^-$$

$$SO^{2+} + \text{base} \rightleftharpoons SO_2 + \text{the base's conjugate acid}$$

But what sort of base could react with SO^{2+} to give SO_2? The candidates in our list of bases are ${SO_4}^{4-}$, ${SO_3}^{2-}$, and SO^{2+} It must be one that donates an oxide ion, such as ${SO_4}^{4-}$. So in other words the $SOCl_2$ is following the pathway:

$$2\,SOCl_2\,(l) \rightleftharpoons SOCl^+ + {SOCl_3}^-$$
$$SOCl^+ + SOCl_2\,(l) \rightleftharpoons SO^{2+} + {SOCl_3}^-$$
$$SO^{2+} + {SO_4}^{4-} \rightleftharpoons SO_2 + {SO_3}^{2-}$$

and ${SO_3}^{2-}$ the pathway

$$2\,{SO_3}^{2-} \rightleftharpoons SO_2 + {SO_4}^{4-}$$

Adding these together gives the following net reaction:

$$3\,SOCl_2\,(l) + {SO_3}^{2-} \rightleftharpoons SO_2 + 2\,{SOCl_3}^-$$

At first glance this seems like it is not the correct equation. However, there is one acid-base reaction we are neglecting. The Cl^- product of the reaction between sodium sulfite and thionyl chloride acts as a base in thionyl chloride:

$$SOCl_2\,(l) + Cl^- \rightleftharpoons {SOCl_3}^-$$

So the net reaction above simply corresponds to the reaction between sodium sulfite and thionyl chloride with additional reactions between the product Cl^- and thionyl chloride added in. However, if a 1:1 ratio of thionyl chloride and sodium sulfate is used in the reaction, then the thionyl chloride will be consumed and the equilibrium between thionyl chloride and chloride ion shifted towards chloride, giving the desired net equation:

$$2\,{SO_3}^{2-} + SOCl_2 \longrightarrow 2\,Cl^- + 2\,SO_2$$

As Example 6.2.3.9.1 illustrates, the application of the solvent system concept to the understanding of acid-base reactions in solution can be quite involved but also serves to allow chemists to apply a detailed understanding of solution chemistry to a wider variety of reactions. However, it is usually much simpler to think about solvent system neutralization reactions using the Lewis acid-base concept.

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6.2.3.10: 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.

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

For example, sulfuric acid ionizes according to the equation:

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

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 $\mathrm{{H_3SO_4}^+}$ and $\mathrm{{HSO_4}^-}$ present in pure sulfuric acid are ~0.02 *M*, much greater than the 10^{-7} *M* H_3O^+ and $\mathrm{OH^-}$ present in pure water.

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

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

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):

$$\mathrm{HA + S} \rightleftharpoons \mathrm{HS^+ + A^-}$$

This equilibrium will favor dissociation of whichever is a stronger acid - HA or $\mathrm{HS^+}$. If the acid is stronger it will mostly dissociate to give $\mathrm{HS^+}$, 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 $\mathrm{HS^+}$ will act as a strong acid and effectively dissociate completely to give the solvent's conjugate acid ($\mathrm{HS^+}$). This also means that the relative acidity of acids stronger than $\mathrm{HS^+}$ 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 $\mathrm{HClO_4}$ 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 $\mathrm{HClO_4}$ and HCl. Both $\mathrm{HClO_4}$ and HCl partly dissociate in MeCN, with the stronger acid $\mathrm{HClO_4}$ 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, $\mathrm{BH^+}$, 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:

$$\mathrm{B + HS} \rightleftharpoons \mathrm{BH^+ + S^-}$$

The position of this equilibrium depends on whether B or $\mathrm{S^-}$ is the stronger base. If the solvent's conjugate base, $\mathrm{S^-}$, is stronger,

then the base B will remain unprotonated and available to act as a base. However, if B is a stronger base than $\mathrm{S^-}$, it will deprotonate the solvent to give $\mathrm{BH^+}$ and $\mathrm{S^-}$. 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 $\mathrm{BH^+}$; otherwise the bases will all be leveled to $\mathrm{S^-}$.

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:

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

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 $\mathrm{LiAlH_4}$).

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6.2.3.11: Non-nucleophilic Brønsted-Lowry Superbases

Non-Nucleophilic Organic Superbases Act as Strong Bases in Organic Solvents but Are Unreactive Towards Other Electrophiles

A variety of strong organic and inorganic bases are available for use in organic synthesis (alkyllithium reagents, diisopropyl amide derivatives, hydrides, and hydroxides). Some of these exhibit poor functional group tolerance owing to their ability to react with electrophilic functional groups. Hence there is considerable interest in the development of bases that can remove hydrogen ions from very weakly acidic organic substrates (*i.e.* like C-H bonds) without reacting with electrophilic functional groups. Classical non-nucleophilic bases used widely in organic chemistry include diisopropylethylamine (DIEA), lithium diisopropylamide (LDA), and the simple and complex ionic hydrides like $\mathrm{CaH_2}^{+2}$ and $\mathrm{LiAlH_4}$. The latter, however, are non-nucleophilic by virtue of their insolubility in organic solvents, on account of which they largely act as bases when an organic substrate interacts with the hydride at a crystal surface.

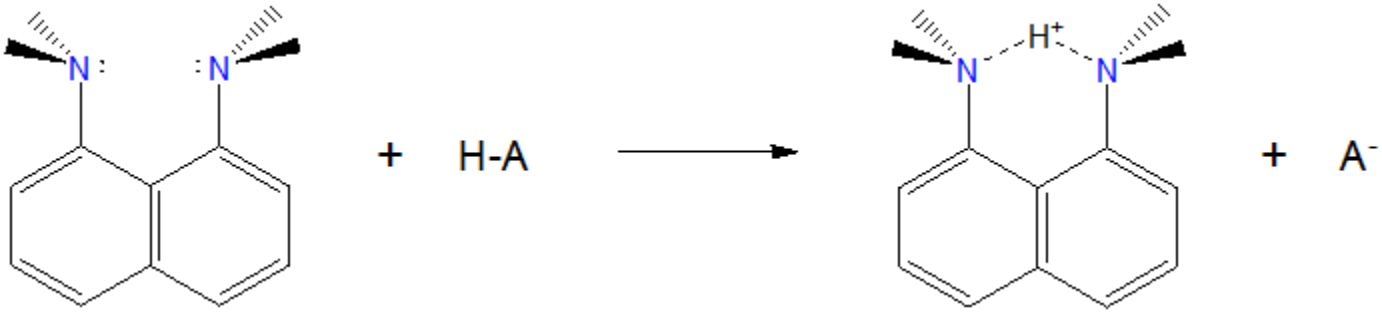
Many strong bases are called superbases in everyday usage. However, more rigorous definitions have been developed to clearly distinguish superbases from simple strong bases. Most of these use some aspect of the thermodynamics of hydrogen ion bonding by 1,8-Bis(dimethylamino)naphthalene as a delimiter between ordinary strong bases and superbases. In other words, by these criteria any base stronger than 1,8-bis(dimethylamino)naphthalene is considered a superbase. By this measure organic superbases may be defined as those having larger proton affinities than 1048 kJ/mol,[1] although most workers use defined superbases as those having a pK_a greater than 1,8-bis(dimethylamino)naphthalene's value of 12.[2]

Non-nucleophilic Organic Superbases Use Charge Delocalization, Proton Chelation, or Both to Tightly Bind Hydrogen Ion

A variety of compounds with a high affinity for hydrogen ions in organic solvents have been specifically developed as strong **non-nucleophilic organic superbases**.[3] Common classes include:

Napthalene-type proton sponges

Napthalene-type proton sponges are two basic groups held in close proximity to one another at the 1 and 8 positions of a napthalene ring. The compound 1,8-Bis(dimethylamino)naphthalene is perhaps the best known superbase of this type and is even sold by the trade name of Proton Sponge™. Its structure is shown below.



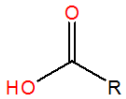
Proton sponge has the typical properties of an organic superbase. Unlike lithium diisopropylamindes and metal hydride reagents, 1,8-Bis(dimethylamino)naphthalene is only weakly basic in water. However, it possesses a very strong affinity for hydrogen ions in organic solvents.

In this case the high basicity of 1,8-Bis(dimethylamino)naphthalene is due to a combination of steric and electronic factors. First, it is a **hydrogen chelator** in that the hydrogen is held in a strong symmetric N---H---N hydrogen bond in its conjugate base. Second, the formation of that hydrogen bond relieves some of the steric strain associated with dimethyl amino groups held close

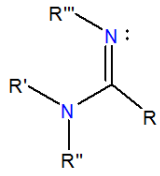
to one another at the 1 and 8 positions on the naphthalene ring.

Aminidines and Guanidenes

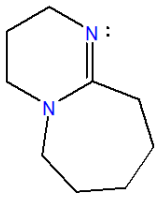
Aminidines are nitrogen derivatives of carboxylic acid derivatives. Acyclic aminidines have pK_a values ~12, similar to that of 1,8-Bis(dimethylamino)naphthalene, although cyclic aminidines are several orders of magnitude higher. For example, DBU is estimated to exhibit a pK_a value of 24.3 in MeCN.[4] Examples of aminidine superbases include the organic catalysts 1,8-Diazabicyclo(5.4.0)undec-7-ene (DBU) and 1,5-Diazabicyclo(4.3.0)non-5-ene (DBN), and vinamidinium superbases, which bind hydrogen ion at the imine nitrogen.



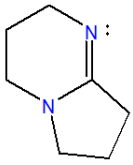
Carboxylic acid



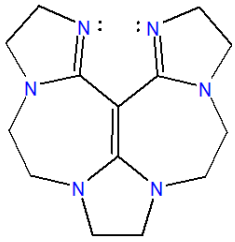
aminidene



1,8-Diazabicyclo(5.4.0)undec-7-ene (DBU)

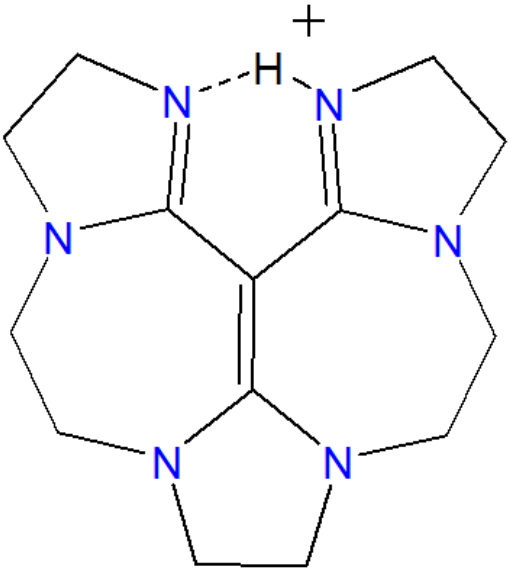


1,5-Diazabicyclo(4.3.0)non-5-ene (DBN)

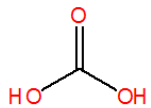


A vinamidinium superbase

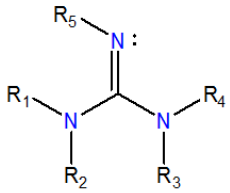
Of these the vinamidinium superbases are hydrogen ion chelators.



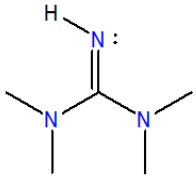
Guanidenes are nitrogen analogues of carbonate and bind hydrogen ion at a nitrogen lone pair just as aminidines do, although monomeric guanidines are slightly more basic (pK_a 13) than analogous aminidines (pK_a 12). Common classes of guanidene superbases include pentalkyl and bicyclic guanidines, shown below.



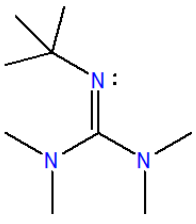
Carbonic acid



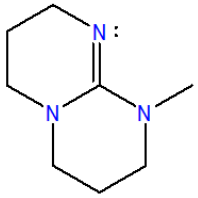
Guanidiene



1,1,3,3-Tetramethylguanidine (TMG)

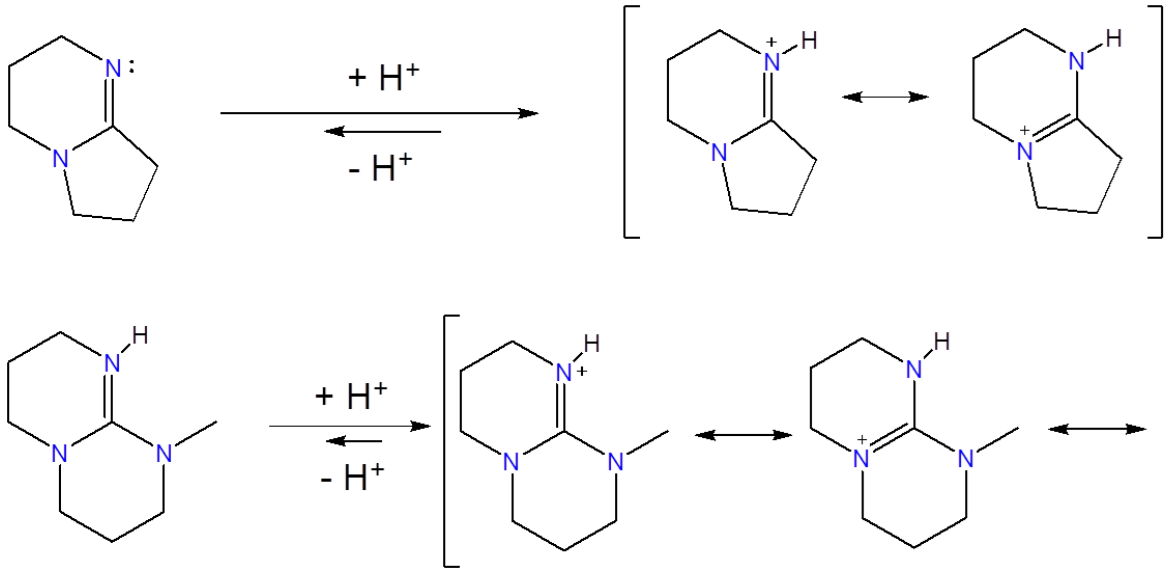


a pentalkyl guanidine superbase



a bicyclic guanidine superbase

The high basicity of aminidines and guanidines is derived from the ability of these systems to delocalize charge in the protonated form.



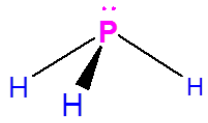
Exercise 6.2.3.11.1

Use the structure of protonated aminidines and guanidines to explain why guanidines are stronger bases than their aminidine analogues.

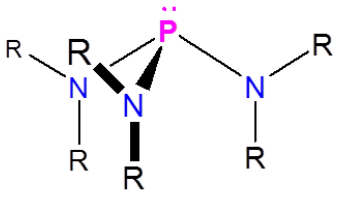
Answer available at the end of this section.

Phosphatrane-type Superbases

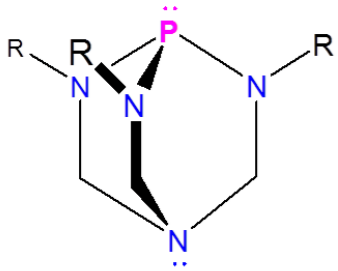
These exhibit enhanced basicity at the phosphorus atom of a special type of azaphosphine called a **proazaphosphatrane**:



phosphine

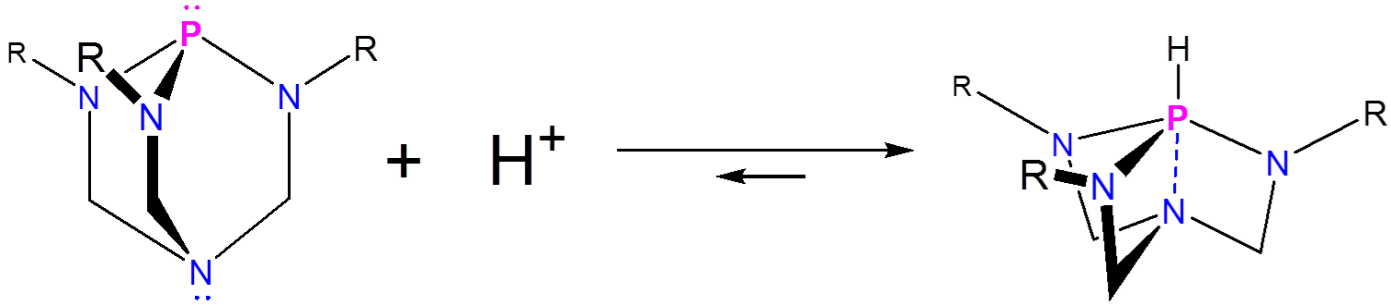


triazaphosphine



proazaphosphatrane
(Verkade-type superbase)

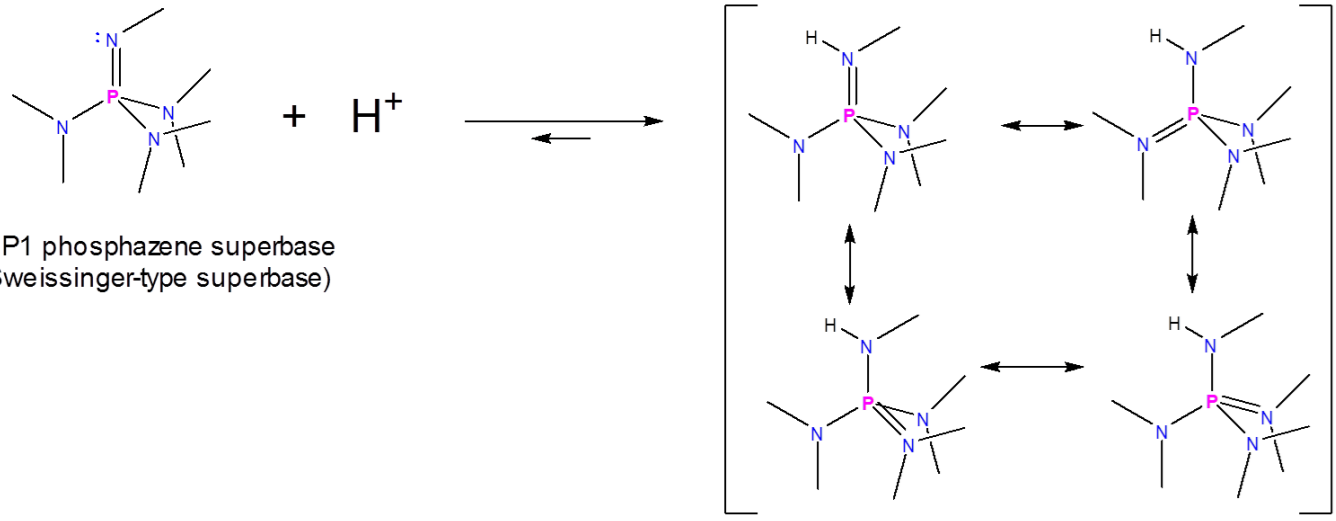
Of these the best known is Verkade's superbase, which is estimated to have a pK_a of 29 in acetonitrile,[5] meaning it is considerably more basic than aminidine and guanidine type superbases. The key to the remarkable basicity of Verkade's superbase is the ability of the proazaphosphoatrane's amine to stabilize the protonated azaphosphine through the formation of a P-N bond, giving a pseudo trigonal bipyramidal phosphorous.



These interactions are so stabilizing that the transannular amine nitrogen exhibit no basicity, even when superacids like Magic Acid are added.[6]

Phosphazene Superbases

Phosphazene superbases, also known as **Schwesinger superbases**, function similarly to aminidines and guanidines in that they bind a hydrogen ion at an imine nitrogen to give a resonance-stabilized cation. It is just that in this case the imine is that of a phosphazene and the greater resonance stabilization of the resulting cation means that they exhibit greater basicity. One phosphazene superbase has been reported to have a pK_a of 42 in acetonitrile.



The P1 phosphazene superbase
(a Sweissinger-type superbase)

References

1. Gal, J.-F.; Maria; P.-C.; Raczynska, E. D. Thermochemical aspects of proton transfer in the gas phase. *Journal of Mass Spectrometry*, 2001; 36: 699–716
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3. Ishikawa, T. Superbases for Organic Synthesis: Guanidines, Amidines, Phosphazenes and Related Organocatalysts; Wiley: New York, 2009.
4. Unless otherwise noted pK_a values other than that reported for 1,8-Bis(dimethylamino)naphthalene are taken from Kaupmees, K.; Trummal, A.; Leito, I. (2014). "Basicities of Strong Bases in Water: A Computational Study". *Croat. Chem. Acta.* **87**: 385–395. doi:10.5562/cca2472
5. Kovačević, B.; Barić, D.; Maksić, Z. B., Basicity of exceedingly strong non-ionic organic bases in acetonitrile —Verkade's superbase and some related phosphazenes. New Journal of Chemistry 2004, 28 (2), 284-288.
6. Akiba, K-Y. Organic Main Group Chemistry; Wiley: New York, 2011.

Answers

Exercise 6.2.3.11.1

There is greater delocalization of charge in guanidinium ions. According to the resonance picture of bonding, in guanidinium ions the positive charge is delocalized over three nitrogen atoms while in amidinium ions it is only delocalized over two.

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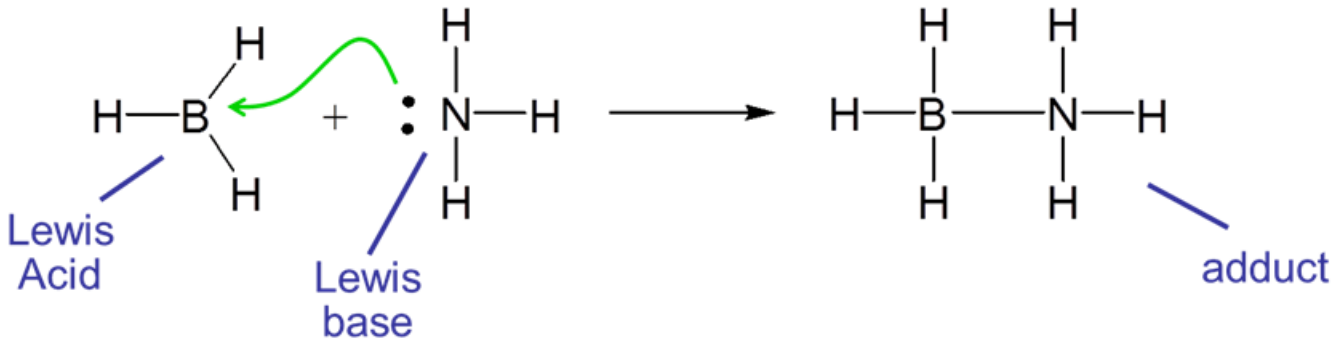
6.2.4: Lewis Concept and Frontier Orbitals

The Lewis acid-base concept generalizes the Brønsted and solvent system acid base concepts by describing acid-base reactions in terms of the donation and acceptance of an electron pair.

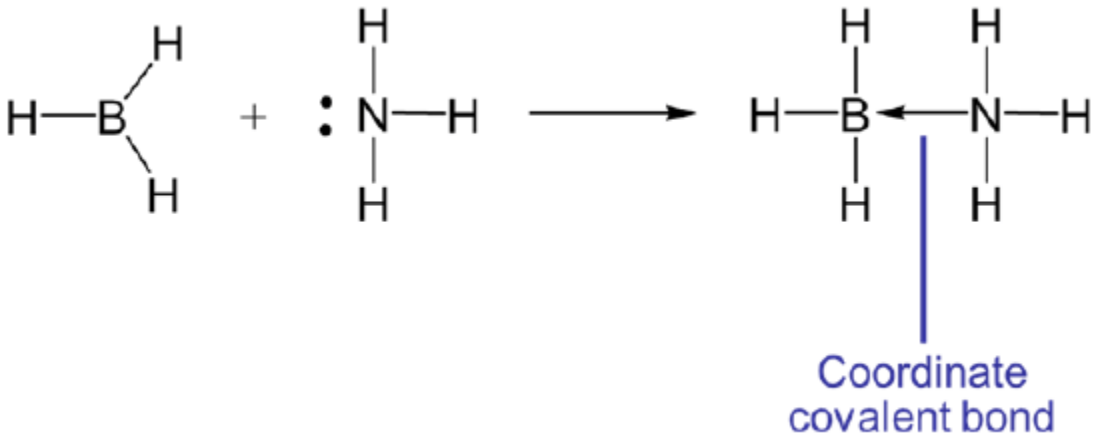
Under the Lewis definition

- **Lewis acids** are electron pair acceptors
- **Lewis bases** are electron pair donors

and in Lewis acid-base reactions, a Lewis base donates an electron pair to the Lewis acid, which accepts it. The reaction between borane, BH_3, and NH_3 is the classic example:



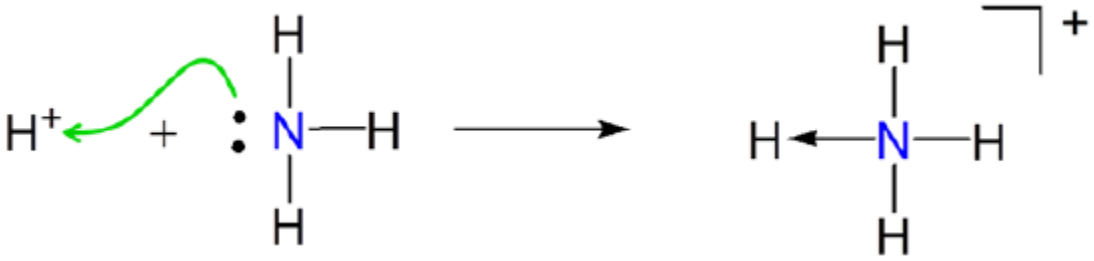
In this case the Lewis acid-base reaction results in the formation of a bond between BH_3, and NH_3. When the acid and base combine to form a larger unit, that unit is said to be an adduct, and the resulting bond is said to be a coordinate covalent or dative bond. Such coordinate covalent bonds are often represented by an arrow that indicates the direction of electron donation from the base to the acid. For instance, the reaction between BH_3 and NH_3 could also have been written as



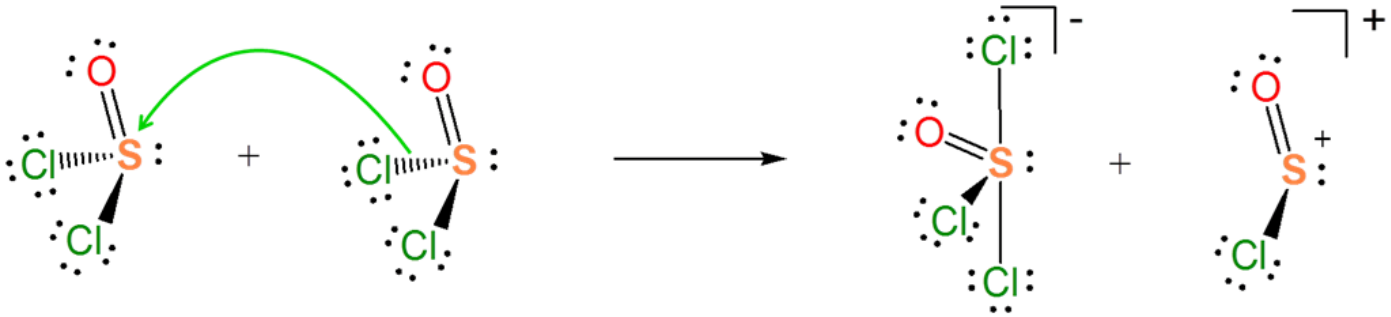
The arrow notation for the coordinate covalent bond is really just a convenient formalism - a bookkeeping tool to help keep track of where the electrons came from and where they might return if the reverse reaction occurs. In actuality a coordinate covalent bond is just an ordinary covalent bond like any other.

For example, in Brønsted acid-base reactions, the hydrogen ion is an acid because it accepts an electron pair from the Brønsted

base. Consequently, under the Lewis acid-base concept, Brønsted acid-base reactions involve the formation of an adduct between H^+ and a base.



The Lewis acid-base concept nicely explains ionization reactions involving nonaqueous solvents. For instance, the autoionization of $SOCl_2$ is an acid-base reaction between two $SOCl_2$ molecules.

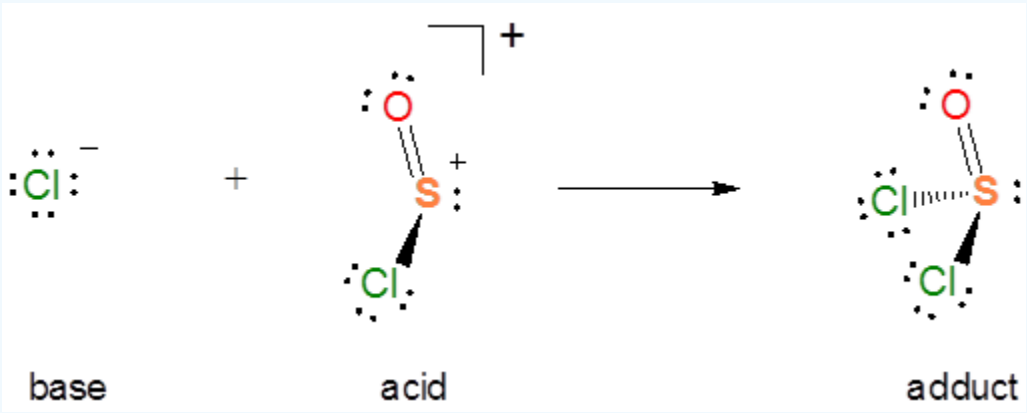


Example 6.2.4.1

Explain how the autoionization of $SOCl_2$ is a Lewis acid-base displacement reaction.

Solution

In the autoionization of $SOCl_2$ the pair of electrons donated comes from the S-Cl bond, and the S-Cl bond is broken to give a lone pair bearing a Cl^- base and an $SOCl^+$ Lewis acid fragment. If you are having trouble seeing how this works, it can be instructive to consider the reverse of this process. It is a Lewis acid-base reaction to give a Lewis acid-base adduct:

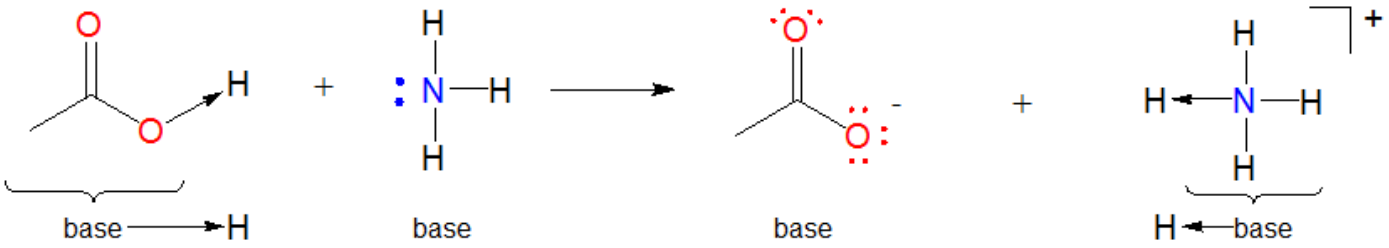


From the autoionization reaction it is also apparent that $SOCl_2$ itself acts as a Lewis acid towards the liberated Cl^-. So the autoionization reaction involves a transfer of the Cl^- base between the two Lewis acids - a Lewis acid-base displacement reaction.



It can be helpful to keep several distinctions in mind when using the Lewis acid-base concept to describe chemical reactions.

1. Many Lewis-Acid base reactions are displacement reactions. This is because the hydrogen ion is usually bound to something at the start of the reaction. In such cases the Lewis acid H^+ unit is transferred from one Lewis base to another :



Such acid-base reactions are sometimes called displacement reactions since the base group in the initial Lewis acid-base complex is displaced by the incoming Lewis base to generate another complex.

2. Substances are sometimes considered amphoteric because they exhibit Lewis acidity and basicity at different types of atomic centers. The classic example is aluminum hydroxide, $\mathrm{Al(OH)_3}$. In water $\mathrm{Al(OH)_3}$ can act as a Lewis acid towards OH^- ion. The reaction occurs by formation of an adduct at $\mathrm{Al(OH)_3}$'s Al^{3+} center:

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

Notice that in addition to acting as a Lewis acid, in this reaction $Al(OH)_3$

- does not act as a Brønsted acid or base since no H^+ ion transfer occurs
- but does act as an Arrhenius acid since OH^- ion is consumed from solution, decreasing $[OH^-]$ and increasing $[H^+]$

In water $\mathrm{Al(OH)_3}$ also acts as a Lewis base towards H^+ through the lone pairs on its hydroxide ligands.

$$\mathrm{Al(OH)_3 + 3\,H^+ + 3\,H_2O \rightarrow Al(H_2O)_6^{3+}}$$

Notice that in addition to acting as a Lewis base, in this reaction $\mathrm{Al(OH)_3}$ also acts as a

- Brønsted base, since a H^+ ion is transferred onto the OH^- ligand
- Arrhenius base, since H^+ ion is consumed from solution, decreasing $[H^+]$
- Lewis acid at its Al^{3+} center, since Al-O metal-ligand bonds are formed

Substances that rapidly undergo Lewis acid-base reactions are called nucleophiles and electrophiles.

Two factors govern the course of chemical reactions - thermodynamics and kinetics. Thermodyamics determines what possible fates of the reaction can take place while kinetics determines which among those possible fates will take place quickly under a particular set of reaction conditions. Because of this, it can be helpful to distinguish Lewis acids and bases that tend to undergo reaction quickly with one another from those which do so more slowly. For this reason, synthetic chemists use the terms electrophile and nucleophile to refer to Lewis acids and bases that react quickly:

- electrophile - Lewis acids that rapidly react with a given Lewis base or class of Lewis bases are said to be good electrophiles
- nucleophile - Lewis bases that rapidly react with a given Lewis acid or class of Lewis acids are said to be good nucleophiles

The electrophile-nucleophile concept is sometimes referred to as the Ingold-Robinson acid-base concept after two organic chemists who did much to illustrate the utility of thinking about Lewis acid-base reactions in kinetic terms.

Several distinctions that should be kept in mind when using the electrophile-nucleophile/Ingold-Robinson concept to think about chemical reactivity:

1. Whether a given Lewis acid or base is able to react rapidly depends on the reaction conditions and the substrate (substance it is reacting with). This means that in principle, the terms nucleophile and electrophile should not be used without appropriately qualifying what the substances act as a nucleophile or electrophile towards and under what conditions. Unfortunately this is rarely done. In such cases, the conditions and substrate must be inferred from the context. For instance, when you learned that the chloride ion is a good nucleophile when studying organic chemistry, what was meant is that chloride is a good nucleophile towards electrophilic carbon atoms in organic molecules.

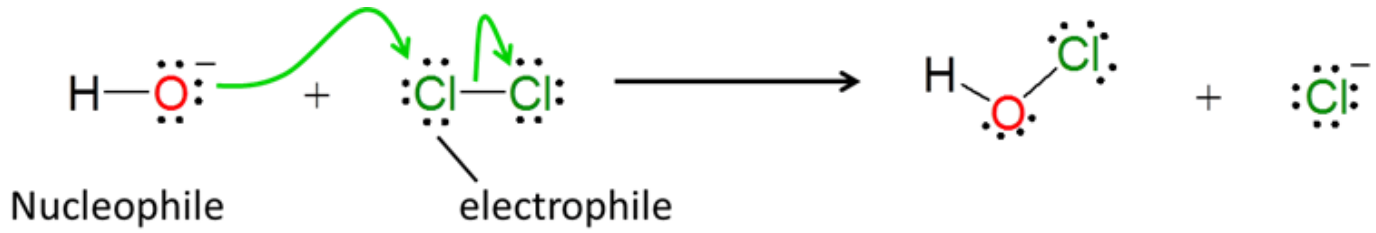
2. Acid and base strength and electrophilicity-nucleophilicity are not exactly the same thing. In many contexts where Lewis acids and bases are classified as electrophilic and nucleophilic substances, it is common to also refer to substances as being good acids or bases on the basis of their Brønsted acidity and basicity. In these contexts, the terms acid and base typically refer to the thermodynamic propensity of a substance to give and accept hydrogen ions while the terms nucleophile and electrophile refer to a substance's kinetic propensity to react with carbon-based Lewis acids and bases, respectively.

A substance may be both a good nucleophile and a strong Brønsted base. For instance, alkyllithium carbanion reagents and alkali metal hydrides are strong bases and good nucleophiles towards electrophilic carbon atoms in organic solvents at moderate temperatures. However, this is not always the case. Under such conditions iodide ion, I^-, is a good nucleophile towards electrophilic carbon atoms but is a poor Brønsted base (it is the conjugate of the strong acid HI). In fact, for the halide ions the order of Brønsted basicity is the opposite of the order of nucleophilicity towards electrophilic carbon:

stronger Brønsted base: F^-, Cl^-, Br^-, I^-: weaker Brønsted base

better nucleophlie: I^-, Br^-, Cl^-, F^-: poorer nucleophile

3. Although the nucleophile-electrophile concept is most often used to describe organic reactions, it is also useful for describing inorganic reactions as well. For instance, the formation of hypochlorite ion in chlorine water possibly involves nucleophilic attack of hydroxide on an electrophilic chlorine atom in an S_N2 type process:



The Usanovich Acid-base Concept

The Usanovich Acid-base concept encompasses a wider range of reactions than the Lewis acid-base concept but is perhaps too general to serve as a convenient framework for understanding reaction chemistry. The Usanovich acid-base concept was developed by the Russian chemist Mikhail Usanovich and extends the Lewis acid-base concept's definition of acids and bases as electron pair donors and acceptors even further. Within the Usanovich definition:

- Acids are anything that accepts electrons, increases cation concentrations, decreases anion concentrations, or reacts with bases
- Bases are anything that donates electrons, increases anion concentrations, decreases cation concentrations, or reacts with acids

These definitions essentially expand the Lewis definition by removing the requirement that the electrons donated or accepted be a pair and practically mean that Usanovich acid-base reactions include Lewis acid-base reactions plus oxidation-reduction reactions. In other words:

- Usanovich acids are Lewis acids plus oxidants
- Usanovich bases are Lewis bases plus reductants

Under this definition BF_3, Fe^{3+}, and $[Fe(CN)_6]^{3-}$ all act as acids, and : NH_3, CN^-, and Zn are all bases:

$$\underset{acid}{BF_3} + \underset{base}{NH_3} \rightarrow F_3B-NH_3$$

$$\underset{acid}{Fe^{3+}} + 6\underset{base}{CN:^-} \rightarrow [Fe(CN)_6]^{3-}$$

$$\underset{acid}{2[Fe(CN)_6]^{3-}} + \underset{base}{Zn} \rightarrow 2[Fe(CN)_6]^{3-} + Zn^{2+}$$

However, notice that while it is easy to think about how any acids might interchangeably react with a given base (and vice versa), under the other acid-base concepts chemists have found it more difficult to think about reactions between oxidants/reductants and Lewis acids and bases. For example, it is difficult to think about how a reaction between BF_3 and Zn metal might occur. Would two Zn donate a pair of electrons to the BF_3? For this reason, most chemists find it more convenient to think about Lewis acid-base and redox reactions under separate categories rather than unite them under the Usanovich definition.

$$\underset{oxidant}{2[Fe(CN)_6]^{3-}} + \underset{reductant}{Zn} \rightarrow 2[Fe(CN)_6]^{3-} + Zn^{2+}$$

Again, it can be helpful to remember Huheey's dictum that deciding between acid-base concepts is not a matter of which concept is the most correct but rather of which is more convenient for a given application.

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6.2.4.1: The frontier orbital approach considers Lewis acid-base reactions in terms of the donation of electrons from the base's highest occupied orbital into the acid's lowest unoccupied orbital.

Another way the Lewis-Acid base concept is widely employed for understanding chemical reactivity is through the frontier orbital approach to chemical reactions. The frontier orbital concept conceptualizes chemical bonding and reactivity in terms of the interactions between frontier orbitals on the chemical species undergoing an interaction (*e.g.* molecules, atoms, ions, or groups as they interact to form a bond or undergo a reaction). Frontier orbitals are those at the frontier between occupied and unoccupied. They are often taken to be the highest energy occupied and lowest energy unoccupied molecular orbitals, called the HOMO and LUMO levels. However, it can sometimes be more convenient to think about them as atomic orbitals or Valence Bond approach-derived orbitals. When developing rough qualitative frontier orbital descriptions of the orbital interactions involved in a given system, the choice of what types of orbitals to use is often a matter of what is the most informative and convenient.

In particular, the frontier orbital concept envisions a Lewis acid-base interaction as involving an interaction between some of the frontier orbitals of the Lewis acid and base, specifically the donation of electrons from the base's HOMO level into the acid's LUMO level. For example, in the frontier orbital approach, adduct formation between NH_3 and BH_3 involves the donation of electrons from ammonia's a_1 HOMO into BH_3's a_2'' LUMO level.

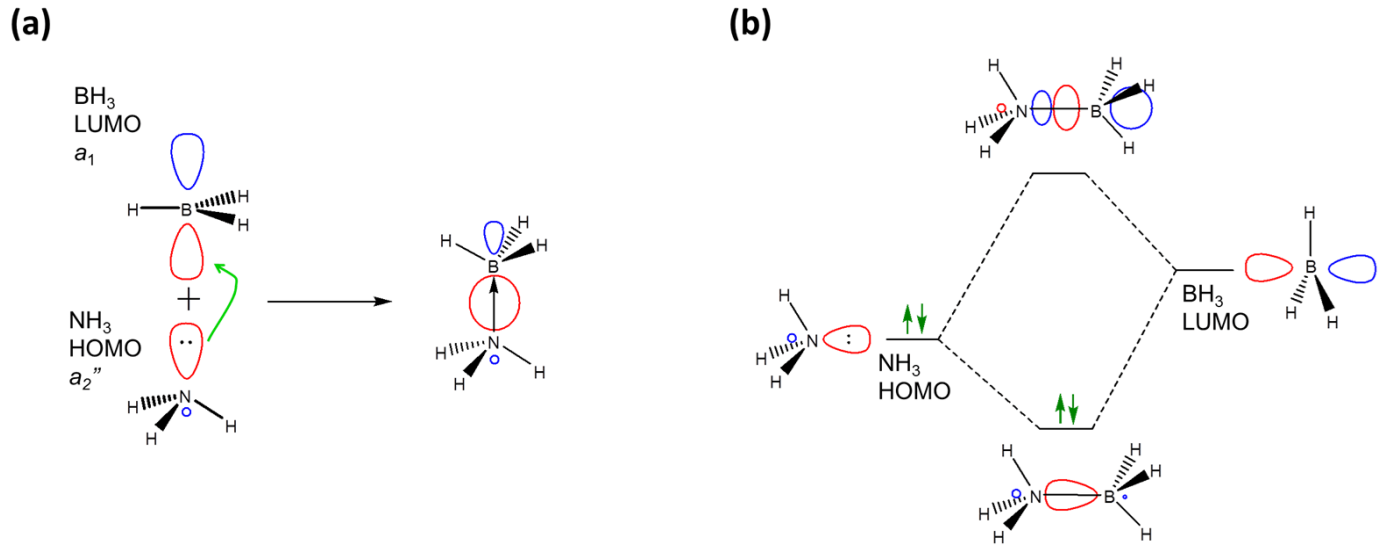


Figure 6.2.4.1.1. Frontier orbital picture of adduct formation between ammonia and borane. (a) As NH_3 and BH_3 approach one another, interaction between the NH_3 HOMO and BH_3 LUMO gives a bonding MO. (b) Partial molecular orbital diagram for $NH_3 \rightarrow BH_3$ showing the stabilization of the base (NH_3) lone pair in a sigma bonding MO upon adduct formation.

As expected when two orbitals of the appropriate symmetry combine, the result of the interaction is the formation of a lower energy bonding orbital between the acid and base (Figure 6.2.4.1.1). Since it is occupied by an electron, the net result of the interaction is the lowering of the base's lone pair energy as it interacts with the Lewis acid. In this case the interaction just follows the general pattern for Lewis-Acid base adduct formation, which is:

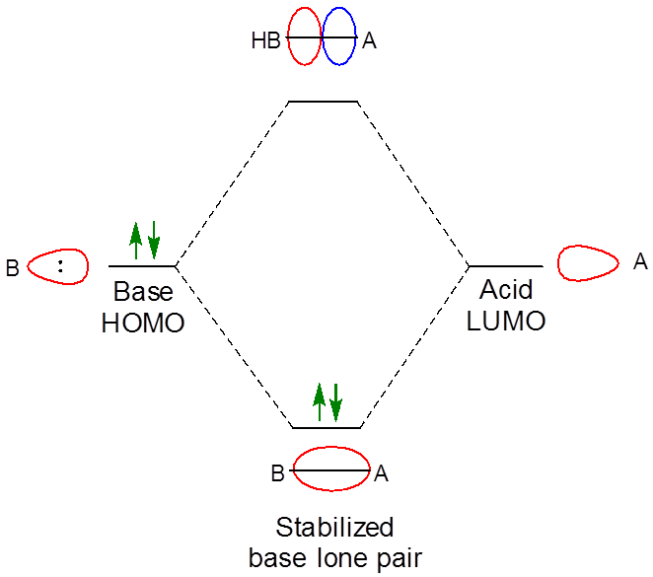
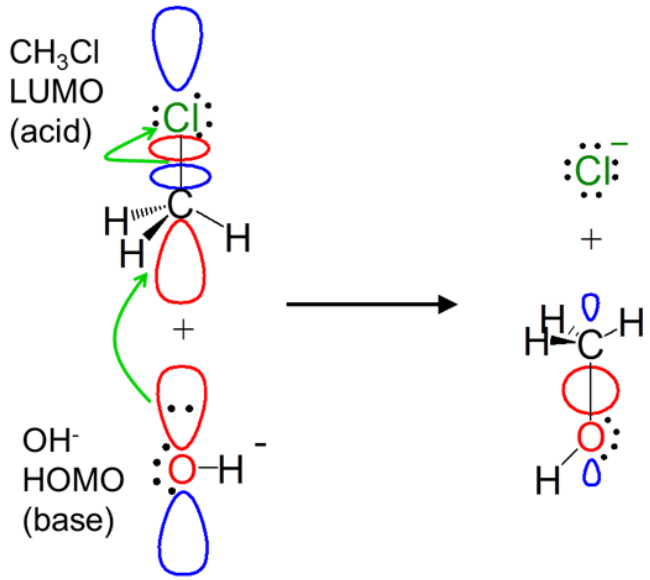


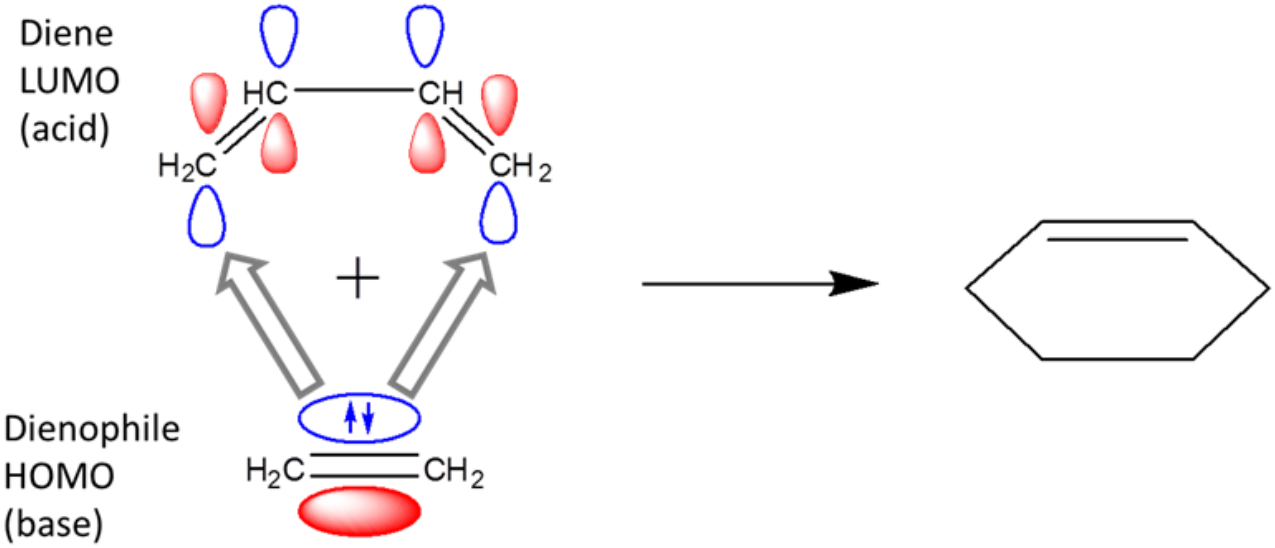
Figure 6.2.4.1.2. Generalized frontier orbital picture for adduct formation between a Lewis base (B) and a Lewis acid (A) involving stabilization of the lone pair of the base HOMO by formation of a bonding orbital with the acid LUMO. The relative energies of the acid LUMO and base HOMO affect the character of the bonding and antibonding MOs but are otherwise unimportant in determining the general features of the interaction. In some cases the base HOMO is higher in energy; in others the acid LUMO is higher in energy; in still others they are equal in energy. In any case the net result is the stabilization of the base lone pair.

The frontier orbital concept illuminates the orbital interactions involved in reactions. For instance, from a frontier orbital perspective the alkyl halide substitution reaction between hydroxide and CH_3Cl via the S_N2 mechanism involves a Lewis acid-base interaction:

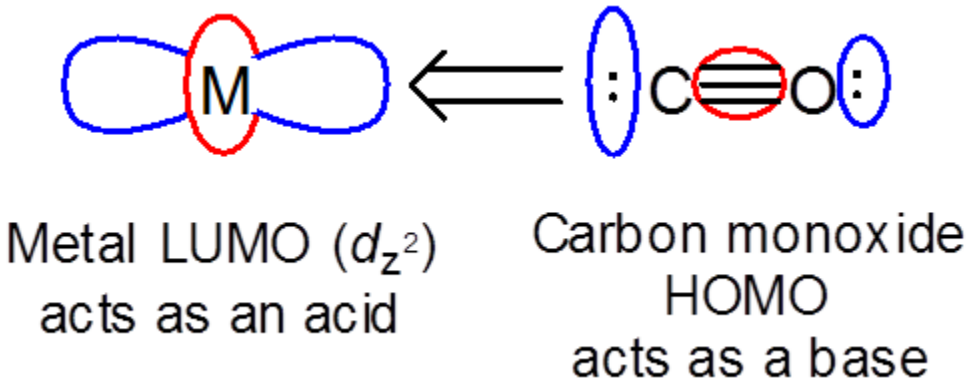


Notice how the frontier orbital approach even explains the displacement of the chloride leaving group. The donation of electrons from the hydroxide HOMO populates the antibonding CH_3Cl LUMO, breaking the C-Cl bond.

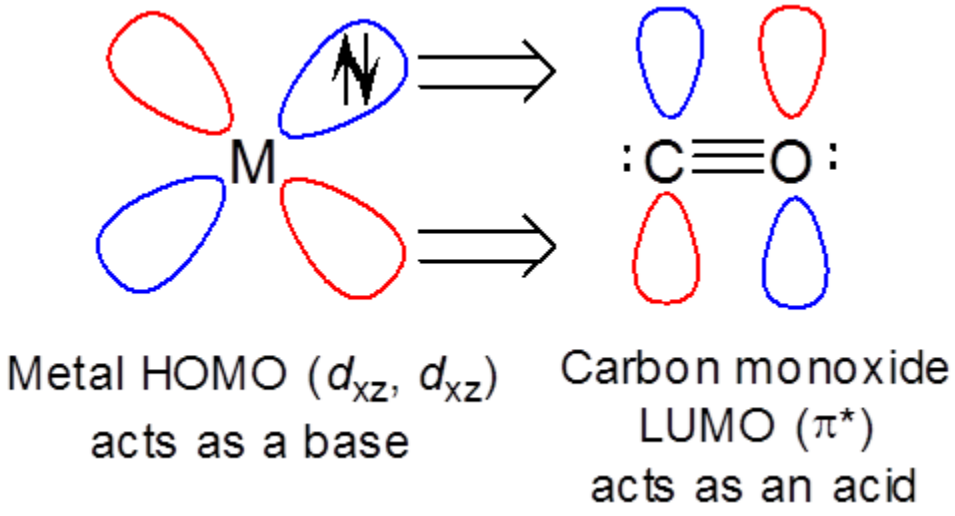
With the frontier orbital approach, it becomes apparent that pericyclic reactions are Lewis acid-base reactions. For example, in the Diels-Alder reaction, the dienophile acts as a Lewis base and the diene as a Lewis acid.



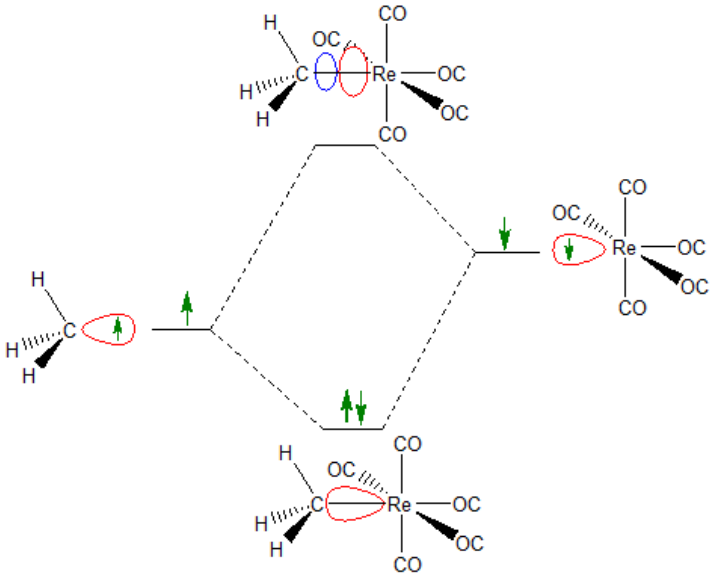
The orbital interactions involved in a given reaction can include both reactants acting as both an acid and base. In these cases the HOMO of each reactant interacts with the LUMO of the other. A good example of this involves Π-type interactions between a metal ion with occupied *d* orbitals and a pi-acceptor ligand. The ligand acts as a base and the metal as an acid to give a M-CO single bond:



However, the metal can also act as a base towards the ligand LUMO (π^*) orbitals.



The frontier orbital concept can also be used to describe interactions between one or more singly occupied frontier orbitals. In fact, when approximate molecular orbital diagrams are being constructed, it can often be helpful to focus on one or two particularly instructive interactions. In these cases, it is sometimes convenient to think about a chemical bond as involving the formation of bonding and antibonding interactions between singly occupied frontier orbitals on different molecular fragments. For instance, when thinking about the chemistry of $CH_3Re(CO)_5$ it can sometimes be helpful to think about the C-Re bond as arising from the interaction between a singly-occupied sp^3 type orbital on a CH_3 group and a singly occupied d^2sp^3 orbital on the Re.



In introducing singly occupied orbitals, the frontier orbital concept formally handles interactions that the Lewis acid-base concept does not, since Lewis acid-base behavior is formally confined to the acceptance and donation of electron *pairs*.

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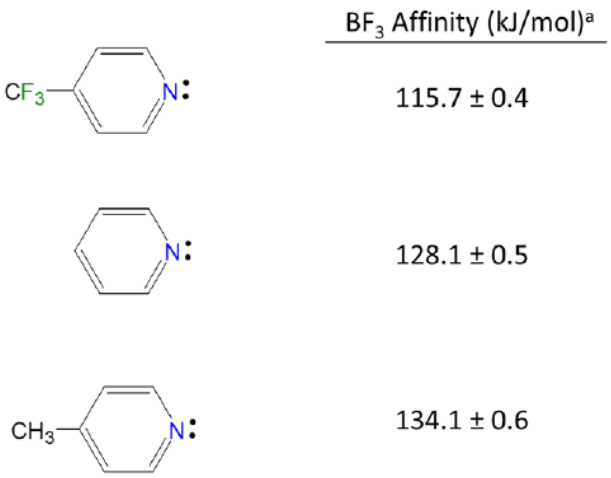
- 6.4.1: The frontier orbital approach considers Lewis acid-base reactions in terms of the donation of electrons from the base's highest occupied orbital into the acid's lowest unoccupied orbital. by Stephen M. Contakes is licensed CC BY 4.0.

6.2.4.2: All other things being equal, electron withdrawing groups tend to make Lewis acids stronger and bases weaker while electron donating groups tend to make Lewis bases stronger and acids weaker

The electrons donated from a Lewis base to a Lewis acid in a Lewis acid-base reaction are donated and accepted at particular atomic centers. For instance, the formation of an adduct between ammonia and BF_3 involves the donation of the lone pair on the ammonia nitrogen atom to the Lewis acid site on BF_3.



Because Lewis acid-base reactions involve electron donation and acceptance at particular sites, substituent groups which alter the electron density at a site through inductively donating or withdrawing electron density will affect the Lewis acid-base properties of that site. For instance, the BF_3 affinities of 4-substituted pyridines increase slightly as the substituent on the aromatic ring is changed from electron donating Me to electron withdrawing CF_3.



a) Data from Laurence, C.; Gal, J.-F. o., *Lewis basicity and Affinity Scales: Data and Measurement. John Wiley: Chichester, West Sussex, U.K., 2010; pp. 91-101.*

Substituent inductive effects are much as one might predict. Since Lewis bases donate electron pairs and Lewis acids accept them:

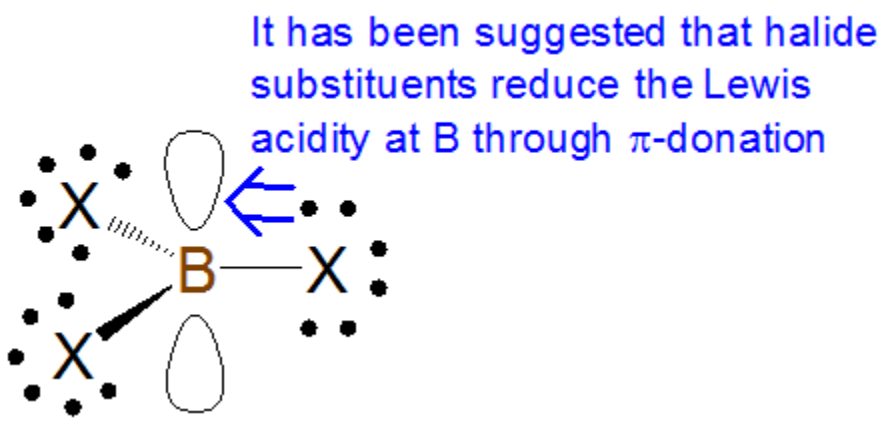
- electron withdrawing substituents tend to decrease the Lewis basicity of basic sites while electron donating substituents increase site Lewis basicity by making them more electron rich.
- electron withdrawing substituents increase the Lewis acidity of acidic sites by making those sites more electron deficient while electron donating substituents tend to decrease Lewis acidity by making sites less electron deficient.

Nevertheless it can be difficult to predict substituent-based trends in Lewis acidity and basicity by inductive effects alone. This is because inductive effects are modest and often exists in competition with other substituent effects, such as

- Steric effects, discussed in section 6.4.7
- Hardness effects, discussed in section 6.6
- π-donation and acceptance effects, which can increase or decrease electron density at a given site as well as create an energy barrier for any structural distortions that might occur upon adduct formation.

Avoid misconceptions about the impact ofπ donation and acceptance on Lewis acid-base affinity

As with σ-based induction effects, π-donation tends to increase Lewis basicity and decrease Lewis acidity while π-withdrawal tends to decrease Lewis basicity and increase Lewis acidity. However, care needs to be taken in assessing the effect of π -donation effects on Lewis acidity and basicity. For example, some textbooks claim that the Lewis acidity of boron trihalides is dominated by the reduction of boron acidity through π-donation from the halide substituents:

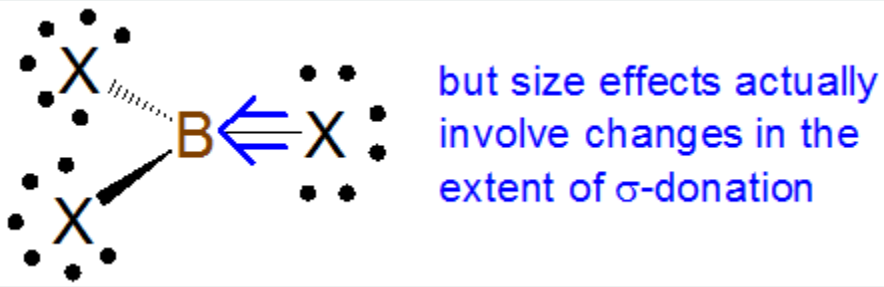


According to this explanation, the extent of this π-donation decreases down the halogen group as the boron-halogen bond distance decreases. This is consistent with the observed trend in Lewis acidity of the boron trihalides towards most bases, which runs counter to that suggested by inductive effects alone:

$$BI_3 > BBr_3 > BCl_3 >> BF_3$$

However, computational work suggests that this explanation is incorrect, since

- atomic size effects are important mainly for substituents in which the connected atom is in row 3+ or higher;
- atomic size effects mainly involve changes in the extent of σ-overlap. In other words, the larger halogens are less able to reduce the electron deficiency at the boron center through σ interactions while π-interactions play little or no role.



References:

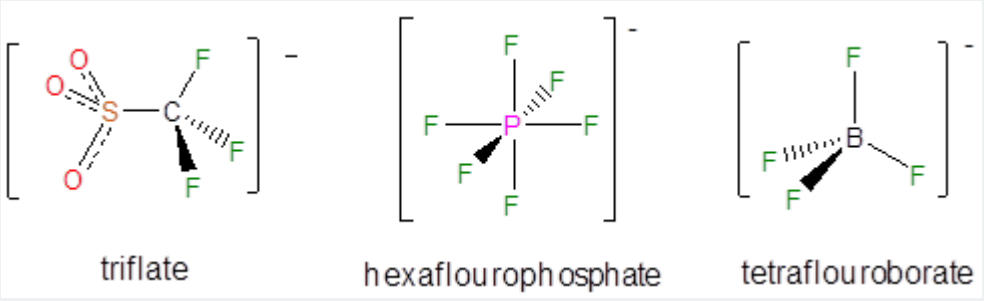
1. Plumley, J. A.; Evanseck, J. D., Periodic Trends and Index of Boron Lewis Acidity. *The Journal of Physical Chemistry A* 2009, 113 (20), 5985-5992.

2. Jupp, A. R.; Johnstone, T. C.; Stephan, D. W., Improving the Global Electrophilicity Index (GEI) as a Measure of Lewis Acidity. *Inorganic Chemistry* 2018, 57 (23), 14764-14771.

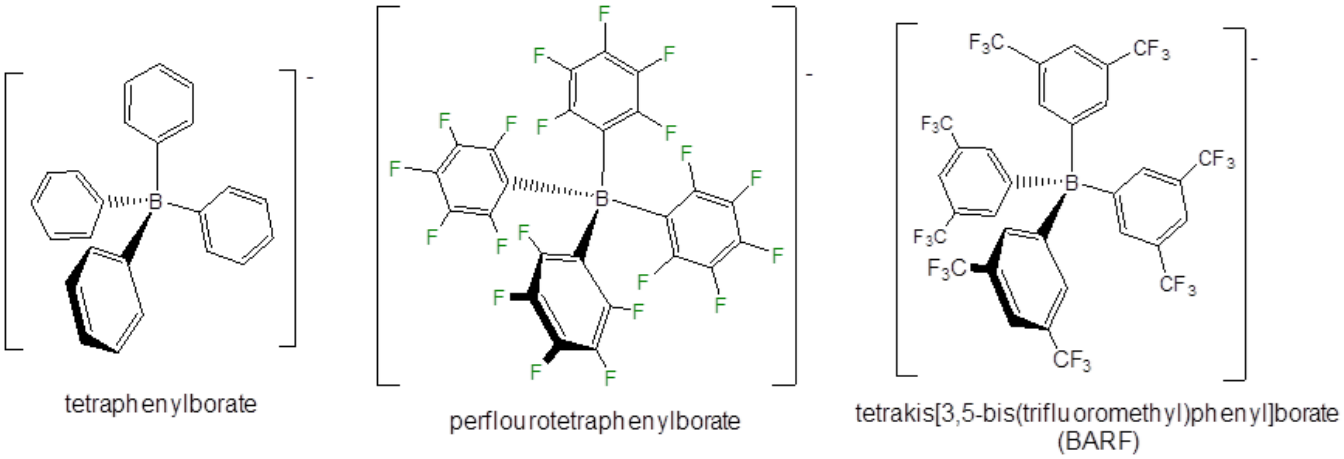
The conjugate bases of many Brønsted superacids have electron-withdrawing substituents that make them such poor Lewis bases that they are useful as noncoordinating anions.

The nonreactivity of Brønsted superacids' conjugate bases towards hydrogen ions is often mirrored in nonreactivity towards other Lewis Acids/electrophiles, most notably metals. This makes these substances useful as inert or noncoordinating ions, although since all are reactive towards suitably electrophilic centers, they are perhaps better understood as weakly coordinating.

A number of noncoordinating anions are commonly used in synthetic and other applications. The conjugate base of perchloric acid, perchlorate, was a common noncoordinating inert anion in classical coordination chemistry and continues to be used widely in electrochemistry. In contrast, the conjugate bases of triflic acid, hexafluoroboric acid, and tetrafluoroboric acid are now more commonly used as counterions for isolating reactive cations.



Even less reactive noncoordination anions include derivatives of tetraphenylborate, particularly those with electron withdrawing substituents.



Other classes of noncoordinating ions include fluoroantimonate clusters, derivatives of the carborane anion ($CB_{11}H_{11}^-$), and fluorinated aluminum tetraalkoxides.

References

Engesser, T. A.; Lichtenthaler, M. R.; Schleep, M.; Krossing, I., Reactive p-block cations stabilized by weakly coordinating anions. *Chemical Society reviews* **2016**, *45 (4)*, 789-899.

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- 6.4.2: All other things being equal, electron withdrawing groups tend to make Lewis acids stronger and bases weaker while electron donating groups tend to make Lewis bases stronger and acids weaker by Stephen M. Contakes is licensed CC BY 4.0.

6.2.4.3: The electronic spectra of charge transfer complexes illustrate the impact of frontier orbital interactions on the electronic structure of Lewis acid-base adducts

When a Lewis acid-base adduct is formed, electron density and negative charge are transferred from the Lewis base to the acid.

The formation of a Lewis-acid base complex involves the transfer of electron density from the base to the acid.



Figure 6.4.2.6.2.4.3.1.

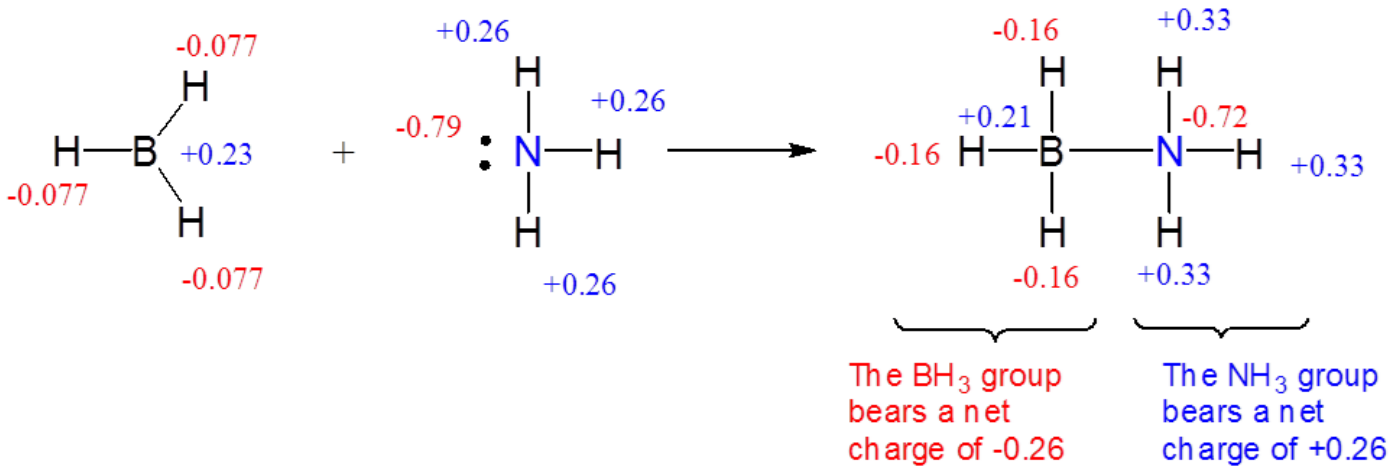


Figure 6.4.2.6.2.4.3.1. Calculated change in atomic charge distribution upon formation of an adduct between BH_3 and NH_3 in the gas phase. All partial charges were calculated for geometry-optimized molecules at the 6-31G** level.

Weakly bound Lewis acid-base adducts in which charge is incompletely transferred are called charge transfer complexes.

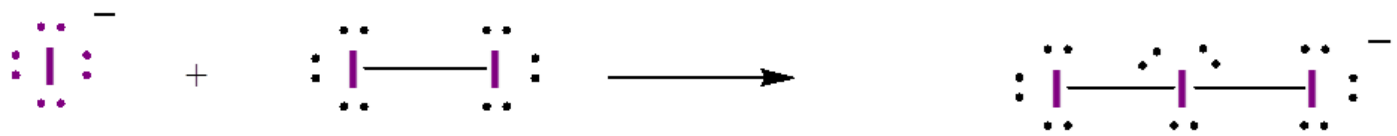
In many weakly bound Lewis acid-base complexes, the transfer of electron density and, consequently, charge from the base group to the acid group is only partial:

$$A + B \rightleftharpoons A^{\delta-}B^{\delta+}$$

Such Lewis acid-base adducts are commonly called **charge transfer complexes (CT complexes)** or **donor-acceptor complexes (DA complexes)**. In these

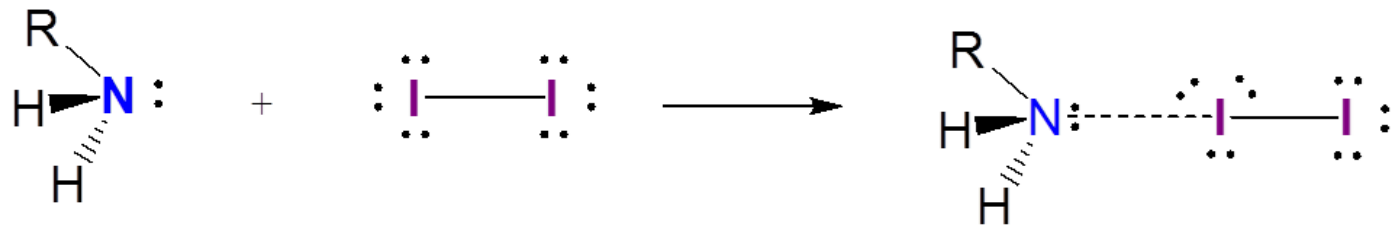
- the base is called the **donor (D)** since it is a net donor of electrons and, consequently, their negative charge
- the acid is called the **acceptor (A)** since it is a net acceptor of electrons and, consequently, their negative charge

A particularly well-known class of charge transfer complexes is the iodine charge transfer complexes. In iodine charge transfer complexes the I_2 acts as a Lewis acid. This is possible since iodine is a Row 3+ element and so is capable of forming hypervalent complexes on reaction with a Lewis base. For example, I_2 reacts with I^- to give the triiodide ion.

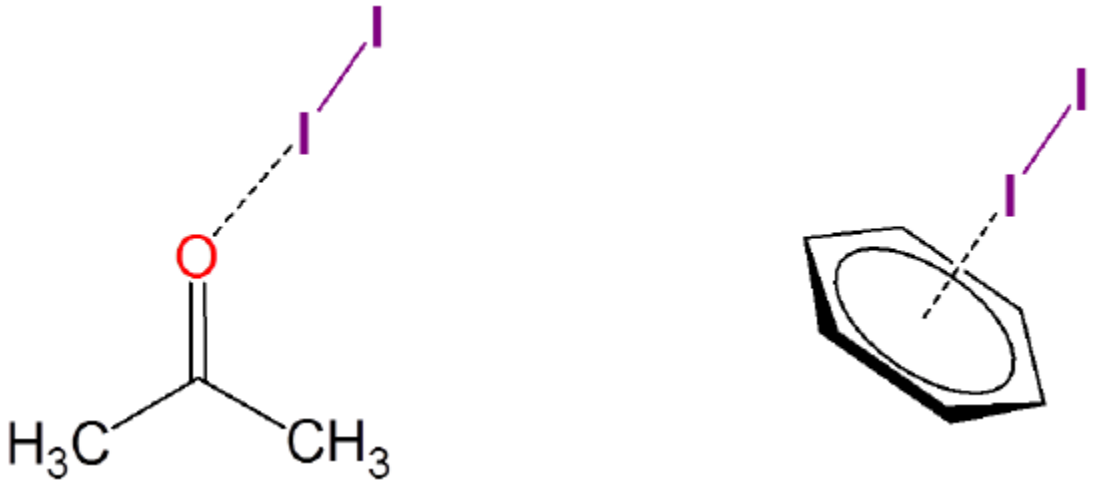


Triiodide is well-known from introductory chemistry from the bright blue color that appears when the triiodide complexes with starch to give the dark blue starch-iodide complex.

In contrast to the stable triiodide anion, iodine charge transfer complexes are only weakly associated. Complexes between iodine and amines are a well known example:

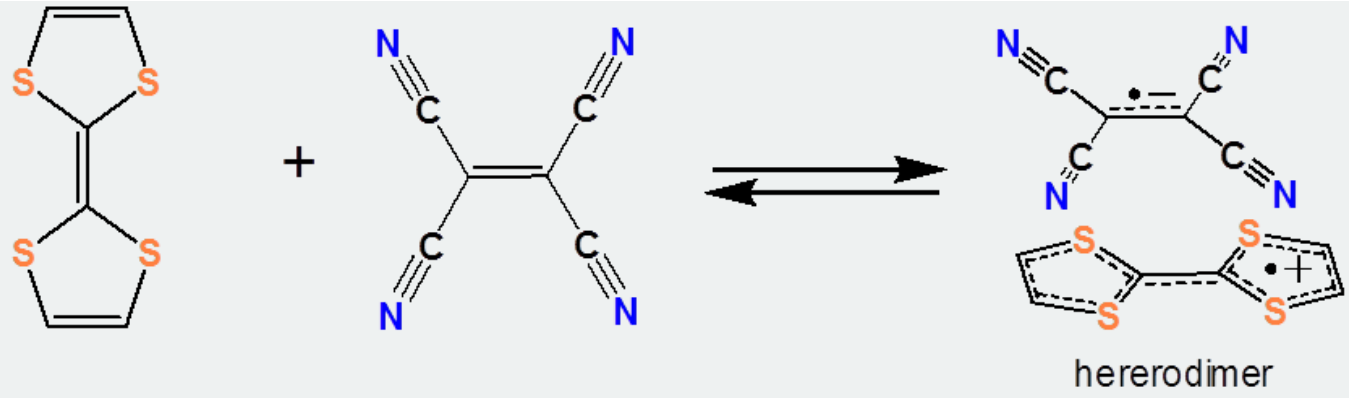


Iodine also forms weakly-associated charge transfer complexes with many solvents. For instance, iodine can weakly associate with both acetone and benzene:

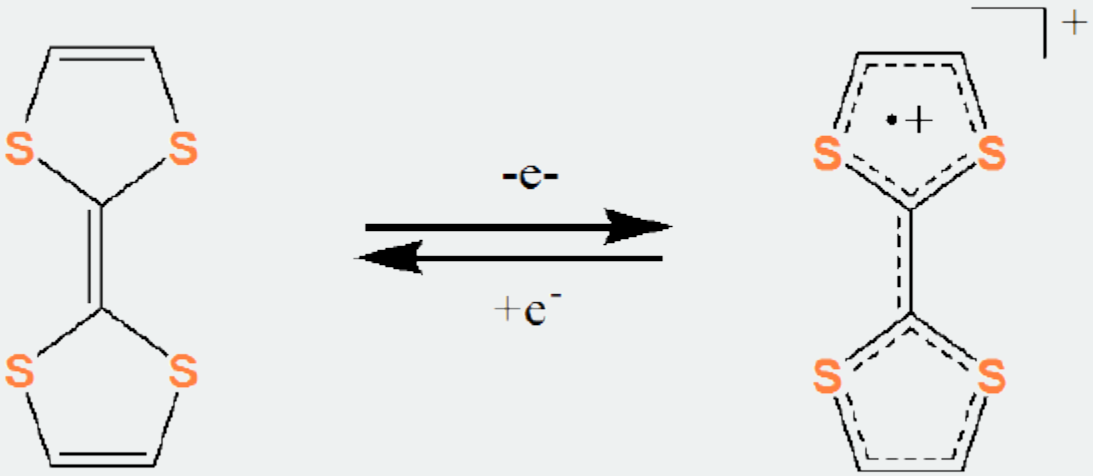


Organic Charge Transfer Complexes

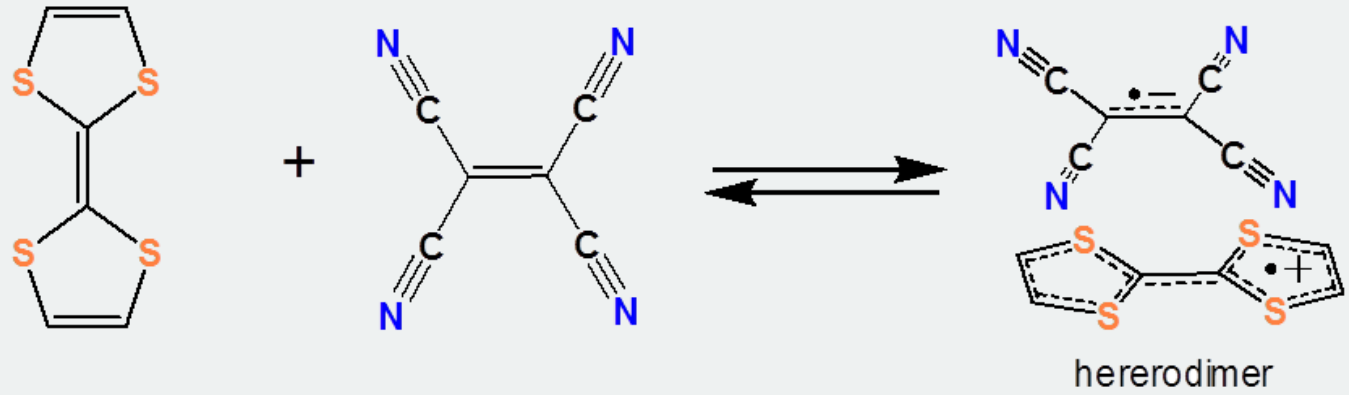
It is worth noting in passing that several organic charge transfer complex systems have been developed in which organic electron donors and acceptors weakly associate with each other. These are of considerable interest for use in molecular electronics applications, and as a result, a large variety of organic electron donors and acceptors have been developed. An example of an organic electron acceptor is tetracyanoethylene (TCNE):



and an example of an organic electron acceptor is tetrathiofulvalene (TTF).



Together they form a charge transfer complex:



Similar organic charge transfer systems have been investigated for use in organic photovoltaic cells. There is considerable interest in developing such organic photovoltaic devices owing to the ease with which organic materials may be fabricated from organic solutions and suspensions.

Charge transfer complexes exhibit charge transfer transitions in which absorption triggers the transfer of an electron from the donor to the acceptor.

When iodine is dissolved in solutions of donor solvents, the striking purple color of molecular iodine is replaced by a yellow-brown color. This is because charge transfer complexes like those formed by I_2 can absorb light in ways that neither the donor nor the acceptor can on their own. Specifically, charge transfer complexes exhibit **charge transfer bands (CT bands)** in their absorption spectra. In the charge transfer transition the initial partial transfer of charge from the donor Lewis base to the acceptor Lewis acid in the charge transfer complex is pushed further by photoexcitation.

$$D^{\delta+} - A^{\delta-} \overset{h\nu_{CT}}{\longrightarrow} D^{+} - A^{-}$$

The nature of these charge transfer transitions is seen from the orbital description of binding for iodine charge transfer complexes. When a donor-I_2 complex forms, the formation of donor-I_2 bonding and antibonding orbitals results in a shift in the $I2\sigma \rightarrow \sigma*$ transition to higher energy, as a new charge transfer band is formed, associated with the excitation of an electron from the largely amine-centered amine-I_2 σ orbital to the largely I_2-centered amine-I_2 $\sigma*$ orbital.

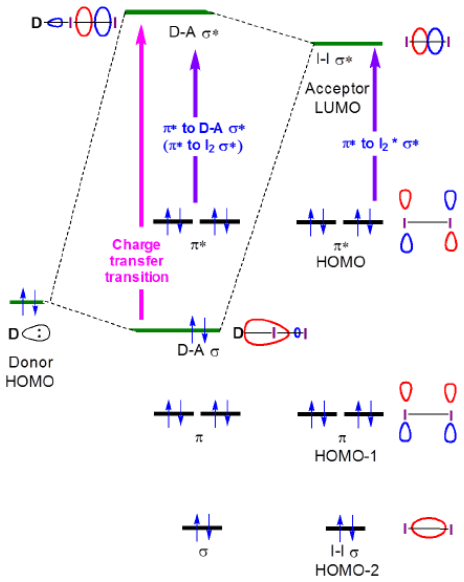


Figure 6.4.2.6.2.4.3.2. Frontier orbital interactions that give rise to changes in the absorption spectra of iodine when it forms a charge transfer complex with a Lewis base donor.

Solutions of I_2 as mixtures with Lewis bases such as amines and in donor solvents clearly have charge transfer bands in their absorption spectra. Several such spectra are given in Figure 6.4.2.3.

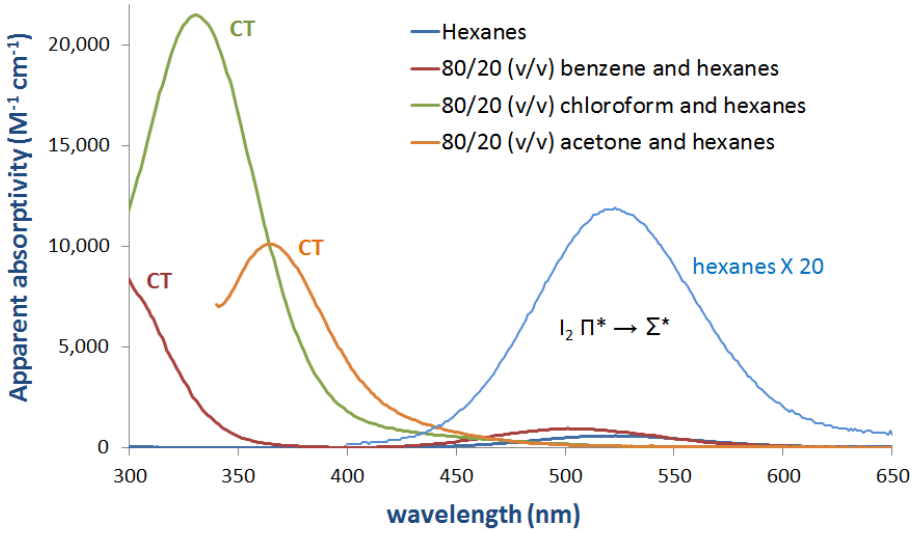


Figure 6.2.4.3.3. Absorption spectrum of molecular iodine (I_2) in various solvents showing the appearance of a CT band in donor solvents.*

In principle, the energies of both the charge transfer and $I_2\ \pi*\ \rightarrow\ D-A\ \sigma*$ transitions both increase with donor strength, as shown in Figure 6.4.2.4.

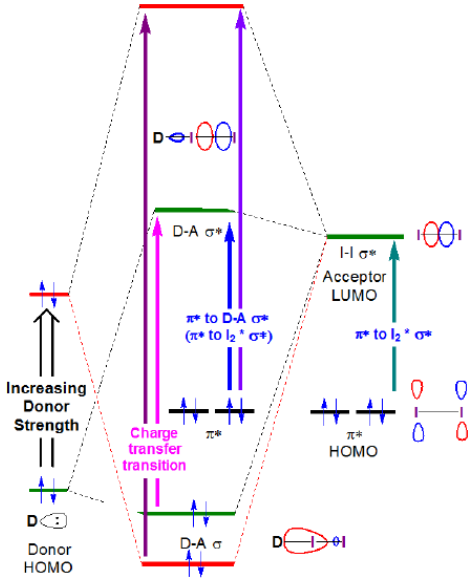


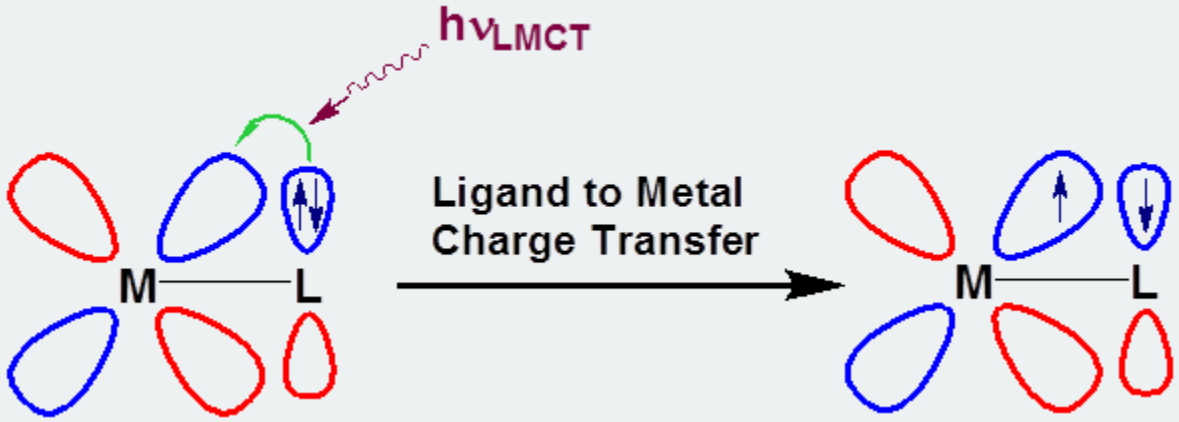
Figure 6.2.4.3.4. Expected change in the frontier orbital energies associated with I_2 donor acceptor complex formation when the HOMO energy of the donor is increased.

As can be seen in Figure 6.4.2, the charge transfer band energy might be expected to increase as the donor HOMO increases in energy to become closer in energy to the acceptor LUMO. Although care should be taken when interpreting the solution phase spectra of I_2, this expectation is borne out by a cursory and qualitative analysis of the spectra in Figure 6.4.2.3. The CT transition energy shifts towards lower wavelengths (and thus higher energy) as the highest occupied atomic orbital energy for the donor atom increases on going from acetone (oxygen, -15.85 eV) to chloroform (chlorine, -13.67eV) and finally benzene (carbon, -10.66 eV).**

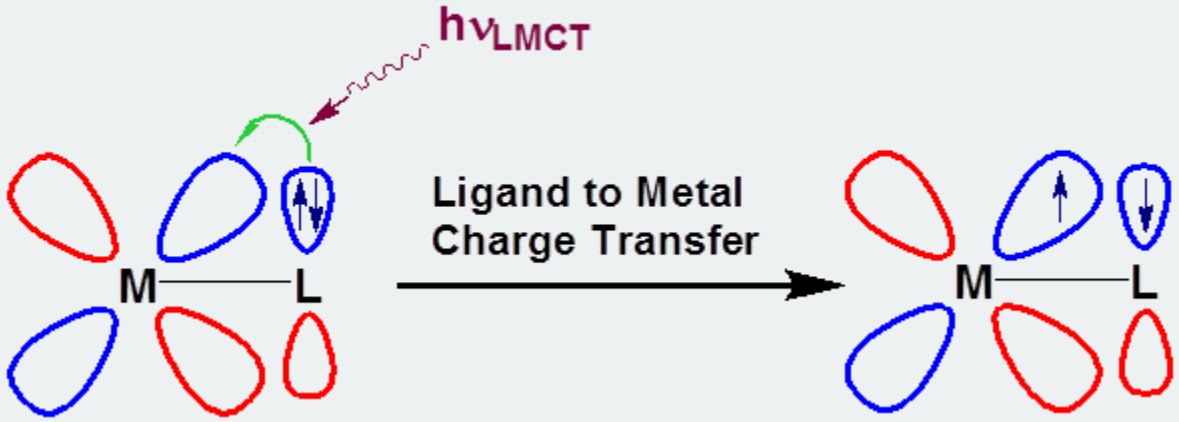
Charge Transfer Bands in Transition Metal Chemistry

Charge transfer transitions are responsible for the intense color of many transition metal complexes. In these cases, however, the weak Lewis acid-base interaction involves incomplete electron donation and acceptance in a $p\pi - d\pi$ (or $p\pi - d\pi *$)-bond between a metal and ligand. The charge transfer bands in the absorption spectra of these complexes involve the transfer of electrons between the metal and ligand. In particular,

- Metal to ligand charge transfer (MLCT or CTTL) bands involve the transfer of an electron from a filled or partly filled metal *d* orbital to a ligand $\pi *$-type orbital.



- Ligand to metal charge transfer (LMCT or CTTM) bands involve the transfer of an electron from a filled or partly filled ligand orbital to a metal *d*-orbital.



- Metal to metal charge transfer bands can be observed in some bimetallic complexes. However, these are usually thought of only as an electron transfer rather than as a shift in the status of a Lewis acid-base interaction.

Because metal-ligand charge transfer bands involve intermolecular electron transfer between the metal and ligand to generate a high energy redox state, the CT excited state is both a better oxidant and reductant than the ground state. Consequently there has been intense research into the development of metal complexes whose charge transfer excited states are powerful oxidants and reductants in the expectation that they will be able to drive the photocatalytic oxidation and reduction of substrates.

* The apparent absorptivity of I_2 in hexanes was calculated from the absorption spectrum of 215 μM I_2 in hexanes. All other apparent absorptivities were calculated from absorption spectra of solutions that were 44 μM in I_2.

** The band positions are not the CT band energies, and the HOMO energies given are atomic energy levels and do not

necessarily correspond to the HOMO of the donor in solution. Because of this and other simplifications this analysis is not intended to replace a rigorous computational analysis of the factors that give rise to CT band positions.

References

1. Meyerstein, D.; Treinin, A., Charge-transfer complexes of iodine and inorganic anions in solution. Transactions of the Faraday Society 1963, 59 (0), 1114-1120.
2. Baskar, A. J. A.; Rajpurohit, A. S.; Panneerselvam, M.; Jaccobb, M.; RoopSingh, D.; Kannappan, V., Experimental and theoretical analysis of substituent effect on charge transfer complexes of iodine and some alkylbenzenes in n-hexane solution at 303K. Chemical Data Collections 2017, 7-8, 80-92.

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6.2.4.4: Substances' solution phase Lewis basicity towards a given acid may be estimated using the enthalphy change for dissociation of its adduct with a reference acid of similar hardness.

A number of spectroscopic and thermodynamic scales have been developed to quantify the strength of Lewis acids and bases.[1,2] For the sake of simplicity only thermodynamic scales will be described. Thermodynamic scales are based on the energetics of Lewis acid-base reactions. When substances act as a Lewis base (B) they form adducts with a Lewis acid (A):

$$B: \ + \ A \ \rightleftharpoons \ B-A$$

Various thermodynamic parameters for this process may be taken as a measure of the strength of the Lewis base towards that acid. For instance, in the case of iodine charge transfer complexes, the equilibrium constant for adduct formation is sometimes used as an informal measure of Lewis base strength.

The thermodynamic parameters used to define Lewis acid and base strength are similar to those used to define Brønsted acidity and basicity. Just as Brønsted acidity and basicity were defined in terms of the free energy change for the dissociation and association of a hydrogen ion, Lewis acidities and basicities are defined in terms of the free energy change for adduct formation:

$$B: \ + \ A_{reference} \ \rightleftharpoons \ B-A \qquad -\Delta G \ = \ Lewis \ basicity \ of \ B \ towards \ A$$

$$B:_{reference} \ + \ A \ \rightleftharpoons \ B-A \qquad -\Delta G \ = \ Lewis \ acidity \ of \ A \ towards \ B$$

The physical meaning of Lewis acidities and basicities may be easier to grasp by considering that Lewis acidities and basicities correspond to the free energy for dissociation of acid-base adducts:

$$B-A \ \rightleftharpoons \ B: \ + \ A_{reference} \qquad \Delta G \ = \ Lewis \ basicity \ of \ B \ towards \ A$$

$$B-A \ \rightleftharpoons \ B:_{reference} \ + \ A \qquad \Delta G \ = \ Lewis \ acidity \ of \ A \ towards \ B$$

Since in practice it is much easier to measure the reaction enthalpies for these processes, many scales use the enthalpy change instead of the free energies. To distinguish these enthalpy changes from Lewis *acidities* and *basicities,* the enthalpy changes are called Lewis acid and base *affinities*. Of these, however, Lewis acid affinities are poorly characterized at present (perhaps one of you readers will help redress this). Thus the remainder of this section will focus on Lewis base affinities.

Before discussing Lewis base affinities it is worth noting that there is no universal reference scale of Lewis base strength. That is because the thermodynamics of a given Lewis acid-base interaction is contingent on a number of factors, including:

- The relative hardness of the acid and base according to Pearson's hard-soft acid base principle. Roughly, Lewis acids tend to associate more strongly with Lewis bases with similar charge densities and polarizabilities. This means that the affinity of a given base for Lewis acids is not a static parameter. Rather it differs markedly with the acid's hardness.
- Steric effects. Sterically hindered Lewis acid-base interactions will be weaker than sterically accessible ones.
- Solvent effects. In solutions, the adduct and the free acid and base pair will in general be differentially stabilized. To avoid solvent effects, some scales quantify Lewis acid and base strength in terms of gas phase adduct formation. However, it is not always possible or desirable to quantify a Lewis acid or base's strength in the gas phase, since gas phase affinities do not always allow for adequate prediction of the strength of a Lewis acid-base interaction in solution.

Because Lewis base affinity depends on hardness, steric effects, and solvent effects care should be taken when acid-base parameters are used to predict the strength of a given interaction. In particular, steric effects should be considered separately, and if predictions are made using scales that employ reference acids or bases that differ markedly in hardness from the interaction to be predicted or which correspond to unrealistic solvent conditions, they should always be taken as tentative.

References

1. Laurence, C.; Graton, J.; Gal, J.-F., An Overview of Lewis Basicity and Affinity Scales. Journal of Chemical Education 2011, 88 (12), 1651-1657.
2. Laurence, C.; Gal, J.-F. o., Lewis basicity and affinity scales: data and measurement. John Wiley: Chichester, West Sussex, U.K., 2010.

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6.2.4.5: In the boron trifluoride affinity scale, the enthalpy change on formation of an adduct between the base and boron trifluoride is taken as a measure of Lewis basicity.

The physical meaning of Lewis acid and base affinities are defined as the negative of the enthalpy for formation of an adduct with a reference base and acid, respectively:

$$B + A_{reference} \rightleftharpoons B-A \qquad -\Delta H = \text{Lewis basicity of B towards A}$$

$$B_{reference} + A \rightleftharpoons B-A \qquad -\Delta H = \text{Lewis acidity of A towards B}$$

Two common scales of Lewis base affinity involve the use of $SbCl_5$ and BF_3 as the reference base. Specifically,

- In the **Guttman donor-acceptor scale,** Lewis bases' **donor numbers** are equal to the negative enthalpy change for formation of the base's $SBCl_5$ adduct in dilute 1,2-dichloroethane (EDC*):

$$Base(EDC\ solution) + SbCl_5(EDC\ solution) \rightarrow Base-SbCl_5(EDC\ solution) \qquad -\Delta H = \text{Guttman Donor Number}$$

- The **BF_3 affinity scale** has largely supplanted the Guttman scale owing to the ease with which its results may be correlated with computational data (it is easier to calculate energies for adducts of BF_3 than of SbF_5). In the BF_3 affinity scale, Lewis bases' **BF_3 affinities** are equal to the negative enthalpy change for formation of a solution phase adduct between the base and gaseous BF_3. The reaction is:

$$Base(solution) + BF_3(g) \rightarrow Base-BF_3(solution) \qquad -\Delta H = BF_3 \text{ Affinity}$$

BF_3 affinity values for a wide range of organic bases were compiled by Laurence, Graton, and Gal in reference 2 and salient trends in this data will be discussed in subsequent sections.

References

1. Laurence, C.; Graton, J.; Gal, J.-F., An Overview of Lewis Basicity and Affinity Scales. Journal of Chemical Education 2011, 88 (12), 1651-1657.
2. Laurence, C.; Gal, J.-F. o., Lewis basicity and affinity scales: data and measurement. John Wiley: Chichester, West Sussex, U.K., 2010.

Notes

* EDC stands for ethylene dichloride, the common name of 1,2-dichloroethane.

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6.2.4.6: Lewis base strength may also be estimated by measuring structural or energy changes upon formation of a Lewis acid-base complex, as illustrated by efforts to spectroscopically assess the strengths of halogen bonds

When a Lewis acid and base form an adduct, it shifts the bond lengths, and strengths in the acid and base also shift.

According to the frontier orbital description of Lewis acid-base interactions, adduct formation results in a net transfer of electron density from the base HOMO to the acid LUMO. This transfer

- increases the electron density between the acid (A) and base (D)
- alters the strength of the bonding within the base as the base LUMO becomes partially populated.

These changes result in structural and spectroscopic shifts on adduct formation that can be taken as a measure of the strength of the Lewis acid-base interaction. Since these shifts depend on the nature of the bonding in the acid and base, in practice structural and spectroscopic measurements of Lewis basicity are applied to a few classes of Lewis acid-base interactions, most notably hydrogen bonding and halogen bonding. Since hydrogen bonds will be discussed in section 6.5.1. the remainder of this subsection will focus on halogen bonds.

Halogen bonds are coordinate covalent bonds formed between a Lewis base and an organohalogen.

The halogens in compounds containing a singly-bonded halogen can engage in a special type of intermolecular interaction called halogen bonding, since the bonded halogens are electrophilic on the opposite side of the bond. This electrophilicity is apparent from the charge distribution in CF_5I shown in Figure 4.5.1, in which the charge is distributed on the I such that the I is Lewis basic perpendicular to the C-I bond and Lewis acidic opposite to it. This region of diminished electron density on the halogen opposite the existing sigma bond is called a σ-hole.*

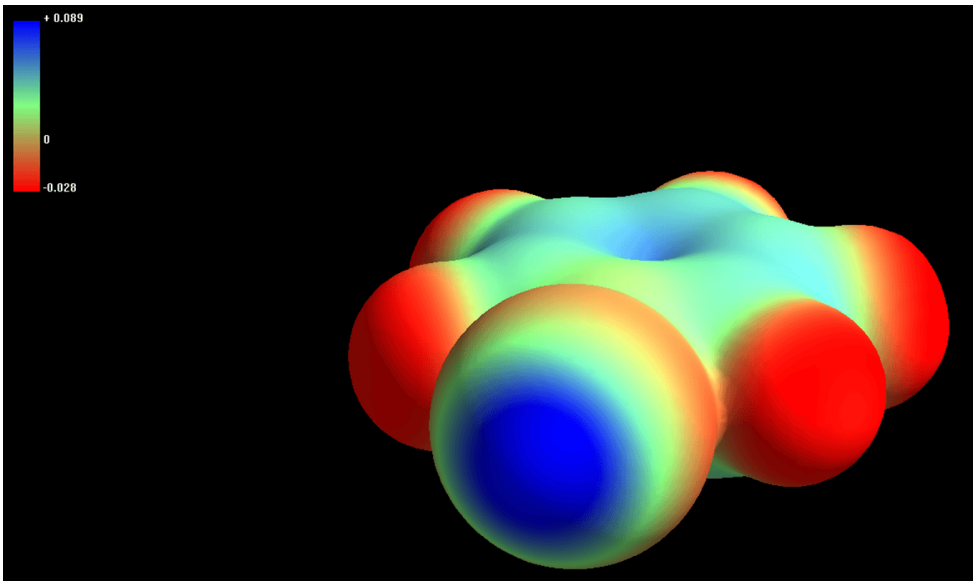
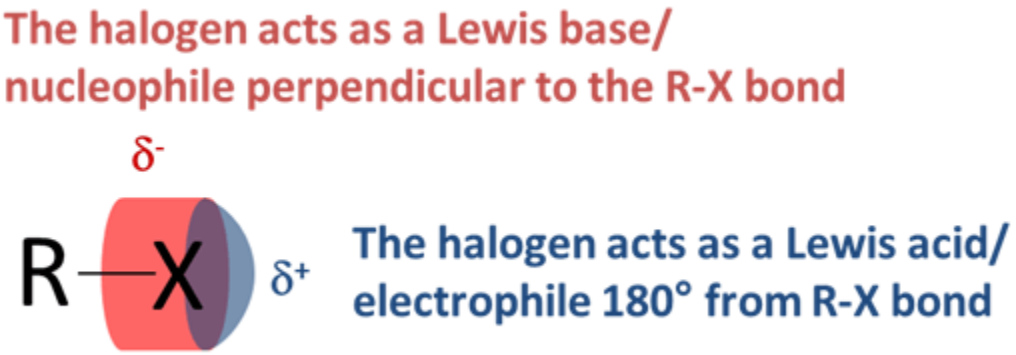
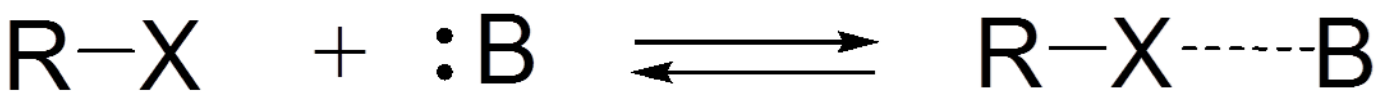


Figure 6.2.4.6.1. Electrostatic surface calculated for CF_5I at the STO-3-21G level oriented so that the C-I bond is facing toward the viewer. The sigma hole shown is the region of positive electron density on the I atom at the front of the image. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

Schematically,



Since the halogen can act as a Lewis acid in the direction opposite the R-X bond it can form adducts with Lewis bases in that direction.



The bonds holding these adducts together are called **halogen bonds**, often abbreviated XB.

The halogen is said to act as a halogen bond donor when it forms a halogen bond with a base along that direction, with the base acting as the halogen bond acceptor. Consequently, the two previous schemes may also be given as:



The ability of singly-bonded halogen atoms to form halogen bonds forms the basis of many efforts to engineer structures in which halogen-containing compounds are held together into chains, sheets, or 3D structures using halogen bonds. One easy-to-see example involves 1D chains formed between *p*-diiodotetrafluorobenzene and *p*-bis(dimethylamino)benzene.[3]

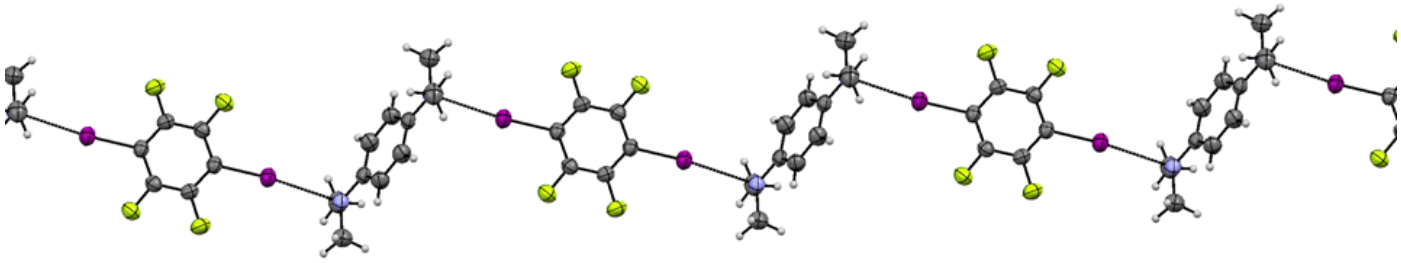
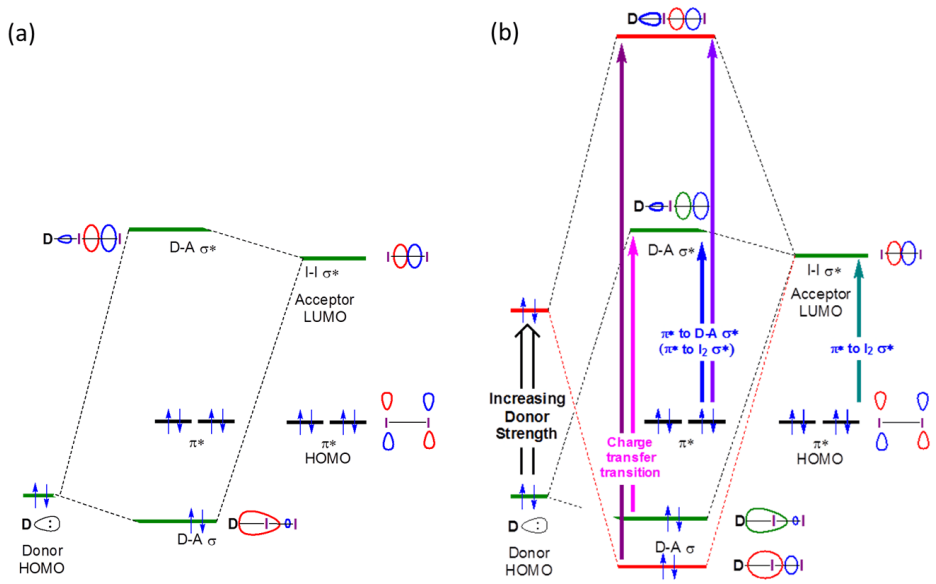


Figure 6.2.4.6.2. 1D chains of *p*-tetrafluorodiiodobenzene and *p*-bis(dimethylamino)benzene molecules in which I is shown in purple, N in blue, F in yellow, and C in grey. The chains are held together by C-I---N halogen bonds with a contact angle of 174 degrees. The figure was produced using Mercury 3.5.1 based on Cambridge crystallographic database entry 172272. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

Trends in halogen bond strength in a closely-related series of compounds may be assessed by examining how the vibrational stretching frequency of I_2 and the I_2 π^* to σ^* transition energy change upon formation of the adduct.

From the description of halogen bonding above it should be apparent that the iodine charge transfer complexes described in section 6.4.2 are held together by halogen bonds. This means that the description of the bonding in I_2 charge transfer complexes given in that section illustrate how vibrational and electronic transitions shift when a halogen-bonded adduct is formed between a halogen bond donor and acceptor.

The orbital interactions involved in halogen bond formation are shown in Figure 6.4.5.3. As can be seen from that figure, the formation of an adduct between I_2 and a Lewis base is expected to result in weakening of the I-I bond and a shift in the I_2 π^* $\rightarrow$ σ^* transition energy to higher energy/shorter wavelengths (*i.e.,* a blueshift). Further, both the weakening of the I-I bond and the I_2 π^* $\rightarrow$ σ^* blueshift are expected to increase with the HOMO energy of the Lewis base.



Figures 6.4.2.2 and 6.4.2.4. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

Because the I-I bond strength and I_2 π^* $\rightarrow$ σ^* blueshift increase with the Lewis basicity of the donor, the blueshift and the I-I vibrational stretching frequency are sometimes used as measures of donor's halogen bond affinity. However, the data obtained from such spectroscopic measurements should be interpreted with a degree of caution. As seen in Table 6.4.5.1, the extent to which the I-I bond is weakened (indicated by $\Delta\nu_{I-I}$) and the $I_2's$ π^* $\rightarrow$ σ^* band is blue shifted are imperfectly correlated overall. However, a careful comparison of the data in 6.4.5.1. reveals that the I-I bond weakening and $I_2's$ π^* $\rightarrow$ σ^* blue shift correlate well for Lewis bases of a given type. Consequently, shifts in the I-I stretching frequency and I_2 π^* $\rightarrow$ σ^* absorption band are not useful as an absolute measure of Lewis basicity but can be used to rank the halogen bond affinity of a closely-related set of donors.**

Table 6.2.4.6.1. *Spectroscopic measures of Lewis basicity for I_2 adducts of selected bases arranged in order of extent of blue shift. The data are excerpted from the extensive compilation given in reference 4.*

Base (type)	$\Delta\nu_{I-I}$ cm^{-1}	Blue shift of $I_2's$ $\pi*$ $\rightarrow$ $\sigma*$
4-methylpyridine (pyridines)	29.1	4730
pyridine (pyridines)	27.4	4560
tetrahydrothiophene (thioethers)	44.5	3640
tetrahydrofuran, THF (ethers)	6.4	2280
diethyl ether (ethers)	5.5	1950
acetone (ketone)	5.0	1850
acetophenone (ketone)	4.6	1650
acetonitrile (nitrile)	4.1	1610
hexamethylbenzene (aromatic)	10.4	1070
benzene (aromatic)	4.3	450

References and Further Reading

1. Cavallo, G.; Metrangolo, P.; Milani, R.; Pilati, T.; Priimagi, A.; Resnati, G.; Terraneo, G., The Halogen Bond. *Chemical Reviews* 2016, *116 (4)*, 2478-2601.
2. Politzer, P.; Murray, J.S. σ-Hole Interactions: Perspectives and Misconceptions. *Crystals* **2017**, *7*, 212.
3. R.Liantonio, S.Luzzati, P.Metrangolo, T.Pilati, G.Resnati, *Tetrahedron*, 2002, 58, 4023, DOI: 10.1016/S0040-4020(02)00264-8

4. Laurence, C.; Gal, J.-F. o., *Lewis Basicity and Affinity scales: Data and Measurement*. John Wiley: Chichester, West Sussex, U.K., 2010.

Notes

* Other compounds also exhibit σ-holes (and π-holes) that can be used in crystal engineering. For details see reference 2.

** for more details consult reference 4, pp. 286-309.

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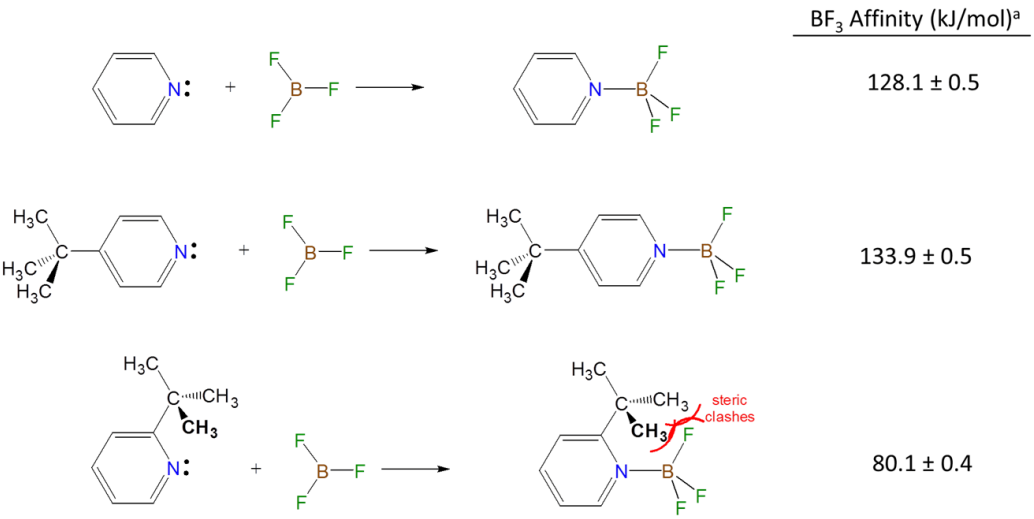
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- 6.4.6: Lewis base strength may also be estimated by measuring structural or energy changes upon formation of a Lewis acid-base complex, as illustrated by efforts to spectroscopically assess the strengths of halogen bonds by Stephen M. Contakes is licensed CC BY 4.0.

6.2.4.7: Bulky groups weaken the strength of Lewis acids and bases because they introduce steric strain into the resulting acid-base adduct.

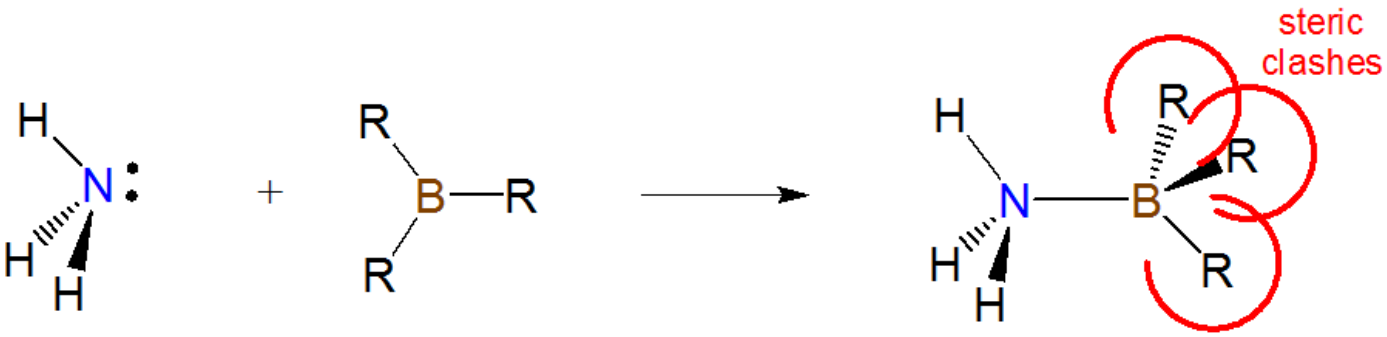
Steric effects can influence the ability of a Lewis acid or base to form adducts by introducing:

- **front strain (F-strain)** whereby bulky groups make it difficult for the Lewis acid and Lewis base centers to approach and interact.



a) Data from Laurence, C.; Gal, J.-F. o., *Lewis basicity and Affinity Scales: Data and Measurement. John Wiley: Chichester, West Sussex, U.K., 2010; pp. 91-101.*

- **back strain (B-strain)** associated with steric interactions that do not directly impede the Lewis acid and base centers from interacting but instead occur as the acid and base rearrange upon adduct formation. For instance, when trivalent boron compounds form adducts with amines, the boron center changes from a more open trigonal geometry to a more hindered tetrahedral one:



- **internal strain (I-strain)** is also associated with the geometry changes incident on adduct formation. However, while B-strain involves direct steric clashes that occur on adduct formation, I-strain is the strain involved in deforming bond and torsional angles away from more stable local geometries. Thus it is more important for Lewis base centers embedded in rings or clusters.

References

1. Alder, R. W., Strain effects on amine basicities. *Chemical Reviews* 1989, 89 (5), 1215-1223.

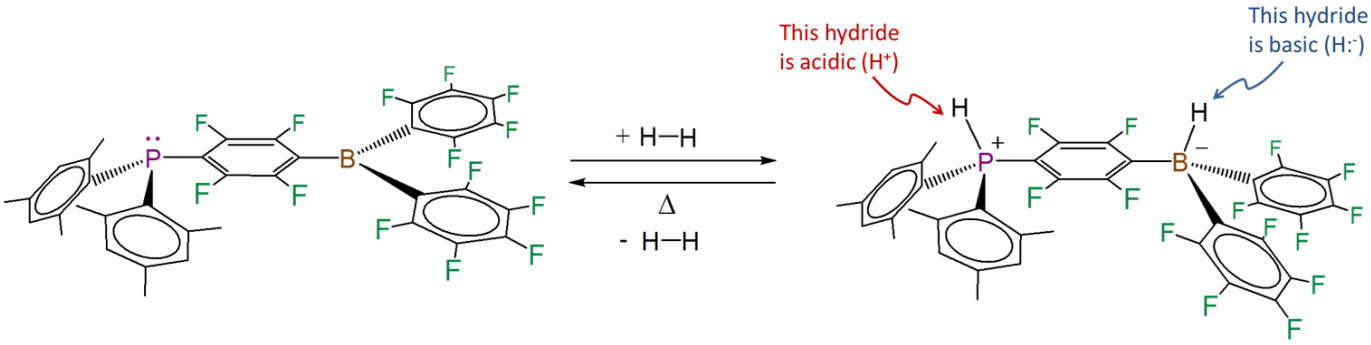
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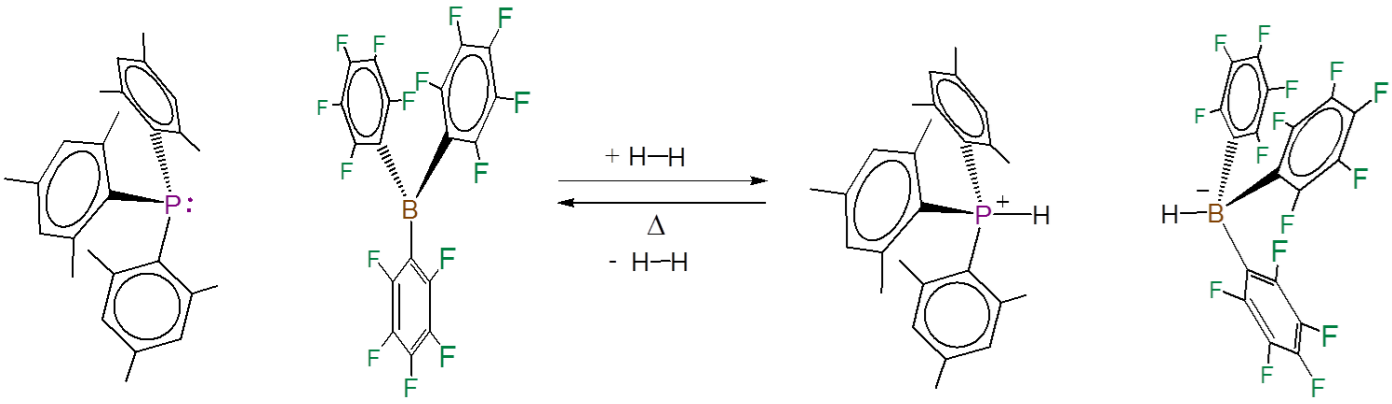
6.2.4.8: Frustrated Lewis pair chemistry uses Lewis acid and base sites within a molecule that are sterically restricted from forming an adduct with each other.

In certain cases when a Lewis acid-base adduct is sterically hindered from quantitatively forming an adduct (and perhaps even when they are so able), the Lewis acid and Lewis base can act together to heterolytically cleave chemical bonds. In such cases the pair of electrons that would otherwise be donated by the base is said to be a **frustrated Lewis pair (FLP)** and in performing the heterolytic cleavage the Lewis acid and base are said to exhibit **frustrated Lewis pair chemistry**.

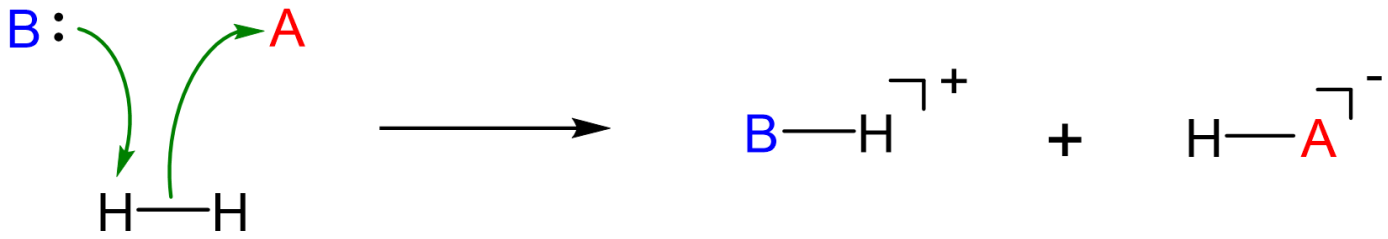
The **Stephan's phosphinoborane** illustrates how FLP chemistry works. It reversibly cleaves dihydrogen to give a zwitterionic species containing both acidic and basic element hydride bonds.



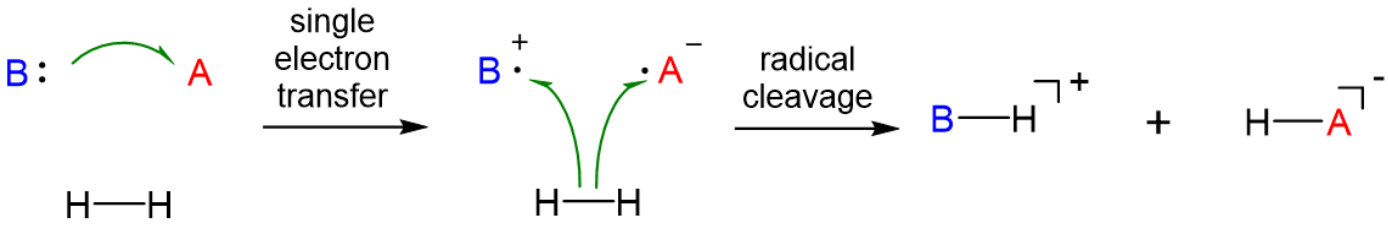
Note that the Lewis acid and base do not need to be part of the same molecule. Hydrogen is also heterolytically cleaved by mixtures of sterically encumbered triarylphosphines and triarylboranes. This time the reaction gives phosphonium and hydroborate ions:



Given the description of FLP systems as frustrated Lewis acid-base adducts, it is natural to think about the cleavage of substrates like H_2 as involving nucleophilic attack by the Lewis base while the Lewis acid acts like an electrophile in a heterolytic cleavage mechanism.



However, only some FLP systems cleave substrates through this mechanism. In others the mechanism involves homolytic cleavage by a diradical intermediate.



In either case, when substrates like H_2 are cleaved by FLPs, they are generally separated into more reactive fragments (e.g., in the case of H_2, H^+ and H^-). Because of this the substrates are said to be activated to undergo further reactions. Because FLP systems can cleave and activate substrates, there is considerable interest in the development of FLP systems that can facilitate reactions of economic or environmental interest. So far FLP systems have been developed that can catalyze various hydrogenations and activate numerous substrates, including CO, SO_2, and N_2.

References

1. Stephan, D. W., Frustrated Lewis Pairs: From Concept to Catalysis. *Accounts of Chemical Research* 2015, 48 (2), 306-316.
2. Fontaine, F.-G.; Stephan D. W., On the concept of frustrated Lewis pairs. *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences* 2017, 375 (2101), 20170004.
3. Jupp, A. R.; Stephan, D. W., New Directions for Frustrated Lewis Pair Chemistry. *Trends in Chemistry* 2019, 1 (1), 35-48.

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- 6.4.8: Frustrated Lewis pair chemistry uses Lewis acid and base sites within a molecule that are sterically restricted from forming an adduct with each other. by Stephen M. Contakes is licensed CC BY 4.0.

6.2.5: Intermolecular Forces

As suggested by the Lewis acid-base concept's ability to describe halogen bonding in terms of the interaction between electrophilic and nucleophilic centers, the Lewis concept can be applied to the understanding of a variety of intermolecular interactions. In the next two sections the utility of Lewis Theory for understanding hydrogen bond and $\pi - \pi$ stacking interactions will be examined.

Contributors and Attributions

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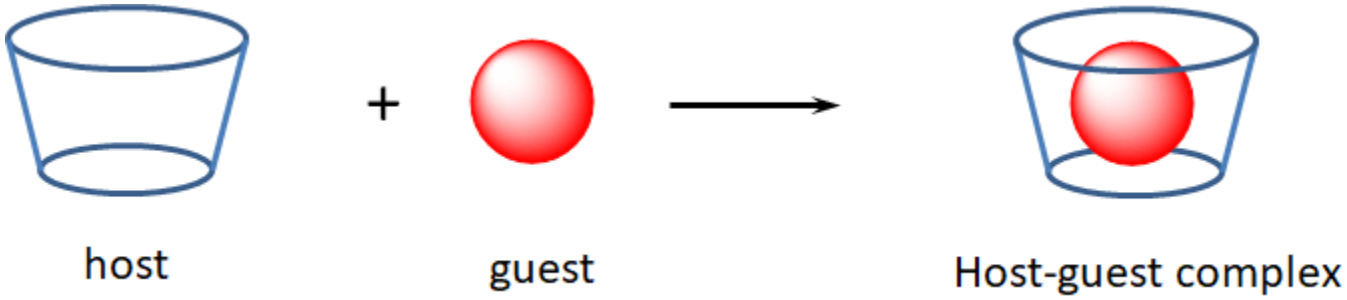
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6.2.5.1: Host-Guest Chemistry and π-π Stacking Interactions

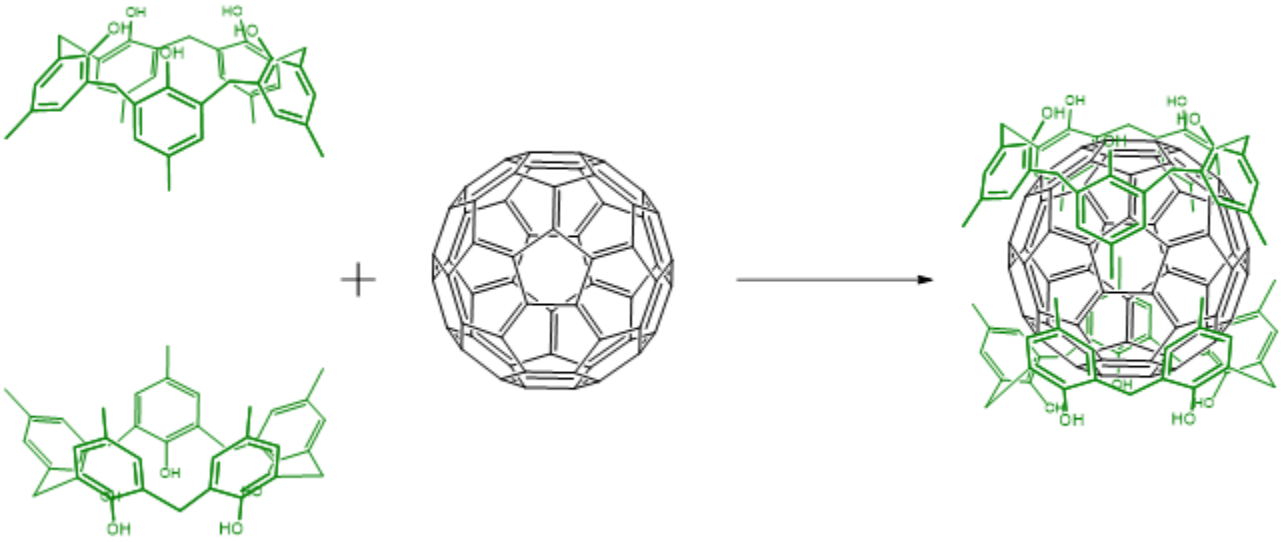
This section sidesteps the discussion of topics related to acid-base chemistry and indulges in a brief aside about one type of intermolecular interaction that is used in host-guest chemistry. This section will first describe the concept of host-guest chemistry, then outline the types of interactions and design principles that can be used to promote host-guest interactions, and finally conclude with a discussion of $\pi - \pi$ interactions.

In Host-Guest Chemistry a large molecule or network material noncovalently binds a smaller molecule in a binding pocket.

In host-guest chemistry, a large molecule or network host uses noncovalent interactions to bind a smaller molecule guest in a binding pocket. Schematically this interaction is often represented as:



Host-guest binding is analogous to the way many biomolecule-substrate interactions occur - *e.g.,* to how antibodies bind antigens and many enzymes bind their substrates. In this way many biomolecular systems can be said to form host-guest complexes, although that terminology is not often used in the biochemistry field. Usually when someone refers to a host-guest complex in inorganic or organic chemistry they are referring to organic or metal-organic cages that bind small organics. A simple example involves the binding of buckminsterfullerene, C_{60}, by calix-[5]-arenes.



In principle any type of intermolecular interaction can hold a host-guest complex together, but whichever one you choose, it helps to pay attention to a few design principles.

The types of interactions that are used to effect host-guest binding are diverse. In the fullerene-calixarene example above, the interactions will primarily involve π stacking interactions between the aromatic rings of the calixarenes and those in the fullerene. Other host-guest systems use some combination of:

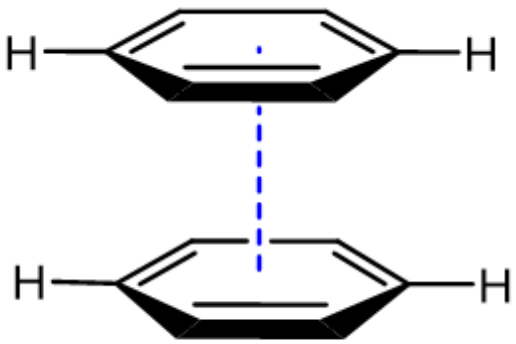
- hydrogen bonds
- halogen bonds
- ionic interactions whereby charged groups from the host attract oppositely charged groups of the guest
- ion-dipole interactions whereby charged groups on one component interact with the appropriate end of a polar group on the other.
- dipole-dipole interactions
- cation-π, X-H-π, and similar interactions in which full or partial positive charges induce a complementary dipole in a π system.
- $\pi - \pi$ interactions
- dispersion forces

Many effective host-guest systems employ a few design principles to favor host-guest binding. These principles include:

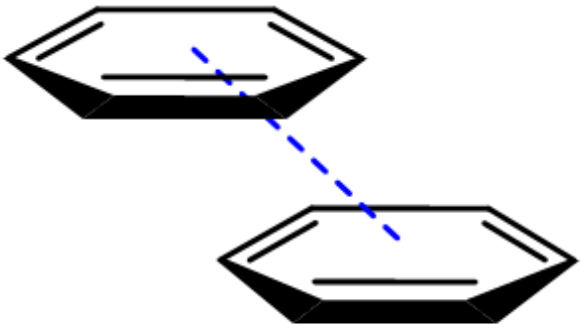
- **host preorganization** - when conformationally flexible (-*i.e.,* floppy) hosts bind a guest, the host will conform to the shape of the guest and so become more rigid. In other words, when a floppy host binds to a guest, a lot of conformational entropy is lost. This will make the ΔS term for the binding free energy more negative and tends to disfavor host-guest binding. To avoid this, effective hosts minimize the loss of conformational entropy on binding. This is usually done by limiting the conformational entropy of the host to begin with by fusing multiple binding sites into a macrocyclic ring, cage, or cluster. The more rigid these are the better.
- **host-guest size and shape complementarity** - this simply means that complexes form when the binding pocket or cavity of the host is complementary to that of the guest. Specifically, its size and shape both fit the guest and allow for tight interactions (*i.e.,* the guest doesn't rattle around inside). Moreover, any charged, polar, or any-directional binding sites on the host are arranged in such a way that they interact favorably with complementary sites on the guest.
- **preferencing of guest desolvation via preferential solvent-solvent interactions*** - $\pi - \pi$ interactions like those which hold the calixarene-fullerene complex together are weak compared to stronger interactions like hydrogen bonds or even water-π bonding (a type of X-H π bonding. However, water-water hydrogen bonds and other interactions between H-bond-capable and polar systems are stronger still. This means that favorable water-water interactions must be broken when a nonpolar host or guest is dissolved in a very polar or ionic solution. Every dipole-induced dipole or X-H π interaction that takes place is a lost opportunity for solute molecules to engage in hydrogen bonding interactions. Thus, when an aqueous solution of a nonpolar host and guest are mixed, the nonpolar parts of these molecules will tend to stick together, freeing water or other polar molecules to interact with one another as they do so.**

$\pi - \pi$ interactions occur when aromatic π systems bind face to face with one another and involve a combination of dispersion and dipole-induced dipole interactions.

Since the electron distribution in aromatic systems is relatively easily distorted, they can engage in atypically strong dispersion and dipole-induced dipole interactions called $\pi - \pi$ **stacking interactions**. These interactions are so named because they occur when the planes of aromatic rings are stacked parallel to one another. This parallel stacking can occur in either a sandwich or a displaced stacking arrangement.

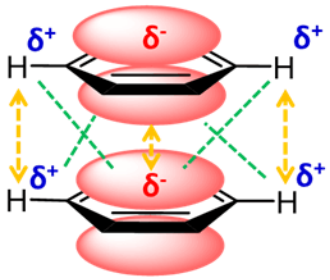


Sandwich
or eclipse stacked

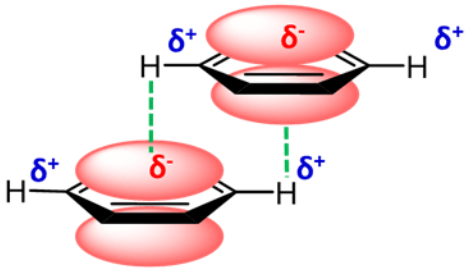


DIsplaced stacked

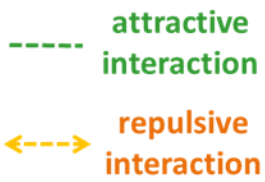
In either case the rings can be attracted to one another by a combination of dispersion and electrostatic interactions. The latter depend on the specific bonding parameters of the system and can be attractive or repulsive. The eclipsed arrangement of the benzene dimer is electrostatically disfavored, while attractions between the positive hydrogen substituents and the π system of an adjacent ring are attractive in the eclipsed arrangement.



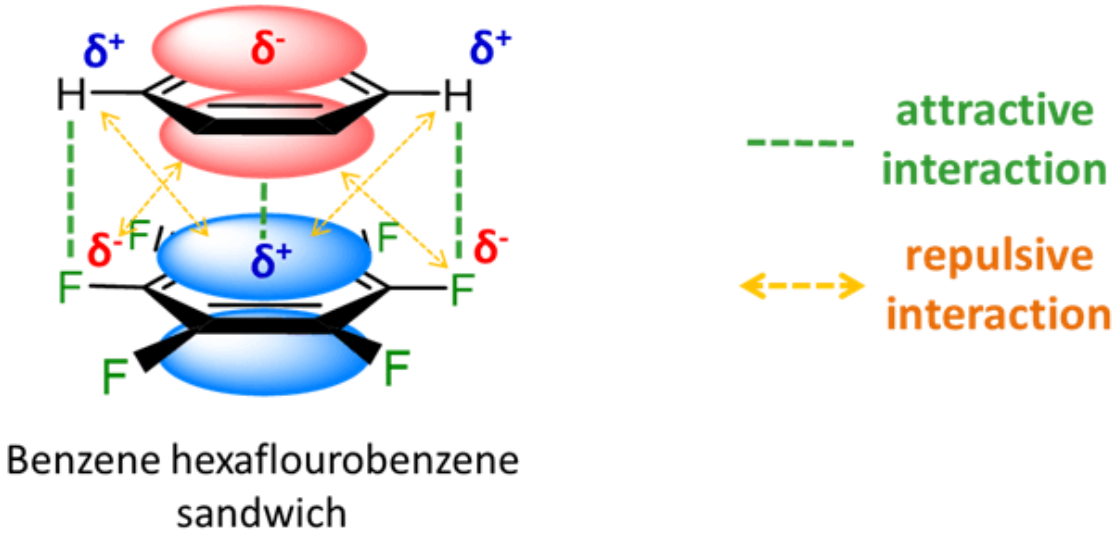
Benzenes sandwich
or eclipse stacked



Benzenes displaced stacked



With electronegative substituents, the polarity of the ring system is reversed so that there are favorable electrostatic interactions in an eclipsed heterodimer of benzene and hexafluorobenzene.



Benzene hexaflourobenzene sandwich

In the heterodimer of benzene and hexafluorobenzene, at last we have an example of a π stacking system that can more readily be described as involving a Lewis acid-base interaction. Specifically, the relatively electron-rich benzene π system acts as a Lewis base in donating "electron pairs" to the electron-poor hexafluorobenzene π system.

Notes

* The most prominent example of desolvation as a driving force is the hydrophobic effect. The hydrophobic effect governs the structure of soaps, micelles, biomolecules, and other amphiphilic or nonpolar systems in water. In the hydrophobic effect, the preference of an aqueous solution of a hydrophobic solute to maximize water-water interactions means that hydrophobic groups tend to stick together in solution.

** A good analogy for this effect is the magnetic marble analogy. When magnetic and ordinary marbles are mixed, the magnetic marbles will tend to stick together because they will attract one another strongly, not because the interactions between the nonmagnetic marbles are somehow disfavored.

† This is not to say that the stacking arrangements lead to attraction in every instance. There are arrangements in which the parallel rings are expected to repel.

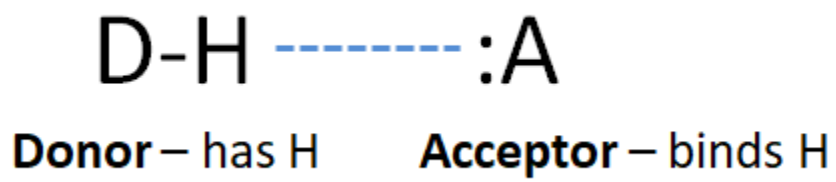
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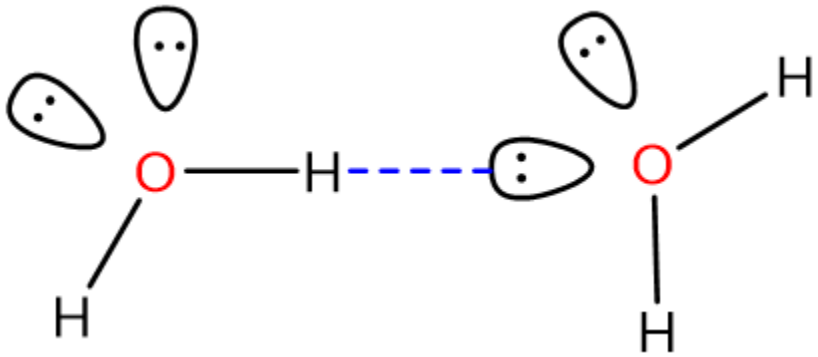
6.2.5.2: Hydrogen bonds may be considered as a special type of Lewis acid-base interaction in which a Lewis acid hydrogen ion is shared between Lewis bases

A hydrogen bond is a bonding interaction in which an E-H hydrogen bond donor unit acts as a Lewis acid in donating a hydrogen ion to a hydrogen bond acceptor, A.

Classically, hydrogen bonds (H-bonds) have been defined as a special type of intermolecular force between D-H and :A, where D & A = N, O, F, and occasionally S. The D-H is said to be the hydrogen bond donor while :A is the hydrogen bond acceptor.



Consider, for instance, a hydrogen bond between two water molecules:



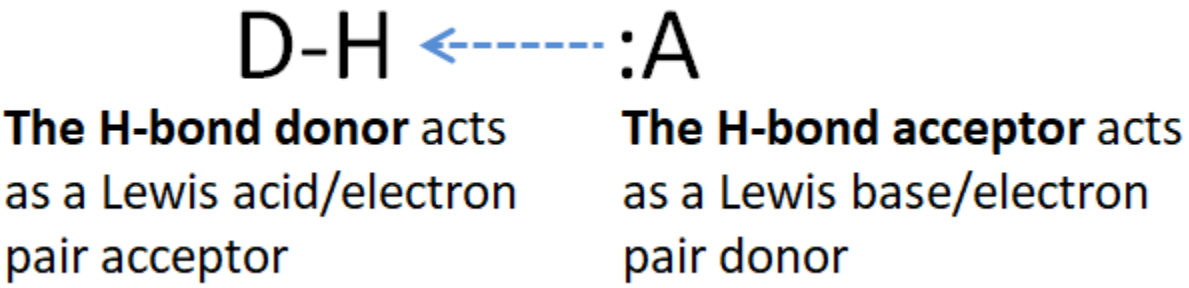
An O-H bond in the water on the left serves as the hydrogen bond donor while one of the lone pairs on the oxygen of the water on the right acts as the hydrogen bond acceptor.* The strength of this classical hydrogen bonding interaction is ~12-20 kJ/mol, much greater than typical dipole-dipole interaction energies (<4 kJ/mol), and even though the hydrogen bonds in water are somewhat flexible, the O-H---O hydrogen bond axis prefers to be linear in many cases [1]. These factors suggest that hydrogen bonds are more than just a special type of dipole-dipole interaction involving hydrogen. Instead, hydrogen bonds involve a combination of factors, including:

- dipole-dipole interactions
- covalent bonding
- dispersion forces
- X-H π-interactions**

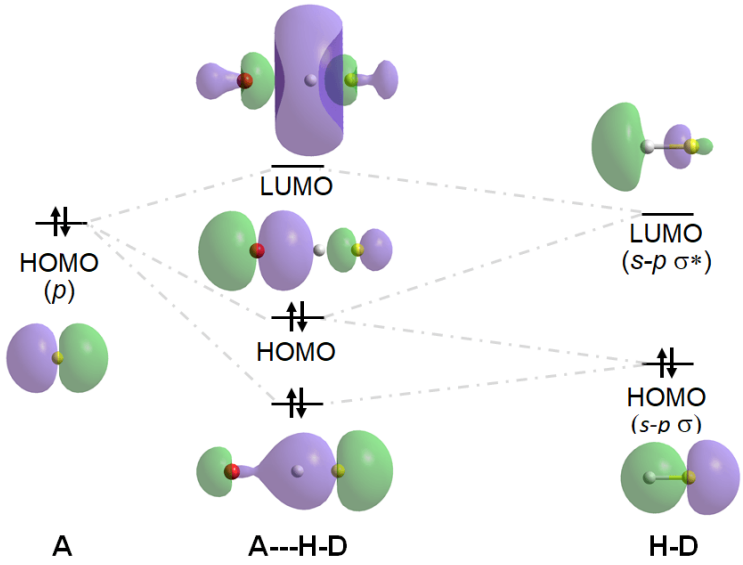
The relative importance of these interactions can differ significantly from one system to another.

In considering how to better understand hydrogen bonding, both Brønsted and Lewis acid-base concepts have been employed. In Brønsted terms, hydrogen bonding has been described as involving a partial transfer of a hydrogen ion from D to A. The

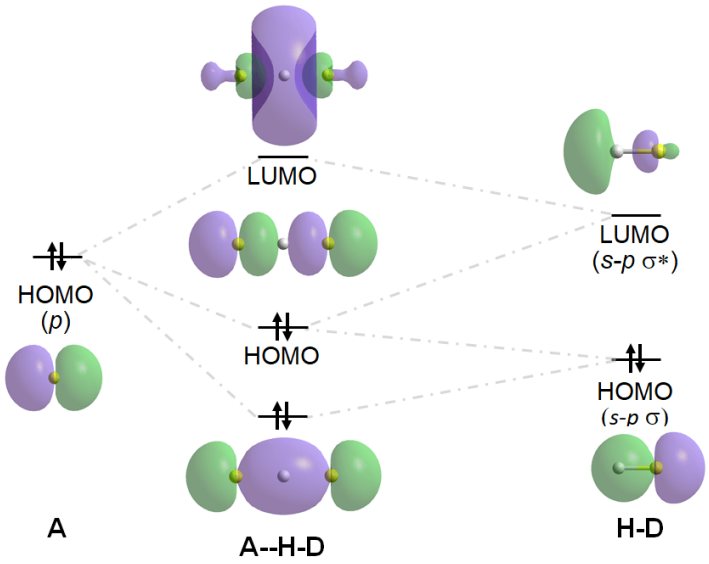
Lewis definition is often more useful for understanding the role of covalency, however, owing to the ease with which Lewis theory accommodates orbital interactions through the Frontier orbital approach to chemical bonding and reactivity. Moreover, from the classical definition of hydrogen bonding as involving donation of H by a D-H unit and its acceptance by a lone pair on A, it is apparent that in some sense D-H is acting as a Lewis acid in donating an electron-deficient H to A while A is acting as a Lewis base in using its lone pair to accept it. In this respect, the hydrogen bond is perhaps better thought of as involving Lewis acid-base adduct formation between a D-H bond and A.



This more expansive definition of a hydrogen bond as involving a Lewis acid-base interaction accommodates the much wider variety of hydrogen bonding interactions that have been recognized since the 1990s. While the classical definition of hydrogen bonding accounts for much of the hydrogen bonding that occurs in water, organic, and biomolecular systems, the large number of multicenter H-bonds[†] and the ability of C-H, P-H, and Au-H to function as hydrogen bond donors and for π systems to function as hydrogen bond acceptors is excluded by the classical definition of a hydrogen bond. In contrast, the Lewis-based definition allows for the understanding of covalent contributions to hydrogen bonding in such systems in terms of the overlap of frontier orbitals on D, H, and A. Consider, for example, the frontier orbital interactions involved in a typical hydrogen bond between D-H and A:[††]



Hydrogen bonds like the one above are called asymmetric hydrogen bonds since the D-H bond is shorter and more stabilized than the A-H bond. When D and A are of equal or similar energy, however, the D-H and A-H interactions are of similar energy, and the H will be centered in between D and A, making it difficult to identify which atom is the donor and which is the acceptor. Such H-bonds are called symmetric H-bonds. An example is the H-bond in $[F{---}H{----}F]^-$, for which the stabilizing and destabilizing frontier orbital interactions are



In general, symmetric hydrogen bonds are stronger and more stable than asymmetric ones. In fact, one approach to predicting the strength of classical hydrogen bonds called Gili's **pKa Slide Rule**‡ considers the pKa of the protonated form of both the neutral donor (D-H) and the neutral acceptor (A, which is then protonated to H-A^+). In this approach the H-bond is considered to involve transfer of a hydronium ion between the donor and acceptor, and the pK_a values of the donor and acceptor serve as proxies for D^- and A's ability to draw the hydrogen ion in the H-bond to itself. When the

- donor is more basic (*i.e.,* its pK_a is higher) relatively little transfer occurs, and the hydrogen bond is better represented as D-H----A
- acceptor is more basic (i.e., its pK_a is higher) the hydrogen ion is transferred from D to A, giving a hydrogen bond better represented as D----H-A
- donor and acceptor are about equally basic (have similar pK_a values) the hydrogen ion is roughly shared equally between D and A in a symmetric H-bond, D--H--A

Specifically, Gili proposed the following criteria for predicting the strength of these ordinary hydrogen bonds:

Hydrogen Bond type	ΔpK_a
Strong (11.5-15.8 kcal/mol)	0-3
Medium Strong (6.8-11.5 kcal/mol)	3-11
Medium (4.1-6.8) kcal/mol	11-21
Medium Weak (2.5-4.1 kcal/mol)	21-31
Weak (1.1-2.5 kcal/mol)	>31

Experimentally, the existence of hydrogen bonds and their approximate strength is inferred from crystallographic bond distances and angles, changes in the D-H vibrational frequency, and shifts in ^{1}H NMR peak positions, although all such measures should be interpreted with caution.

If hydrogen bonds involve full or partial coordinate covalent bond formation between a D-H bond and an acceptor site, then the resulting adduct should exhibit evidence of bond formation. In practice such evidence is sought from three main sources:

1. *Crystallographic bond distances and angles.* In the structure of crystalline solids, hydrogen bonds can be distinguished from

Van der Waals contacts in that

- the D----A distance is closer than that expected from the Van der Waals surfaces of D and A.
- when the H can be located, the D-H distance is longer than non-hydrogen-bonded D-H bonds in similar systems.
- for two-centered hydrogen bonds unconstrained by external factors, the D-H---A angle will approach linearity, as VSEPR theory would predict for a D:H:A unit.

2. *D-H vibrational frequencies*. Since hydrogen bonding involves weakening of the D-H bond and the formation of an H-A bond, in theory both the D-H and A-H vibrational modes will be found in the IR spectrum of a hydrogen-bonded system, albeit redshifted to lower wavenumbers than the unweakened D-H and A-H bonds. In practice, the shift in the D-H vibrational band to lower wavenumbers (along with a broadening and intensifying of the band) is taken as evidence for hydrogen bonding (Figure 6.5.1.1).

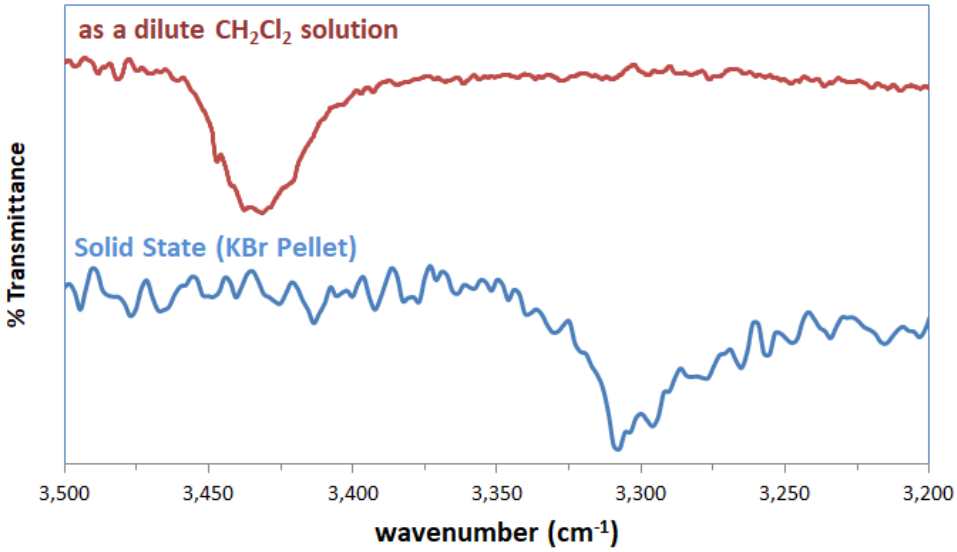
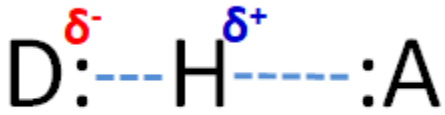


Figure 6.5.1.1. N-H vibrational bands in the IR spectrum of *N*-ferrocenylisonicotinamide. In dilute solution the N-H stretch of isolated molecules occurs at 3430 cm^{-1} but in the solid it shifts to 3307 cm^{-1} as the molecules form a network of H-bonded chains.

3. Shifts in the ^{1}H NMR peak position of the donor hydrogen. As the hydrogen is partially transferred from D to A it becomes deshielded and so is shifted downfield, sometimes by as much as several ppm.



Care should be taken in applying these criteria since:

- The criteria work best for classical hydrogen bonded systems. Other aspects of the bonding in a given system can influence apparent bond strengths and NMR chemical shifts, particularly for intramolecular H-bonds and in nonclassical hydrogen bonding systems.
- Stronger hydrogen bonds are more likely to adhere to these criteria than weaker ones. Moreover, stronger hydrogen bonds generally exhibit greater linearity, shorter distances relative to those expected from Van der Waals radii, larger stretching frequency lowering for D-H, and greater downfield shifts in their NMR spectra.

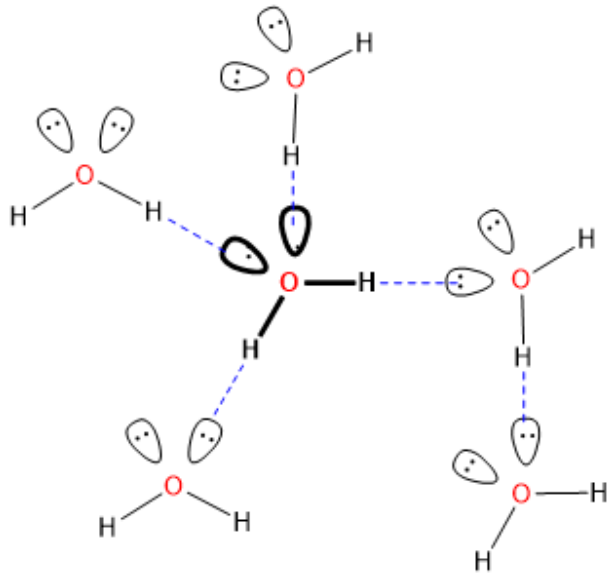
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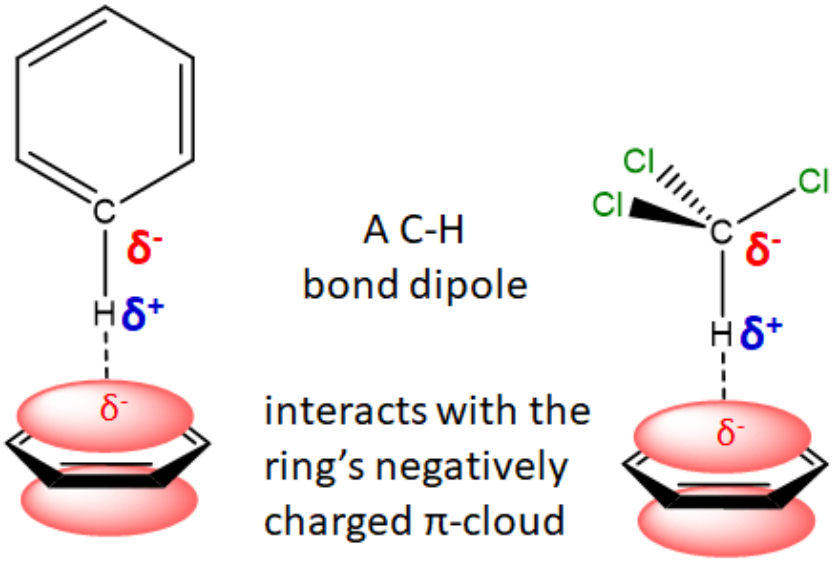
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Notes

* Of course in solutions where there are many hydrogen bonding interactions many of the water molecules might simultaneously act as a hydrogen bond donor and acceptor.



** X-H π interactions are interactions between the partial positive charge on the H end of a polar X-H bond and a negatively-charged π-bond. These are particularly for understanding hydrogen bonded systems in which as π-system serves as the hydrogen bond acceptor,. Examples of X-H interactions in which benzene is the acceptor are illustrated below.



† In a multicenter H-bond the D-H is donated to multiple acceptors simultaneously.

†† The MOs shown in the diagrams were calculated by performing *ab initio* calculations at the 6-31G** level. Those for the symmetric H-bond correspond to FHF^- and the assymetric H bond to OHF^-.

‡ So called because it involves a sliding bar chart with common classes of H-bond donors and acceptors that may be slid along the rule in a manner similar to the operation of a pre-late 20th Century device for performing mathematical computations called a slide rule.

‡‡ for example, intramolecular hydrogen bonds are sometimes constrained to by the overall geometry of the interacting groups.

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6.2.6: Hard and Soft Acids and Bases

Origin of the Hard-Soft Acid-Base Principle

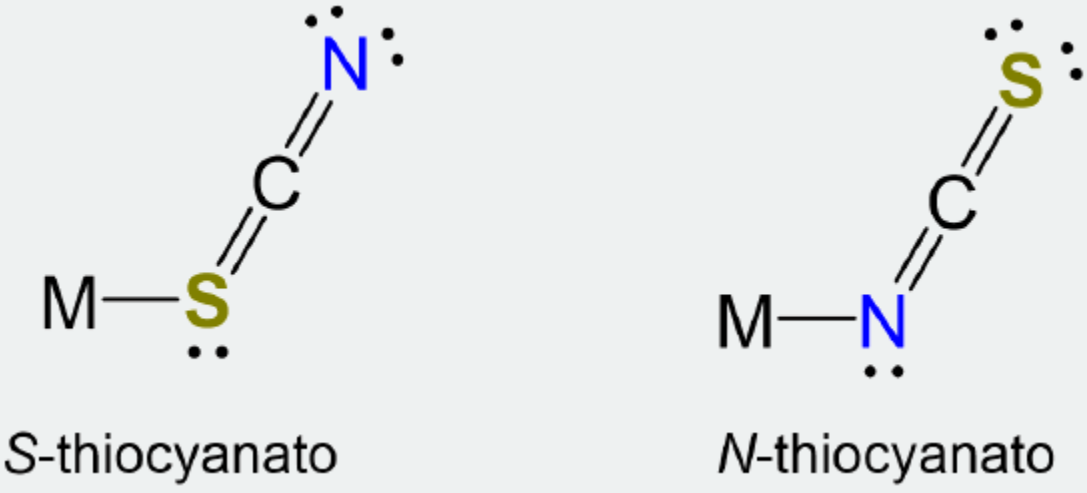
One of the strengths of the Lewis acid-base concept is the readiness with which it illuminates the role that covalent and electrostatic interactions in acid base behavior, specifically through its ability to explain chemical interactions in terms of frontier orbitals and the interactions between charged groups as electrons are donated from a base to an acid. However, simply acknowledging the presence of such interactions does little to illuminate the degree to which each mode of explanation best explains the bonding in a given system? To what extent is a given adduct better described as held together by covalent bonds as opposed to ionic ones - *e.g.* better described as a molecule rather than an ion pair? Moreover, does it even matter, given that the orbitals of quantum mechanics result from the combination of electrons' wavelike behavior with their electrostatic attraction to nuclei in either case?[1] These questions and more are addressed by one of the most important conceptual tools in contemporary inorganic chemistry, 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 even 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 bound 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 forms S-thiocyanato complexes, giving species like $[Hg(SCN)_4]^{2-}$.

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.



- 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

$$X = F << Cl < Br << I \text{ (for the solubility of LiX)}$$

Notes

1. Albeit suitably fudged through such niceties as the Aufbau principle and other approximations.

* 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.

† This can be predicted based on the relative hardness of BF_3, BR_3, and BH_3 in the list of hard and soft acids. However, for those of you who may be confused as to why H is considered a better electron donor for the purposes of softening a Lewis acid center while alkyl groups are better electron donors for the purposes of stabilizing carbocations in organic chemistry, the dominant effect is the lower electronegativity of H relative to carbon (in CH_3). The effect of electron donation due to hyperconjugation isn't as great for thermodynamically stable bases like BX_3/BR_3.

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6.2.6.1: Quantitative Measures of Hardness, Softness, and Acid-Base Interactions from a Hard Soft Acid-Base Principle Perspective Involve Orbital Energies and/or Apportioning Acid-Base Bonding in Terms of Electrostatic and Covalent Factors

Pearson Absolute Hardness is a useful metric of hardness based on orbital energies

The recognition that hard acids and bases possess a large HOMO-LUMO gap suggests that the gap size itself might serve as a useful index of hardness. The basis for this idea may be found by considering Pearson's definition of absolute hardness, η.[1] **Pearson's absolute hardness, η**, is half the second derivative of a species' energy with respect to changes in total number of electrons, N_{e^-}.

$$\text{Pearson's absolute hardness} = \eta = \frac{1}{2}\frac{d^2E}{dN_{e^-}^2}$$

$$(in \;\; eV)$$

and, since acids' and bases' hardness and softness are inversely related, Pearson's absolute softness, σ, is just the inverse of hardness.

$$\text{Pearson's softness} = \frac{1}{\eta}$$

Of these, Pearson's absolute hardness is related to the **Mulliken definition of electronegativity** as the first derivative of a species' energy with respect to changes in total number of electrons.

$$\text{Mulliken electronegativity} = \chi = \frac{dE}{dN_{e^-}}$$

$$(in \;\; eV)$$

Operationally, both the Pearson hardness and Mulliken electronegativity are approximated in terms of the energies associated with unit changes in the number of electrons – *i.e.,* in terms of ionization energies and electronegativities. Specifically,

$$\text{Pearson's absolute hardness} = \eta \approx \frac{IE–EA}{2}$$

$$\text{Mulliken electronegativity} = \chi \approx \frac{IE + EA}{2}$$

where IE and EA are in eV.

The connection between Pearson's absolute hardness/softness and the HOMO-LUMO gap then follows from Koopman's theorem, in which the ionization energy (IE) is just the opposite of the HOMO energy.

$$IE = -E_{HOMO}$$

Similarly, the electron affinity (EA), defined as the opposite of the energy released on absorption of an electron, may be taken as an approximation of the LUMO energy.

$$E_{LUMO} \approx -EA$$

So Pearson's absolute hardness is just half the HOMO-LUMO gap (band gap) size in electron volts:

$$\text{Pearson's absolute hardness} = \eta \approx \frac{E_{LUMO} - E_{HOMO}}{2}$$

where all values are given in eV,

and the Mulliken electronegativity is just the average of the HOMO and LUMO energies (~Fermi energy):

$$Mulliken\ electronegativity, \chi \approx -\frac{E_{LUMO} + E_{HOMO}}{2}$$

$$where\ all\ values\ are\ given\ in\ eV$$

The relationships between the Pearson absolute hardness, Mulliken electronegativity, and HOMO and LUMO energies are depicted schematically for the group 1A monocations in Figure 6.2.6.1.1.

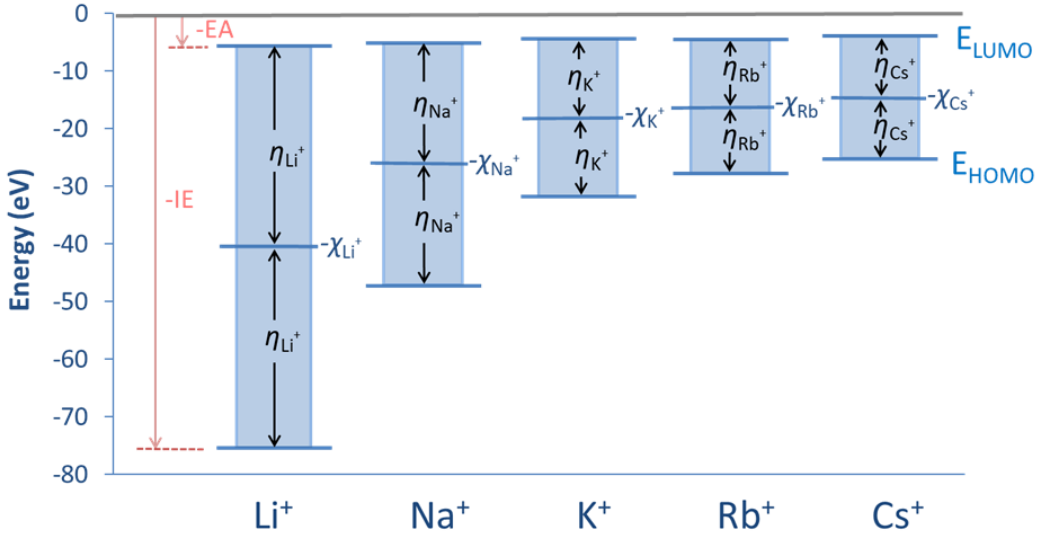


Figure 6.2.6.1.1. Relationships between Pearson absolute hardness, Mulliken electronegativity, and HOMO and LUMO energies for the group 1A monocations.

Values of the Pearson hardness and Mulliken electronegativity for several acids and bases are given in Table 6.2.6.1.1. The values in the table confirm the expected trends, showing an increase in hardness with size (down a group), with increasing charge, and as substituent electronegativity increases for a series of isolobal ions.

Table 6.2.6.1.1: Pearson Absolute Hardness and Related Parameters for Selected Acids and Bases.[2] *Taken from Pearson, R. G., Absolute electronegativity and hardness: application to inorganic chemistry. Inorganic Chemistry 1988, 27 (4), 734-740.*

Species	Ionization Energy, IE or I (eV)	Electron Affinity, EA or A (eV)	Mulliken Electronegativity, χ (eV)	Pearson Absolute Hardness, η (eV)
Selected Acids				
Group 1A monocations				
Li^+	75.64	5.39	40.52	35.12
Na^+	47.29	5.14	26.21	21.08
K^+	31.63	4.34	17.99	13.64
Rb^+	27.28	4.18	15.77	11.55
Cs^+	25.1	3.89	14.5	10.6

Species	Ionization Energy, IE or I (eV)	Electron Affinity, EA or A (eV)	Mulliken Electronegativity, χ (eV)	Pearson Absolute Hardness, η (eV)
Group 11 monocations				
Cu^+	20.29	7.73	14.01	6.28
Ag^+	21.49	7.58	14.53	6.96
Au^+	20.5	9.23	14.9	5.6
Isoelectronic Row 3 Metal Cations				
Na^+	47.29	5.14	26.21	21.08
Mg^{2+}	80.14	15.04	47.59	32.55
Al^{3+}	119.99	28.45	74.22	45.77
Changes with Transition Metal Ion Charge				
Fe^{2+}	30.65	16.18	23.42	7.24
Fe^{3+}	54.8	30.65	42.73	12.08
Co^{2+}	33.50	17.06	25.28	8.22
Co^{3+}	51.3	22.5	42.4	8.9
Boron trihalides				
BF_3	15.81	-3.5	6.2	9.7
BCl_3	11.60	0.33	5.97	5.64
BBr_3	10.51	0.82	5.67	4.85
CO_2	13.8	-3.8	5.0	8.8
CS_2	10.08	0.62	5.35	5.56
Selected Bases				
Group 17 monoanions (taken to be identical to the free atom values; for arguments as to why this is reasonable see Pearson, R. G., Inorg. Chem. 1988, 27 (4), 734-740.)				
F^-	17.42	3.40	10.41	7.01
Cl^-	13.01	3.62	8.31	4.70
Br^-	11.84	3.36	7.60	4.24
I^-	10.45	3.06	6.76	3.70
Group 15 hydrides				
NH_3	10.7	-5.6	2.6	8.2
PH_3	10.0	-1.9	4.1	6.0
Trimethylpnictides				
NMe_3	7.8	-4.8	1.5	6.3
PMe_3	8.6	-3.1	2.8	5.9
$AsMe_3$	8.7	-2.7	3.0	5.7
Group 16 hydrides				

Species	Ionization Energy, IE or I (eV)	Electron Affinity, EA or A (eV)	Mulliken Electronegativity, χ (eV)	Pearson Absolute Hardness, η (eV)
H_2O	12.6	-6.4	3.1	9.5
H_2S	10.5	-2.1	4.2	6.2
Phosphorous trihalides				
PF_3	12.3	-1.0	5.7	6.7
PCl_3	10.2	0.8	5.5	4.7
PBr_3	9.9	1.6	5.6	4.2

Drago-Wayland Acid-Base Parameters allow for estimation of the electrostatic and covalent contributions to the enthalpy of formation of a Lewis acid-base adduct.

Although Pearson hardness values are a useful metric of acids' and bases' hardness, they cannot easily be used to estimate the Lewis acid-base interaction energy. This is not the case for the EC model developed by Drago and Wayland.[3] In the **Drago and Wayland's EC Model,** the enthalpy of formation of an acid-base adduct, AB,

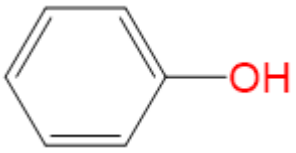
$$A + B \rightleftharpoons AB \qquad \Delta H_{AB\ adduct}$$

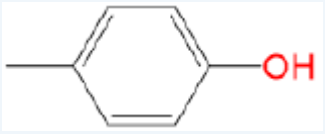
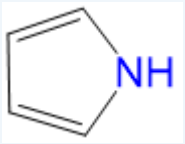
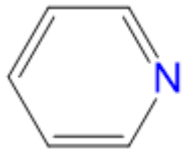
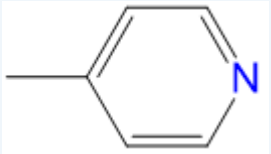
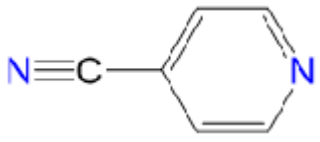
from the acid (A) and base (B) can be calculated as the sum of products of electrostatic (E) and covalent (C) factors that reflect the propensity of the acid and base to engage in strong electrostatic and covalent interactions with one another:

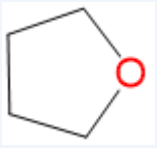
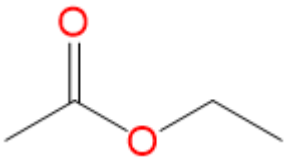
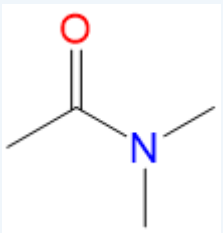
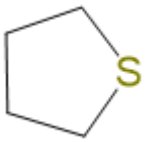
$$-\Delta H_{AB\ adduct} = E_A E_B + C_A C_B$$

where E_A and C_A are the electrostatic and covalent parameters for the acid and E_B and C_B the electrostatic and covalent parameters for the base given in units of kcal^{½} mol$^{-½}$. E and C parameters for selected acids and bases are given in Table 6.2.6.1.2 .

Table 6.2.6.1.2: E and C Parameters for selected Lewis acids and bases according to the ECW model.[4,5] Taken from Vogel, G. C.; Drago, R. S., The ECW Model. Journal of Chemical Education 1996, 73 (8), 701 and Drago, R. S. A modern approach to acid-base chemistry. Journal of Chemical Education 1974, 51 (5), 300 (for BF_3).

Species	E (kcal^{½} mol$^{-½}$)	C (kcal^{½} mol$^{-½}$)	W (kcal mol^{-1})	C/E
Acids				
I_2	0.5†	2†	0	4
ICl	2.92	1.66	0	0.57
H_2O	1.31	0.78	0	0.59
SO_2	0.51	1.56	0	3.1
$HCCl_3$ (chloroform)	1.56	0.44	0	0.28
$(CH_3)_3COH$	1.07	0.69	0	0.65
$(CF_3)_3COH$	3.06	1.88	-0.87	0.61
	2.27	1.07	0	0.47

Species	E (kcal^{½} mol$^{-½}$)	C (kcal^{½} mol$^{-½}$)	W (kcal mol^{-1})	C/E
	2.23	1.03	0	0.46
	2.30	1.11	0	0.48
	1.38	0.68	0	0.49
BF_3	1.62	9.88		6.10
$B(CH_3)_3$	2.90	3.60	0	1.2
$Al(CH_3)_3$	8.66	3.68	0	0.43
$Ga(C_2H_5)_3$	6.95	1.48	0	0.21
$In(CH_3)_3$	6.60	2.15	0	0.33
$Zn[N(Si(CH_3)_3)]_2$	2.75	2.32	0	0.84
$Cd[N(Si(CH_3)_3)]_2$	2.50	1.83	0	0.73
Bases				
NH_3	2.31	2.04		0.88
CH_3NH_2	2.16	3.13		1.4
$(CH_3)_2NH$	1.80	4.21		2.3
$(CH_3)_3N$	1.21	5.61		4.6
	1.78	3.54		2.0
	1.81	3.73		2.0
	1.53	2.94		1.9
CH_3CN	1.64	0.71		0.43
$ClCH_2CN$	1.67	0.33		0.20
$CH_3C(O)CH_3$	1.74	1.26		0.72

Species	E (kcal^{½} mol$^{-½}$)	C (kcal^{½} mol$^{-½}$)	W (kcal mol^{-1})	C/E
$(C_2H_5)_2O$	1.80	1.63		0.91
	1.64	2.18		1.3
 (EtOAc)	1.63	0.95		0.58
	2.35†	1.31		0.56
$(CH_3)_2S$	0.25	3.75		15
$(CH_3CH_2)_2S$	0.24	3.92†		15
	0.26	4.07		16
$(CH_3)_2Se$	0.05	4.24		83
$(CH_3)_2SO$	2.4	1.47		0.61
$(CH_3)_3P$	0.25	5.81		24
$(CH_3O)_3P$	0.13	4.83		37
$(C_6H_5)_3PO$	2.59	1.67		0.64
$(C_6H_5)_3PS$	0.35	3.65		10
C_6H_6	0.70	0.45		0.64

† These values were fixed to parameterize the rest of the E and C parameters.

Trends in the relative values of C and E for the acids and bases in Table 6.2.6.1.2 are very roughly consistent with the trends in hardness and softness outlined earlier. However, the parameters suggest that some trends in hardness reflect changes in species' ability to engage in ionic interactions while others reflect changes in species' ability to engage in strong covalent interactions. For example, C_B for the dimethylchalcogenides increases steadily from 1.5 to 4.25 kcal^{½} mol$^{-½}$ on going from Me_2O to Me_2Se while E_B decreases from 1.68 to 0.05 kcal^{½} mol$^{-½}$, suggesting that electrostatic and covalent factors are both involved in a decrease in base hardness down group 16. However, in the case of phosphines and amines it appears that electrostatic factors are primarily responsible for the decrease in hardness down group 15. On going from Me_3N to Me_3P, C_B only increases slightly from 5.61 to 5.81 kcal^{½} mol$^{-½}$ while E_B decreases from 1.21 to 0.25 kcal^{½} mol$^{-½}$ - *i.e.*, to 20% of the Me_3N value.

However, some species tend to have very high values for both E and C, reflecting their ability to engage in strong electrostatic

and covalent interactions, while others have small values for both, reflecting their relative stability as free species in solution.

As can be seen by comparing the acids and bases listed in the absolute hardness table (Table $6.2.6.1.1$) and the EC parameters table (Table $6.2.6.1.2$). The EC model has primarily been applied to organic and main group organometallic acids and bases. However, a variety of extensions have been proposed that enable its wider applicability.

The simple EC model only includes electrostatic and covalent considerations and thus ignores steric, lattice energy, and other contributions to the interaction energy. Thus it is only useful for analyzing the interaction energies of sterically unhindered adducts in which solvation energy and other contributions to the overall interaction energy are insignificant. However, additional refinements of the model attempt to extend its usefulness by accomodating various factors, such as

- *Steric strain*. Specifically, Hancock and Martell[6] introduced a D parameter to account for any additional steric strain introduced upon adduct formation,* giving

$$-\Delta H_{AB\ adduct} = E_A E_B + C_A C_B - D_A D_B$$

- *Charge transfer upon adduct formation*. As discussed in section 6.4.2, the formation of a Lewis acid-base complex results in a net transfer of electron density from the electron donor (base) to the acceptor (acid). Drago and Wong[7] extended the EC model to include that charge transfer by adding what they called receptance factors that account for the acid's ability to receive electron density (R_A) and transference factors that account for the base's ability to donate electron density (T_B), giving

$$-\Delta H_{AB\ adduct} = E_A E_B + C_A C_B + R_A T_B$$

  This extension of the EC model is called the **electrostatic-covalent-transfer or ECT model**. Notably, it has been applied successfully to adducts involving ions, for which the R_AT_B term can account for as much as 31% of the interaction energy.

- *Any constant energy term, such as the energy needed to cleave a dimer in order to make the Lewis acid (e.g., $Al_2Cl_6 \rightarrow 2AlCl_3$).* Drago and Vogel[4] extended the EC model to accommodate these constant energy terms, which they designated W. The resulting model is called the **ECW model,** for which

$$-\Delta H_{AB\ adduct} = E_A E_B + C_A C_B + W$$

where

$$W = W_A + W_B$$

A simple application of EC and extended EC models is that they allow the enthalpy of adduct formation to be calculated. These enthalpy calculations based on the EC model are consistent with the superior interaction energy of hard-hard and soft-soft interactions compared to hard-soft ones. Consider, for example, the transfer of I_2 between BF_3 and $InMe_3$, H_3N-BF_3, and H_3N-$InMe_3$.

$$H_3N - BF_3 + InMe_3 \rightleftharpoons BF_3 + H_3N - InMe_3$$

Since H_3N is a hard base and BF_3 and $InMe_3$ are harder and softer acids, respectively, the equilibrium is expected to favor the reactant, H_3N-BF_3. Assuming the equilbrium is enthalpically driven, this qualitative analysis is consistent with the expected endothermic enthalpy of the reaction, as may be seen from the calculated enthalpies of adduct formation for both H_3N-BF_3 and H_3N-$InMe_3$.

For H_3N-BF_3:

$$-\Delta H_{H_3N-BF_3} = E_{BF_3}E_{NH_3} + C_{BF_3}C_{NH_3}$$

$$-\Delta H_{H_3N-BF_3} = (1.62)(2.31) + (9.88)(2.04)$$

$$-\Delta H_{H_3N-BF_3} = 3.74\ kcal/mol + 20.1\ kcal/mol = 23.8\ kcal/mol$$

$$\Delta H_{H_3N-BF_3} = -23.8\ kcal/mol$$

For H_3N-$InMe_3$:

$$-\Delta H_{H_3N-InMe_3} = E_{InMe_3}E_{NH_3} + C_{InMe_3}C_{NH_3}$$

$$-\Delta H_{H_3N-InMe_3} = (6.6)(2.31) + (2.15)(2.04)$$

$$-\Delta H_{H_3N-InMe_3} = 15.25\ kcal/mol + 4.39\ kcal/mol = 19.63\ kcal/mol$$

$$\Delta H_{H_3N-InMe_3} = -19.63\ kcal/mol$$

So H_3N-BF_3 is enthalpically favored by -4.2 kcal/mol [=-23.8 kcal/mol - (-19.63 kcal/mol) according to Hess' Law].

In addition to their utility for estimating enthalpies of Lewis acid-base complex formation, EC and related models serve as a useful tool for estimating the relative importance of ionic, covalent, and steric factors in complex formation. Specifically,

- The relative contributions of ionic and covalent factors can be calculated directly, as from the E and C terms. This can provide insight into why some complexes are more stable than others. Such calculations reveal that the hard-hard adduct H_3N-BF_3 is favored over the hard-soft adduct H_3N-$InMe_3$ because of the strong covalent interaction holding together H_3N-BF_3. The covalent term accounts for 84% of the energy of the H_3N-BF_3 interaction and is largely lost upon formation of H_3N-$InMe_3$, for which it contributes only 22% of the interaction energy. When the electrostatic term is accounted for, it can be seen that the formation of H_3N-$InMe_3$ from H_3N-BF_3 is disfavored, since it would result in a loss of 15.7 kcal/mol of covalent stabilization that would be incompletely compensated for by a gain of 11.5 kcal/mol of electrostatic stabilization.
- The role of other contributions to the bonding in a Lewis acid-base complex may be estimated from the discrepancy between the experimental and EC model calculated stabilization energies. This is because the EC parameters assume sigma bonding and so any deviation between the calculated and experimental enthalpies of complex formation can be attributed to non-sigma contributions.
  - This is done explicitly in extensions of the EC model. For instance, in the case of the Hancock and Martell, ECT, and ECW extensions of the EC model, the contributions of the steric, charge transfer, and constant energy factors (like dimer dissociation) are directly computed in the model.
  - Comparisons of the difference between the energies calculated using ordinary EC parameters and the observed enthalpies has also been used as an estimate of the
    - steric strain energy in strained adducts, which exhibit a less exothermic heat of adduct formation than expected
    - π-backbonding energy in adducts which are capable of such interactions and exhibit a more exothermic heat of formation than expected.[8-10]
  - For examples see (a) Drago, R. S., The interpretation of reactivity in chemical and biological systems with the E and C model. Coordination Chemistry Reviews 1980, 33 (3), 251-277; (b) Drago, R. S.; Bilgrien, C. J., Inductive transfer and coordination of ligands in metal—metal bonded systems. Polyhedron 1988, 7 (16), 1453-1468; (c) Drago, R. S., The question of a synergistic metal-metal interaction leading to .pi.-back-bond stabilization in dirhodium tetrabutyrate adducts. Inorganic Chemistry 1982, 21 (4), 1697-1698.
- The role of electrostatic, covalent, and other contributions to the spectroscopic behavior of Lewis acid-base complexes can be assessed similarly using specialized versions of the ECW or ECT model that allow for calculation of changes in spectroscopic parameters upon adduct formation - *e.g.,* OH stretching frequencies. Details are beyond the scope of this text but may be found in the original literature,[11] for example, Drago, R. S.; Vogel, G. C. *JACS* 1992, 114 (24), 9527-9532; Vogel, G. C.; Drago, R. S., *J. Chem. Educ.* 1996, 73 (8), 701; Drago, R. S.; Wong, N. M., *J. Chem. Educ.* 1996, 73 (2), 123.).

Pearson Softness Parameters have been proposed as a means of calculating the equilibrium constant for formation of a Lewis acid-base adduct, although they are more commonly used to estimate metal toxicity

Pearson also proposed a softness parameter that can be used to estimate the thermodynamics of Lewis acid-base complex formation, this time in the form of the equilibrium constant for

$$A + B \overset{K}{\rightleftharpoons} AB$$

for which Pearson proposed

$$logK = S_A S_B + \sigma_A \sigma_B$$

where S_A and S_B are acid and base parameters related to the strength of the acid-base interaction and σ_A and σ_B are acid and base parameters related to softness. This approach hasn't found as wide an acceptance in studies of chemical reactivity as the Drago-Wayland and absolute hardness parameters. However, because the toxicity of metal ions sometimes depends on their propensity to bind soft Lewis bases in living systems, the softness parameters which Pearson and Mawby subsequently proposed based on the relative energies of metal fluorine and metal iodine bonds[12] have been widely used as a tool for predicting metal ion toxicity.[13]

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11. Drago, R. S.; Vogel, G. C., Interpretation of spectroscopic changes upon adduct formation and their use to determine electrostatic and covalent (E and C) parameters. *Journal of the American Chemical Society* 1992, 114 (24), 9527-9532.

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Notes

* More precisely, the D parameters account for the difference in steric strain in the adduct relative to a water adduct of the Lewis acid.

This page titled 6.2.6.1: Quantitative Measures of Hardness, Softness, and Acid-Base Interactions from a Hard Soft Acid-Base Principle Perspective Involve Orbital Energies and/or Apportioning Acid-Base Bonding in Terms of Electrostatic and Covalent Factors is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Stephen M. Contakes.

- 6.6.1: Quantitative Measures of Hardness, Softness, and Acid-Base Interactions from a Hard Soft Acid-Base Principle Perspective Involve Orbital Energies and/or Apportioning Acid-Base Bonding in Terms of Electrostatic and Covalent Factors by Stephen M. Contakes is licensed CC BY 4.0.

6.2.6.2: 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

The Hard Soft Acid Base Principle is a Conceptual Tool for Thinking About Patterns of Lewis Acid-Base Reactivity

The explanation of the trends in metal distribution, halide salt solubility, and preferred metal coordination patterns is rooted in Arland, Chatt, and Davies' observation 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).[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 class b acids and bases soft. These terms reflect how "soft" these substance's electron clouds are towards distortion or, in other words, their polarizability (Figure 6.2.6.2.1). Pearson terms acids and bases which are relatively polarizable **soft** and those which are difficult to polarize **hard.**

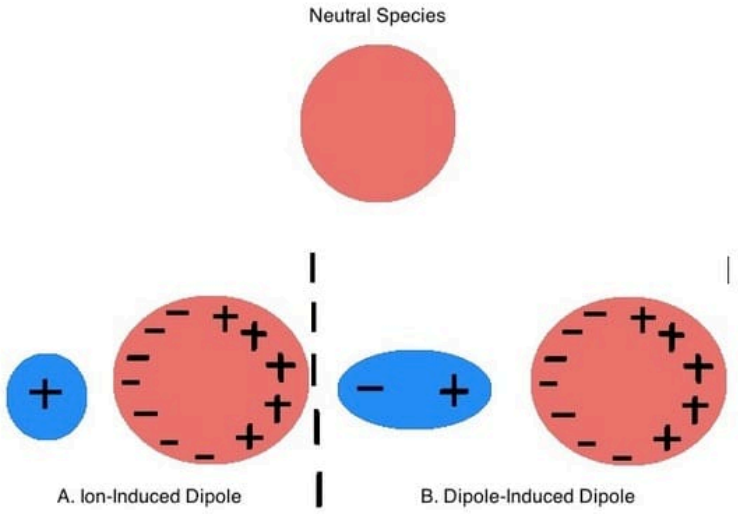


Figure 6.2.6.2.1: Polarizability refers to the ease with which a substance's electron cloud may be distorted under the action of an electric field. A fragment's polarizability determines the degree to which its electron cloud is distorted by A.) an Ion and B.) a polar molecule to induce a dipole moment. The figure is taken from (and the caption expanded from) Cox, Kelly and Dana Reusser "Polarizability"

Recognizing Hard and Soft Acids and Bases

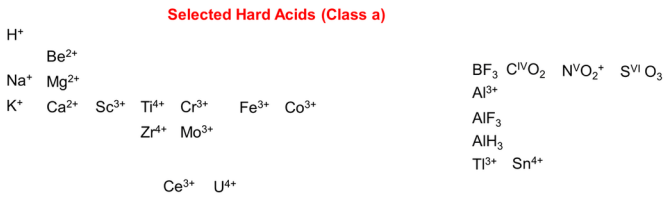
Hard acids and bases come in two varieties:

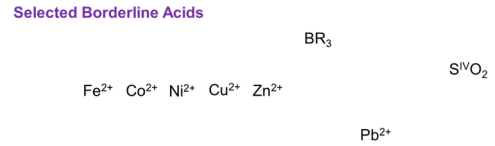
1. hard acid and base sites that possess few valence electrons and for which polarization therefore involves distorting core electrons, which are difficult to distort because they are close to the nucleus and experience a high nuclear charge. The most common examples of such substances are Lewis acid hard acids towards the left of the periodic table.
2. hard acid and base sites with a high charge density (highly charged relative to size) and/or which are electron deficient. In these cases polarization involves distorting electrons that already experience strong unshielded electrostatic interactions.

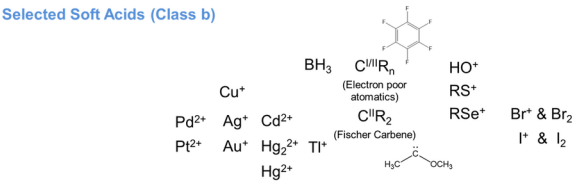
Soft acids and bases also come in two varieties

1. soft acids and bases which posses many valence electrons and so are more readily polarized. In consequence, all other things being equal, soft acids and bases are more likely to be found towards the middle or right of the periodic table.
2. soft acids and bases with little charge density and/or which are relatively electron rich.

Note that the hard-soft classification should not be thought of as if all hard acids and bases are equally hard and all soft acids and bases equally soft. There is a graduation in hardness and softness and a number of intermediate acids and bases which do not fit neatly in either category. With this caveat in mind, representative **hard, soft, and borderline acids** are given below. Notice how they illustrate the trends just outlined.

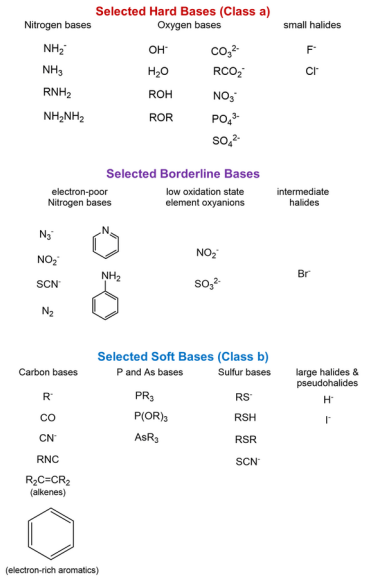






As expected, hard acids tend to be found towards the left side of the periodic table and involve higher oxidation states and/or electron donating substituents while soft acids are more common to the right of the periodic table and involve lower oxidation states and/or electron donating substituents.

Illustrative hard, soft, and borderline bases are given below. Again, notice how these substances illustrate the general trends.



Qualitative Estimation of the Relative Hardness and Softness of Lewis Acids and Bases

As can be seen from the examples above, **hard acids are relatively electron-poor and hard bases electron-rich** since they have comparatively

- small frontier orbitals, reflective of their relatively small atom/ion/fragment sizes
- high (for acids) or low (for bases) oxidation states on the base atom, reflected in a large positive formal charge (for acids) or negative formal charge (for bases)
- low polarizability, due to loss or gain of substantial numbers of electrons, or the localization of
  - positive charge on an electropositive element or an atom bearing electron-withdrawing substituents
  - negative charge on an electronegative element or an atom bearing electron-donating substituents

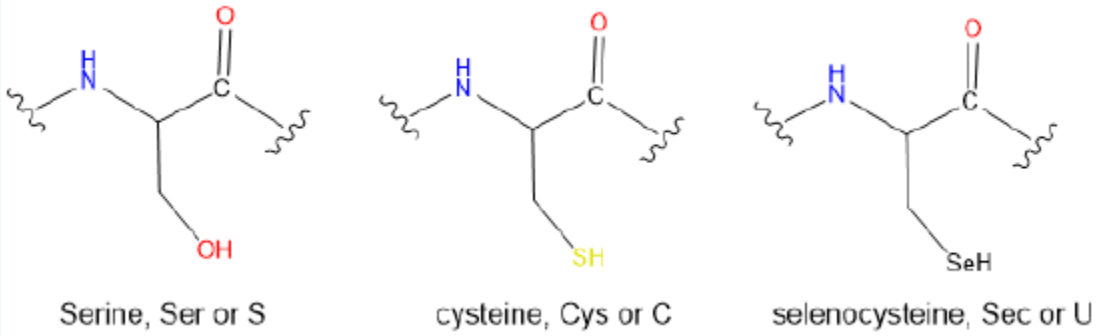
In contrast to hard acids and bases, **soft acids are relatively electron-rich and soft bases larger and more electron poor** since they have comparatively

- large frontier orbitals, reflective of their relatively large atom/ion/fragment sizes
- low oxidation states, often resulting in small or nonexistent atomic charges
- high polarizability, as might be expected of species in which electron-electron repulsions are lower and electrons are spread over a large volume. Sometimes this is indicated by
  - positive charge on an electronegative element or an atom bearing electron-donating substituents
  - negative charge on an electropositive element or an atom bearing electron-withdrawing substituents

Exercise 6.2.6.2.1

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 available at the end of this section.

The Hard-Soft Acid-Base Principle (HSAB Principle)

The **Hard-Soft acid-base principle (HSAB Principle) explains patterns in Lewis acid-base reactivity in terms of 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 stronger acid-base complexes with hard bases while soft acids form stronger 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/neucleophiles.

Applications of the HSAB principle include

1. Predicting the equilibrium or speed of *Lewis acid-base metathesis and displacement reactions*. In a Lewis acid-base **metathesis reaction** the acids and bases swap partners

$$\mathrm{A_1 : B_1 + A_2 : B_2 \overset{k_1,\ K_{eq}}{\rightleftharpoons} A_1 : B_2 + A_2 : B_1}$$

For example, the equilibrium position of the metathesis reaction between TlF and $\mathrm{K_2S}$ favors the products:

$$\mathrm{2\,TlF + H_2S \rightleftharpoons Tl_2S + 2\,KF}$$

consistent with the HSAB's hard-hard and soft-soft preference.



The HSAB principle also allows for prediction of the position 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 HI and methylmercury cation

$$\mathrm{HI + HgSCH_3^+ \rightleftharpoons CH_3SHgI + H^+}$$

involves displacement of an iodide from HI to give $\mathrm{CH_3HgI}$. The position of the equilibrium favors $\mathrm{CH_3HgI}$ since both $\mathrm{CH_3Hg^+}$ and $\mathrm{I^-}$ are soft, while $\mathrm{H^+}$ is a hard acid.



Exercise 6.2.6.2.2

Predict the position of equilibrium for the following reaction.

$$\mathrm{Fe_2O_3 + 3\,Ag_2S \rightleftharpoons Fe_2S_3 + 3\,Ag_2O}$$

Answer available at the end of this section.

Exercise 6.2.6.2.3

Predict whether K for the following equilibria will be <<1, ~1, or >>1.

a. $\mathrm{2\,HF + (CH_3Hg)_2S \rightleftharpoons 2\,CH_3HgF + H_2S}$
b. $\mathrm{Ag(NH_3)_2^+ + 2\,PH_3 \rightleftharpoons Ag(PH_3)_2^+ + 2\,NH_3}$

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 available at the end of this section.

2. Predicting the relative strengths of a given set of *Lewis acids or bases towards a particular substrate*. Consider, for example, the relative strengths of a BH_3, BMe_3, and BF_3 towards group 15 hydrides like NH_3, PH_3, and AsH_3. Of the boranes listed, the hardest acid BF_3 is the strongest acid towards the hard base NH_3 while BH_3 is the strongest towards AsH_3.[†]

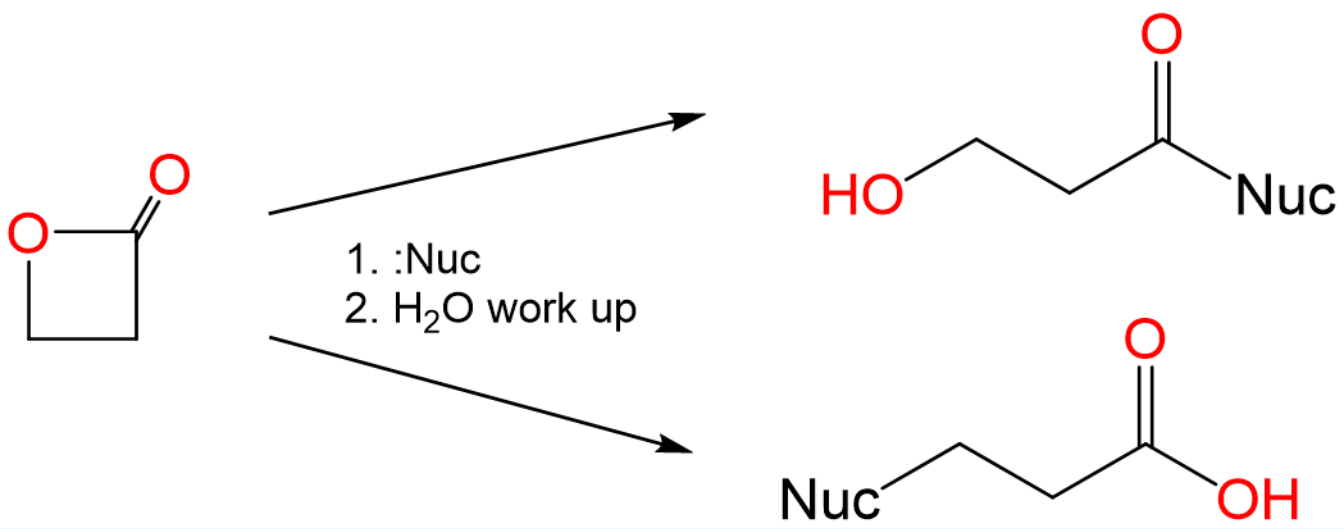
Exercise 6.2.6.2.4

Which acid will form the most stable complex with CO: BH_3, BF_3, or BMe_3?

Answer available at the end of this section.

Exercise 6.2.6.2.5

When lactones react with nucleophiles, they can undergo ring opening reactions to give either an alcohol or a carboxylic acid, as shown for propiolactone below:



In the reaction above, sterically unhindered alkoxides give one product and sterically unhindered thioalkoxides the other. Explain why this is the case and predict the products of the reaction between propiolactone and the sodium salts of ethoxide and thioethoxide.

Answer available at the end of this section.

The theoretical interpretation of the hard-soft acid-base principle is that hard-hard preferences reflect superior electrostatic stabilization while soft-soft preferences reflect superior covalent stabilization.

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.

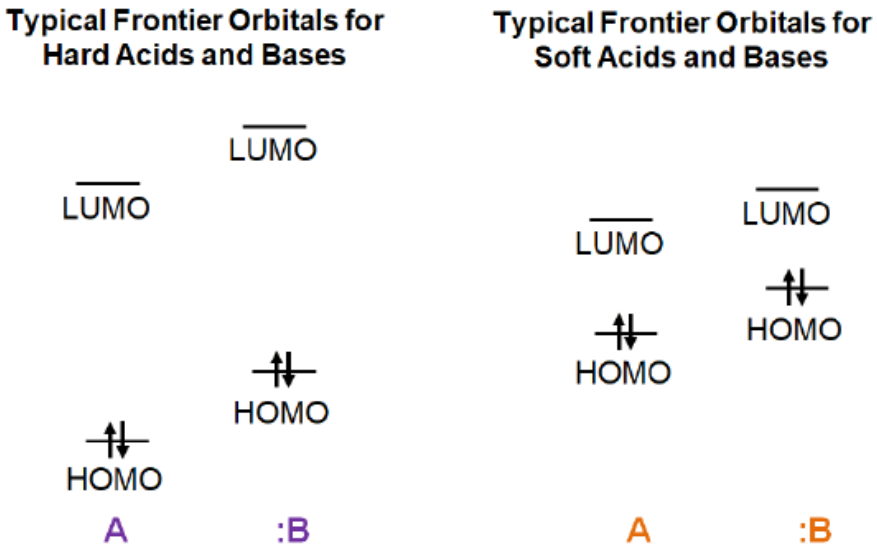
- The lone pair of a hard or soft base is comparatively weakly stabilized by an acid opposite to it in hardness or softness since the overall electrostatic and covalent stabilization of the adduct is comparatively weak.

To see why this is the case it is helpful to divide the contributions to the interaction energy between an acid and a base as follows:

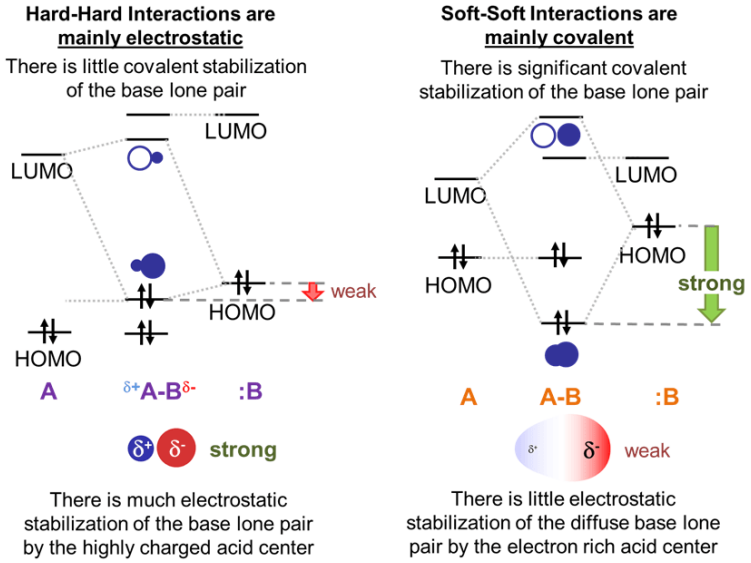
Interaction Energy = Electrostatic attractions and repulsions of partial atomic charges (Ionic term) + Interactions between filled orbitals on one fragment and unfilled orbitals on the other (Covalent term) + Electrostatic repulsions between filled orbitals on the two fragments (Steric term)

Of the three contributions to the interaction energy, only the ionic and covalent terms directly relate to the hardness of the interacting acid and base. One approach to thinking about how hardness influences the ionic and covalent contributions is to consider the frontier orbitals involved in the acid-base interaction. This is sometimes done through the use of the Salem-Klopman equation,[1,*] although in the treatment which follows a more qualitative approach will be employed.

Both hard acids and bases will have comparatively low energy HOMO levels and high energy LUMO levels, with a correspondingly high HOMO-LUMO gap. In contrast, soft acids and bases will have comparatively high-energy HOMO levels and low-energy LUMO levels, giving a comparatively smaller HOMO-LUMO gap.



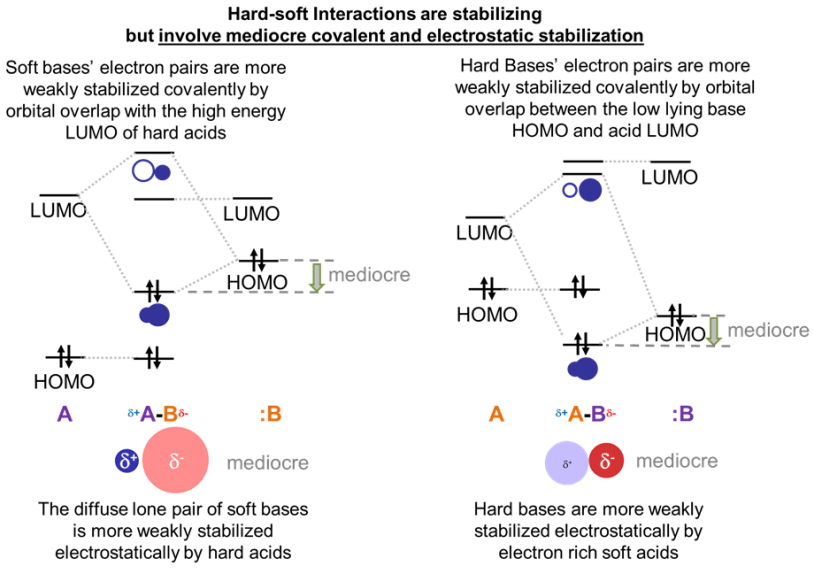
Given this, consider the frontier orbital interactions involved in the formation of an acid-base complex for the possible cases, as illustrated schematically below.



The large gap in energy between hard bases' highly stabilized HOMO lone pairs and the high energy LUMO of hard acids ensures that in **hard acid-hard base adducts the dominant stabilizing interaction will involve electrostatic attraction between the base lone pair and the electropositive Lewis acid center**. Fortunately, since the electron clouds in hard bases are relatively dense and electron rich while hard Lewis acids are highly charged and small, these electrostatic interactions are strong.

In contrast, in **soft acid-soft base adducts, the dominant stabilizing interaction will be covalent.** This is because the small gap in energy between a soft base HOMO and soft acid LUMO enables the formation of a well-stabilized bonding orbital with significant electron density between the acid and base.

The orbitals' interactions between hard acids and soft bases and soft acids and hard bases are intermediate between the hard acid-hard base and soft acid-soft base cases.



This means that the adducts are stable relative to free acid and base – just not as well stabilized as in the hard acid and hard base case. In the case of hard acids and soft bases the hard acids are less able to stabilize the soft bases' relatively diffuse electron pair electrostatically and there isn't as much covalent stabilization as in adducts of soft acids and bases due to the hard acid's high energy.

References

1. Ahrland, S.; Chatt, J.; Davies, N. R., The relative affinities of ligand atoms for acceptor molecules and ions. Quarterly Reviews, Chemical Society 1958, 12 (3), 265-276.

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.

† This can be predicted based on the relative hardness of BF_3, BR_3, and BH_3 in the list of hard and soft acids. However, for those of you who may be confused as to why H is considered a better electron donor for the purposes of softening a Lewis acid center while alkyl groups are better electron donors for the purposes of stabilizing carbocations in organic chemistry, the dominant effect is the lower electronegativity of H relative to carbon (in CH_3). The effect of electron donation due to hyperconjugation isn't as great for thermodynamically stable bases like BX_3/BR_3.

†† For more on the Salem-Klopman equation see Fleming, I., Molecular orbitals and organic chemical reactions. Reference ed.; Wiley: Hoboken, N.J., 2010; pp. 138-143.

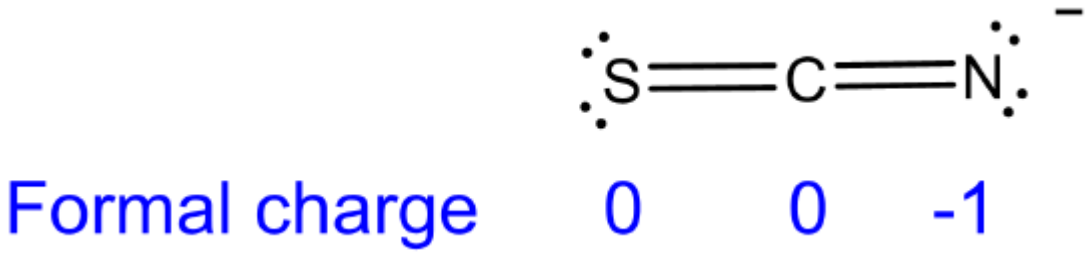
Answers

Exercise 6.2.6.2.1

(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 6.2.6.2.2

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 6.2.6.2.3

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.

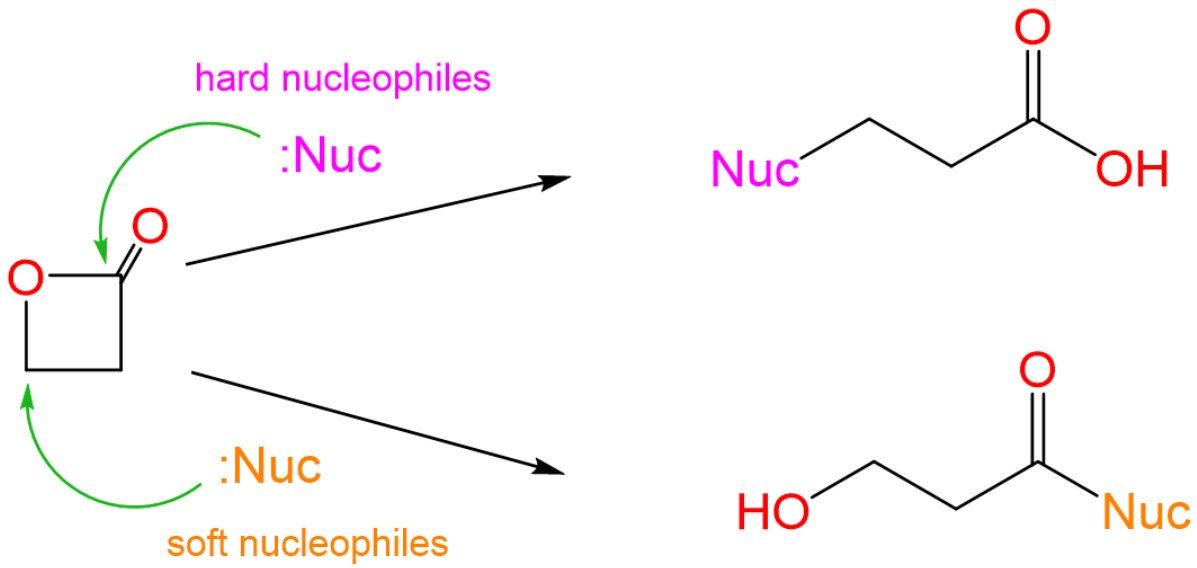
d. K>>1 since BH_3 is a softer acid than BF_3, so it will form a stronger complex with the softer base H_2S while the harder BF_3 forms a stronger complex with the harder base NH_3.

Exercise 6.2.6.2.4

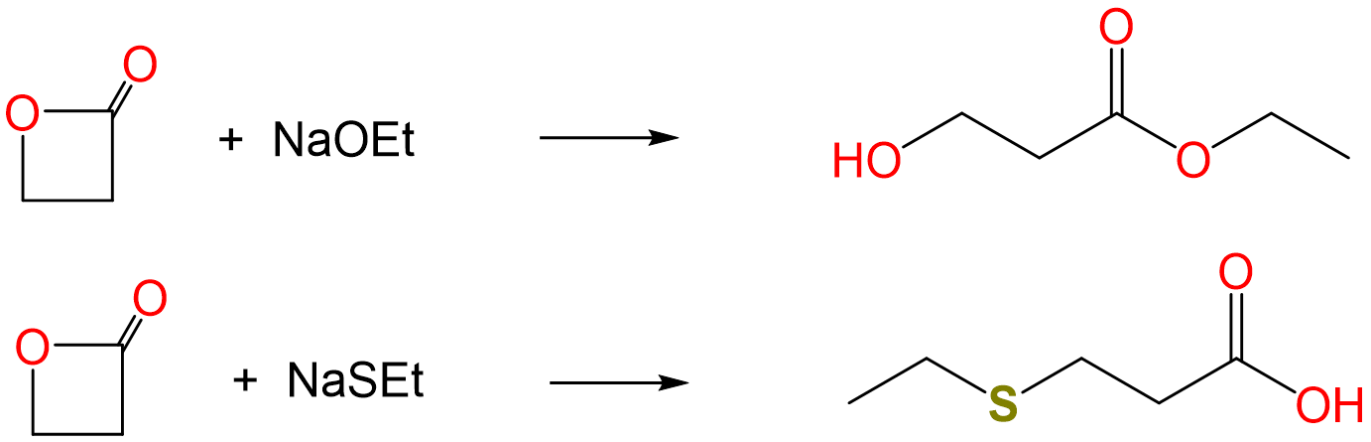
BH_3. Since CO forms complexes primarily through its carbon lone pair, it is a soft base and so will form the strongest complex with the softest Lewis acid.

Exercise 6.2.6.2.5

The two reaction products correspond to nucleophilic attack at the lactones' two electrophilic carbon centers. Specifically, the acid is produced by attack at the softer C^I center of the CH_2 directly attached to the ester oxygen and the alcohol by nucleophilic attack at the harder C^{III} center of the ester carbonyl.



Consequently, it is reasonable to expect that the harder base ethoxide will nucleophilically attack the harder carbonyl carbon while the softer thioethoxide will attack the softer methylene carbon.



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6.3: ACID-BASE CHEMISTRY

Learning Objectives

- Understand the Brønsted and Lewis definitions of acids and bases.
- Identify conjugate acids and bases, and rules for strong & weak acids/bases, in both Brønsted and Lewis acid-base systems.
- Use Pauling's rules to predict the pK_as of oxoacids.
- Understand the periodic trends of acidic, basic, and amphoteric compounds
- Predict, describe, and rationalize acid/base chemistry in non-aqueous systems, including acidic and basic solvents, aprotic solvents, and molten salts.
- Apply the principles of acid-base chemistry to the design of molecules and Lewis acids with target functions.
- Understand the connection between acid-base chemistry and the stabilization of oxidation states.
- Predict favorable and stable compounds using hard-soft acid-base (HSAB) theory.
- Understand the applications of the ECW model.

Acid-base reactions form the basis of the most common kinds of equilibrium problems which you will encounter in almost any application of chemistry. There are three major classifications of acids and bases: (1) The Arrhenius definition states that an acid produces H^+ in solution and a base produces OH^- and the (2) Brønsted-Lowry and (3) Lewis definitions of acids and bases. Of particular importance in inorganic chemistry is the "hard and soft (Lewis) acids and bases" (HSAB) theory that is widely used for explaining stability of compounds, reaction mechanisms, and reaction pathways.

6.3.1: Prelude to Acid-Base Chemistry

6.3.2: Brønsted and Lewis Acids and Bases

6.3.3: Hard and Soft Acids and Bases

6.3.4: The Electrostatic-Covalent (ECW) Model for Acid-Base Reactions

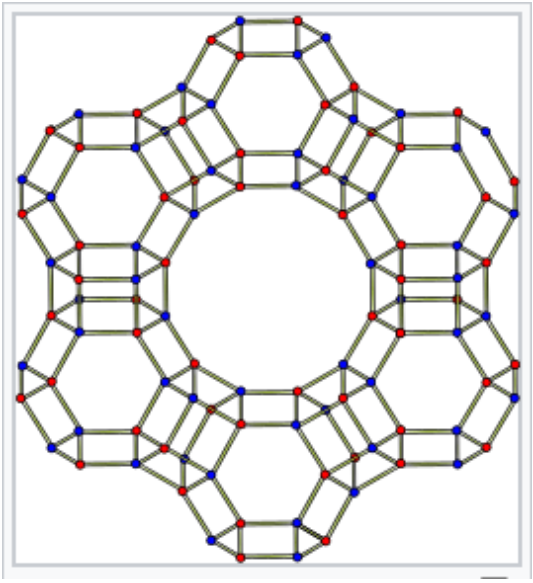
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6.3.1: Prelude to Acid-Base Chemistry

Acids and bases are important for a number reasons in inorganic chemistry.

- Many industrially useful catalytic reactions involve inorganic acids and superacids, such as zeolites, anhydrous hydrogen fluoride, and sulfated zirconia. These acids are sufficiently strong in anhydrous media that they can protonate olefins and alcohols to produce carbocations. Carbocations are key intermediates in the transformations of hydrocarbons.
- Inorganic compounds are sometimes synthesized in strongly acidic or basic media. For example, ternary metal oxides can be synthesized and crystallized in molten NaOH or KOH, which are strongly basic. Organic fluorination reactions are often done in strongly acidic media, such as anhydrous HF. Understanding the familiar chemistry of acids and bases in water helps us understand how these non-aqueous media work.
- The acidic or basic environment of metal ions affects the stability of their oxidation states. We will learn more about this in Chapter 4.
- Transition metal complexes (coordination compounds and organometallic compounds) are essentially Lewis acid-base complexes. We can understand a great deal about their stability and reactivity by considering the acid-base character of metals and ligands. We will learn about this in Chapter 5.



Solid acid catalysts, such as zeolite Y, are used to isomerize hydrocarbons in the processing of crude oil into gasoline. Edith Flanigen(below with President Barack Obama) received the 2014 National Medal of Technology for her research on the synthesis of zeolite Y.



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6.3.2: Brønsted and Lewis Acids and Bases

Three theories of acids and bases

There are three major classifications of substances known as acids or bases. The Arrhenius definition states that an acid produces H^+ in solution and a base produces OH^-. This theory was developed by Svante Arrhenius in 1883. Later, two more sophisticated and general theories were proposed. These are the Brønsted-Lowry and the Lewis definitions of acids and bases. The relationship between these theories is illustrated in the figure below.

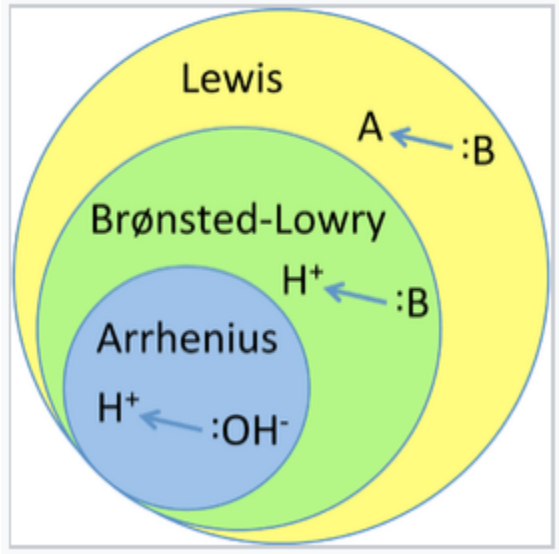


Illustration of the hierarchy of acid-base theories. Arrhenius acids and bases are a sub-class of Brønsted acids and bases, which are themselves a subclass of Lewis acids and bases.

The Arrhenius theory, which is the simplest and least general description of acids and bases, includes acids such as $HClO_4$ and bases such as NaOH or $Mg(OH)_2$. This theory successfully describes how acids and bases react with each other to make water and salts. However, it does not explain why some substances that do not contain hydroxide ions, for example F^- and NO_2^-, can make basic solutions in water. The Brønsted-Lowry definition of acids and bases addresses this problem. In this theory an **acid is a substance that can release a proton** (like in the Arrhenius theory) and a **base is a substance that can accept a proton**. A basic salt such as Na^+F^- generates OH^- ions in water by taking protons from water itself (to make HF):

$$\mathrm{F^-_{(aq)} + H_2O_{(l)} \rightleftharpoons HF_{(aq)} + OH^-} \tag{6.3.2.1}$$

When a Brønsted acid dissociates, it increases the concentration of hydrogen ions in the solution, $[H^+]$; conversely, Brønsted bases dissociate by taking a proton from the solvent (water) to generate $[OH^-]$.

Acid Dissociation: $\mathrm{HA_{(aq)} \rightleftharpoons A^-{}_{(aq)} + H^+{}_{(aq)}}$

$$K_a = \frac{[A^-][H^+]}{[HA]} \tag{6.3.2.2}$$

Base dissociation: $\mathrm{B_{(aq)}{}^+ \ H_2O_{(l)} \rightleftharpoons HB^+{}_{(aq)} + OH^{-+}(aq)}$

$$K_b = \frac{[HB^+][OH^-]}{[B]} \tag{6.3.2.3}$$

Conjugate acids and bases

One important consequence of these equilibria is that every **acid** (HA) has a **conjugate base** (A-), and vice-versa. In the base dissociation equilibrium above the conjugate acid of base B is HB^+.

For a given acid or base, these equilibria are linked by the water dissociation equilibrium:

$$\mathrm{H_2O_{(l)} \rightleftharpoons H^+{}_{(aq)} + OH^-{}_{(aq)}} \tag{6.3.2.4}$$

$$K_w = [H^+][OH^-] \tag{6.3.2.5}$$

for which the equilibrium constant K_w is 1.00 x 10^{-14} at 25°C. It can be easily shown that the product of the acid and base dissociation constants K_a and K_b is K_w.

Strong and weak acids and bases

Acids and bases that dissociate completely are said to be strong:

$$\mathrm{HClO_{4\,(aq)} \longrightarrow H^+{}_{(aq)} + ClO_4{}^-{}_{(aq)}} \tag{6.3.2.6}$$

$$\mathrm{HBr_{(aq)} \longrightarrow H^+{}_{(aq)} + Br^-{}_{(aq)}} \tag{6.3.2.7}$$

$$\mathrm{CH_3O^-{}_{(aq)} + H_2O_{(l)} \longrightarrow CH_3OH_{(aq)} + OH^-{}_{(aq)}} \tag{6.3.2.8}$$

$$\mathrm{NH_2{}^-{}_{(aq)} + H_2O_{(l)} \longrightarrow NH_{3\,(aq)} + OH^-{}_{(aq)}} \tag{6.3.2.9}$$

Here the right-handed arrow (→) implies that the reaction goes to completion. That is, a 1.0 M solution of $HClO_4$ in water actually contains 1.0 M H^+(aq) and 1.0 M ClO_4^-(aq), and very little undissociated $HClO_4$.

Conversely, weak acids such as acetic acid (CH_3COOH) and weak bases such as ammonia (NH_3) dissociate only slightly in water - typically a few percent, depending on their concentration and the values of K_a and K_b - and exist mostly as the undissociated molecules.



Antacid tablets typically contain calcium salts of the bicarbonate ion (HCO_3^-), a weak base. Its conjugate acid, carbonic acid (H_2CO_3) is a weak acid. The acid-base equilibrium between carbonic acid and bicarbonate is important in maintaining blood pH.

Example

Household ammonia is a solution of NH_3 in water that ranges from about 5-10% by weight. Let's calculate the percent ionization and the pH of the solution.

Solution

For a solution that is 8% ammonia by weight, assuming that the density is about the same as that of liquid water, the analytical concentration of ammonia is (80 g/L) / (17 g/mol) = 4.7 M.

The other thing we need to know to solve this problem is the base dissociation constant, K_b.

$$\mathrm{NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-} \quad K_b = 1.8 \times 10^{-5}$$

We can solve this problem rigorously by invoking both charge balance ($[H^+] + [NH_4^+] = [OH^-]$) and mass balance (4.7 M = $[NH_3] + [NH_4^+]$) and using $K_W = [H^+][OH^-]$. But because the algebra becomes complicated with that method - leading to a cubic equation that is hard to solve - we'll invoke two simplifying assumptions:

$[NH_4^+] \approx [OH^-] \gg [H^+]$ (which is a reasonable assumption for a basic solution)

and

$[NH_3] \gg [NH_4^+]$ (also reasonable if the percent ionization is small)

Now we can write:

$$[NH_4^+][OH^-] \approx [OH^-]^2 = (4.7M)(K_b) = 8.4 \times 10^{-5}$$

$$[OH^-] = 9.2 \times 10^{-3} M \;\; (\approx [NH_4^+]), \;\; [H^+] = \frac{K_w}{[OH^-]} = 1.1 \times 10^{-12} M, \quad \mathbf{pH = 11.97}$$

The percent ionization is:

$$100\% \times 9.2 \times 10^{-3} M / 4.7M = \mathbf{0.19}$$

This example illustrates that it is technically incorrect to label a bottle of aqueous ammonia as “ammonium hydroxide,” since only about 2/10 of one percent of the weak base exists in that form.

Conjugate acids and bases

A common misconception is that strong acids have weak conjugate bases, and that weak acids have strong conjugate bases. It is easy to see that this is incorrect by remembering that $K_aK_b = K_w$. Our definition of a strong acid or base is that $K >> 1$, i.e., that the substance dissociates completely. Our definition of a weak acid or base is $1 > K > K_w$. It follows that if $K_a >> 1$ (strong) then K_b cannot be $> K_w$ (weak).

In fact, **strong acids** such as HCl dissociate to produce **spectator ions** such as Cl^- as conjugate bases, whereas **weak acids** produce **weak conjugate bases**. This is illustrated below for acetic acid and its conjugate base, the acetate anion. Acetic acid is a weak acid ($K_a = 1.8 \times 10^{-5}$) and acetate is a weak base ($K_b = \frac{K_w}{K_a} = 5.6 \times 10^{10}$)



The strength of a conjugate acid/base varies inversely with the strength or weakness of its parent acid or base. Any acid or base is technically a conjugate acid or conjugate base also; these terms are simply used to identify species in solution (i.e acetic acid is the conjugate acid of the acetate anion, a base, while acetate is the conjugate base of acetic acid, an acid).

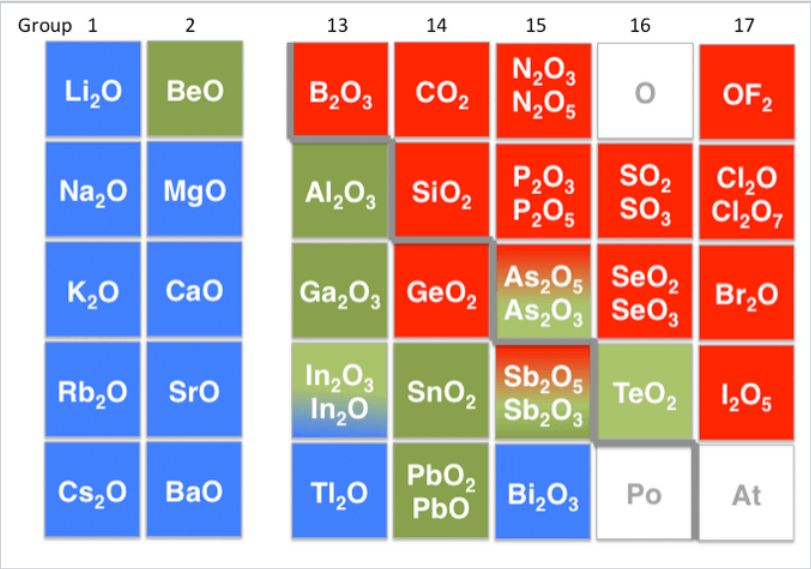
Neutral oxyacids (H_2SO_4, H_3PO_4, HNO_3, $HClO_2$, etc.) can be classified as strong or weak following a simple rule first noted by Linus Pauling. If the number of oxygen atoms exceeds the number of hydrogen atoms by two or more, then the acid is strong; otherwise it is weak. For example $HClO_4$ and $HClO_3$, where the difference is 3 and 2, respectively, are both strong acids. HNO_2 and $HClO_2$ are both weak because the difference is 1 in both cases. For weak acids, the relative strength depends on this difference (i.e., $HClO_2$ is a stronger weak acid than HOCl) and on the electronegativity of the central atom (HOCl is stronger than HOI).

Acids that can donate more than one proton are called **polyprotic acids**. For example, sulfuric acid, H_2SO_4, is a strong acid that has a conjugate base that actually happens to be a weak acid itself. This means that every mole of H_2SO_4 in aqueous solution donates more than 1 mole of protons. Carbonic acid (H_2CO_3) and phosphoric acid (H_3PO_4) are weak polyprotic acids. Typically, the sequential pK_a's of polyprotic acid are separated by about 5 pH units, because it becomes progressively more difficult to remove protons as the ion becomes more negatively charged. For example, the three pK_a's of phosphoric acid are 2.15, 7.20, and 12.35.

Amphoteric compounds

Some substances can act either as an acid and as a base. An example is water. H_2O molecules may either donate a hydrogen ion or accept one. This property makes water an **amphoteric** solvent. In the situation where an acid dissociates in solution, water is acting as a base. Conversely, water acts as an acid when bases dissociate. The strongest acid we can make in H_2O is H^+ (aq), and the strongest base we can make in H_2O is OH^- (aq).

Other examples of amphoteric compounds are oxides and hydroxides of elements that lie on the border between the metallic and non-metallic elements in the periodic table. For example, aluminum hydroxide ($Al(OH)_3$) is insoluble at neutral pH, but can accept protons in acid to make $[Al(H_2O)_6]^{3+}$ or accept an OH^- ion in base to form $Al(OH)_4^-$ ions. Consequently, aluminum oxide is soluble in acid and in base, but not neutral water. Other examples of amphoteric oxides are BeO, ZnO, Ga_2O_3, Sb_2O_3, and PbO. Increasing the oxidation state of a metal increases the acidity of its oxide by withdrawing electron density from the oxygen atoms. Thus, Sb_2O_5 is acidic, but Sb_2O_3 is amphoteric.



Periodic table showing basic (blue), amphoteric (green) and acidic (red) oxides. The metal-nonmetal boundary is indicated by the gray staircase line.

Solvent leveling

Solvent leveling is an effect that occurs when a strong acid is placed in a solvent such as (but not limited to) H_2O. Because strong acids donate their protons to the solvent, the strongest possible acid that can exist is the conjugate acid of the solvent. In aqueous solution, this is H_3O^+. This means that the strength of acids such as HCl and HBr cannot be differentiated in water as they both are dissociated 100% to H_3O^+. In the context of our discussion of conjugate bases above, we would say that both Cl^- and Br^- are spectator ions in water: neither one is a strong enough base to accept a proton from H_3O^+. In order to differentiate the acidities of strong acids such as $HClO_4$ and HCl, or the basicities of strong bases such as CH_3O^- and NH_2^-, we must typically work in non-aqueous solvents, as explained below.

Nonaqueous solutions

The Brønsted theory encompasses any type of solvent that can donate and accept H^+ ions, not just aqueous solutions. The strength of an acid or a base varies depending on the solvent. Non-aqueous acid-base chemistry follows similar rules to those developed for acids and bases in water. For example in liquid ammonia, the solvent autodissociates in the reaction:

$$2\,NH_{3\,(l)} \rightleftharpoons NH_4{}^+ + NH_2{}^- \tag{6.3.2.10}$$

This equilibrium is analogous to the autodissociation of water, but has a smaller equilibrium constant ($K \approx 10^{-30}$). It follows by analogy to water that NH_4^+ is the strongest acid and NH_2^- is the strongest base that can exist in liquid ammonia. Because ammonia is a basic solvent, it enhances the acidity and suppresses the basicity of substances dissolved in it. For example, the ammonium ion (NH_4^+) is a weak acid in water ($K_a = 6 \times 10^{-10}$), but it is a strong acid in ammonia. Similarly, acetic acid is weak in water but strong in ammonia. Solvent leveling in fact makes HCl, CH_3COOH, and NH_4Cl all strong acids in ammonia, where they have equivalent acid strength.

Strong acids that are leveled in water have different acid strengths in acidic solvents such as HF or anhydrous acetic acid. For example, acid dissociation of HX in acetic acid (CH_3COOH) involves protonating the solvent to make its conjugate acid ($CH_3COOH_2^+$) and the X^- anion. Because $CH_3COOH_2^+$ is a stronger acid that H_3O^+, the anion X^- (which is a spectator in water)

can become a weak base in CH_3COOH:

$$\mathrm{HX + CH_3COOH \rightleftharpoons CH_3COOH_2^+ + X^-} \tag{6.3.2.11}$$

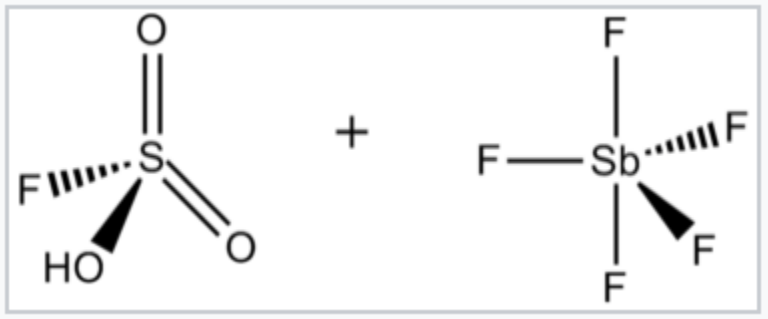
It follows that acidic solvents magnify the Brønsted basicities of substances that cannot accept protons in water. Conversely, basic solvents magnify the acidity of substances that cannot donate a proton to OH^-.

The acidity and basicity of non-aqueous solvents is difficult to quantify precisely, but one good relative measure is the Hammett acidity function, H_o. H_o is defined analogously to pH according to the Henderson-Hasselbach equation:

$$H_o = pK_a + \log(\frac{[base]}{[conjugate\ acid]}) \tag{6.3.2.12}$$

For non-aqueous solvents, or for acidic or basic compounds in dissolved in solvents that do not themselves dissociate, H_o is a rough measure of the pH of the solvent or compound in question. Anhydrous HF and H_2SO_4 have H_o values of approximately -10 and -12 respectively.

Superacids and superbases. The term *superacid* was originally coined by James Bryant Conant in 1927 to describe acids that were stronger than conventional mineral acids.[1] George A. Olah prepared the so-called magic acid, so-named for its ability to attack hydrocarbons, by mixing antimony pentafluoride (SbF_5) and fluorosulfonic acid (FSO_3H). The name was coined after a candle was placed in a sample of magic acid. The candle dissolved, showing the ability of the acid to protonate hydrocarbons, which under aqueous acidic conditions cannot be protonated.



Magic acid is made by mixing FSO_3H and SbF_5. Their reaction generates the $H_2SO_3F^+$ cation, which can protonate hydrocarbons.

At 140 °C , FSO_3H–SbF_5 converts methane into the tertiary-butyl carbocation, a reaction that begins with the protonation of methane:[2]

$$\mathrm{CH_4 + H^+ \longrightarrow CH_5^+} \tag{6.3.2.13}$$

$$\mathrm{CH_5^+ \longrightarrow CH_3^+ + H_2} \tag{6.3.2.14}$$

$$\mathrm{CH_3^+ + 3\,CH_4 \longrightarrow (CH_3)_3C^+ + 3\,H_2} \tag{6.3.2.15}$$

Fluoroantimonic acid, $HSbF_6$, can produce solutions with H_0 down to –28.[3] Fluoroantimonic acid is made by combining HF and SbF_5. In this system, HF releases its proton (H^+) concomitant with the binding of F^- by antimony pentafluoride, which (as described below) is a Lewis acid. The resulting anion (SbF_6-) is both a weak nucleophile and an extraordinarily weak base.

Superacids are useful in reactions such as the isomerization of alkanes. Industrially, anhydrous acid-exchanged zeolites, which are superacid catalysts, are used on a massive scale to isomerize hydrocarbons in the processing of crude oil to gasoline. Superbases such as lithium diethylamide ($LiNEt_2$), alkyllithium compounds (RLi), and Grignard reagents (RMgX) useful in a broad range of organic reactions. $LiNEt_2$ deprotonates C-H bonds to generate reactive carbanions. RLi and RMgX are powerful

nucleophiles.

The use of superbases in nonaqueous media allows us to rank the acidities (and measure the pKa's) of different classes of molecules. This ranking is particularly important in understanding the reactions of organic molecules. Note that the order of acidities for hydrocarbons is alkynes >> alkenes, aromatics >> alkanes. This ordering has to do with the hybridization of the carbon atom that forms the carbanion. The negatively charged lone pair of the carbanion is stabilized in orbitals that have high s character (e.g., sp vs. sp^2 or sp^3). This is because s orbitals have finite probability density at the nucleus and "feel" the positive nuclear charge (thereby stabilizing the extra negative charge on carbon) more than p orbitals. Resonance effects also stabilize carbanions. Thus, cyclopentadiene is more acidic than even an alkyne because the negative charge is delocalized over the entire (aromatic) $C_5H_5^-$ ring when the C_5H_6 is deprotonated.

name	formula	structural formula	pKa
Methane	CH_4	Methane-2D-dimensions.svg	56
Propene	C_3H_6	Propylene skeletal.svg	44
Benzene	C_6H_6	Benzol.svg	43
Acetylene	C_2H_2	Acetylene-CRC-IR-dimensions-2D.png	25
Cyclopentadiene	C_5H_6	Cyclopentadiene.png	18

Table 1. Carbon acid acidities in pKa in DMSO [4].

Acid-base equilibria in molten salts

When a solid salt melts, it forms a solution of the cations and anions. For example, KOH melts at temperatures above 400 °C and dissociates into K^+ and OH^- ions which can act as a solvent for chemical reactions. Because of the autodissociation of the OH^- solvent, water is always present in a molten KOH flux, according to the acid-base equilibrium:

$$2\,OH^- \rightleftharpoons H_2O + O^{2-} \tag{6.3.2.16}$$

It follows that in this very basic solvent, water (the conjugate acid of the solvent) is the strongest acid that can exist. The conjugate base of the solvent, O^{2-}, is the strongest base. This autodissociation equilibrium allows for the acidity of a flux to be easily tuned through the addition or boiling off of water. A "wet" flux is more acidic, and can dissolve metal oxides that contain the basic O^{2-} anion. Conversely a "dry" flux is more basic and will cause oxides to precipitate. Molten hydroxide fluxes can thus be used in the synthesis of oxide crystals, such as the perovskite superconductor ($K_{1-X}Ba_XBiO_3$).[5]. Eutectic mixtures of NaOH and KOH are relatively low melting (≈ 200 °C) and can be used as solvents for crystallizing a variety of basic oxides.

Lewis Acids and Bases

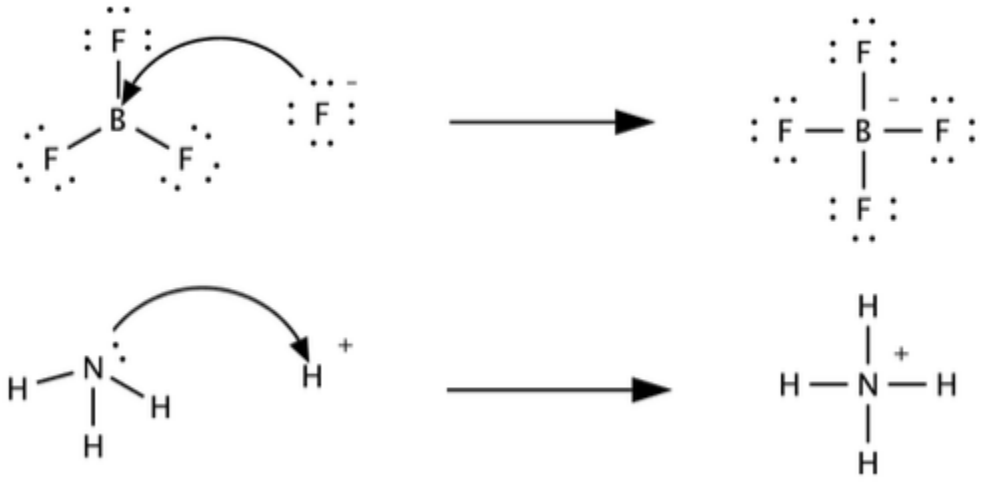
The Lewis classification of acids and bases is broader than the Brønsted-Lowry definition, and encompasses many more substances. Whereas the Brønsted-Lowry and the Arrhenius classifications are based on transfer of protons, Lewis acidity and basicity are based on the sharing of an electron pair. **Lewis acids** can accept an electron pair, while **Lewis bases** can donate an electron pair. This definition encompasses the Brønsted-Lowry definition, in that H^+ is an electron pair acceptor (when interacting with a base), and a base is an electron pair donor in its interaction with H^+. This is illustrated below for the protonation of ammonia.

Boron trifluoride, BF_3 acts as a Lewis acid when it combines with a basic ion or molecule that can donate an electron pair. Such a reaction is shown below.

\[\ce{BF3 + F^{-} <=> BF4^{-}

Here, the acid is BF_3 and the base is F^-. This acid-base reaction allows boron (which is electron-deficient in BF_3) to complete its octet. Similarly, $AlCl_3$ is a Lewis acid that can react with Cl^- (a Lewis base) to make the Lewis "salt" $AlCl_4^-$. Note that in water Cl^-

is a spectator ion (a weaker base than the solvent) in Brønsted acid-base reactions.



Additional examples of Lewis acid base reactions. In each, try to identify the acid, the base, and the salt, based on the concept that the base is the molecule or ion that donates an electron pair. In cases where you are not sure, it may help to draw the VSEPR structures of the molecules:

$\mathrm{I_2 + I^- \rightleftharpoons I_3^-}$

$\mathrm{AuCl_3 + Cl^- \rightleftharpoons [AuCl_4]^-}$

$\mathrm{Fe^{3+} + 6\,H_2O \rightleftharpoons [Fe(H_2O)_6]^{3+}}$

$\mathrm{TiF_4 + 2\,F^- \rightleftharpoons [TiF_6]^{2-}}$

$\mathrm{SF_4 + SbF_5 \rightleftharpoons SSbF_9}$

In other Lewis acid base reactions both acid and base are molecules and the product is referred to as an adduct.

$\mathrm{(CH_3)_3B + N(CH_3)_3 \longrightarrow (CH_3)_3B{-}N(CH_3)_3}$

$\mathrm{I_2 + S(CH_3)_2 \longrightarrow I_2{-}S(CH_3)_2}$

$\mathrm{C_5N_5N + Cu(HFacac)_2 \longrightarrow C_5N_5N{-}Cu(HFacac)_2}$

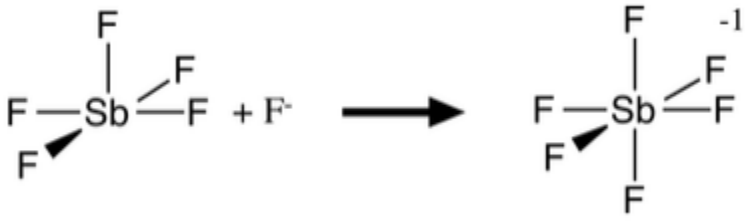
Lewis acidity is the basis for coordination chemistry, a topic we will discuss in more detail in Chapter 5. This is because coordination chemistry involves **metal ions** that are Lewis acids, which bond to ligands that are Lewis bases.

Determining the strength of metal ion Lewis acids

There are three determining factors in the Lewis acid strength of a metal ion:
1. The higher positive charge on the metal, the more acidic it is. For example, Al^{3+} and Fe^{3+} are good Lewis acids and their salts make acidic solutions in water, but $K^+$and Na^+ are not.
2. The smaller the atomic radius of the metal ion, the more acidic it is. Going down the periodic table, the Lewis acidity of metal ions decreases (e.g., Al^{3+} > Ga^{3+} > In^{3+}) because the ionic radius increases.
3. For transition metal ions, more electronegative metals tend to make stronger Lewis acids. The electronegativity has maxima at W and Au in the 5d series, so metal ions near in that part of the periodic table are good Lewis acids.

Molecules with five coordinate geometries (e.g., PCl_5, AsF_5, SbF_5) are typically strong Lewis acids, because when accepting another pair of electrons from a base, they form an octahedral molecule or anion. Neither of the common five-coordinate

geometries (trigonal bipyramidal or square pyramidal) is efficient in terms of packing. The Lewis acid-base reaction forms an additional bond with a relatively small energetic penalty of stretching the existing bonds:



Because F^- is a good Lewis base, and also a small anion, it can form stable octahedral anions with both main group elements and transition metals. For this reason, TiO_2 and SiO_2 dissolve in HF (but are unreactive with aqueous HCl and other strong acids):

$$\mathrm{TiO_2 + 4\,HF + 2\,F^- \rightleftharpoons {TiF_6}^{2-} + 2\,H_2O} \tag{6.3.2.17}$$

$$\mathrm{SiO_2 + 4\,HF + 2\,F^- \rightleftharpoons {SiF_6}^{2-} + 2\,H_2O} \tag{6.3.2.18}$$

Lewis bases stabilize high oxidation states.

An interesting example of using Lewis acid-base chemstry to drive reactions is the chemical synthesis of fluorine gas, which was devised by Karl O. Christe in 1986.[6] Christe at the time was organizing a symposium to commemorate the 100th anniversary of the isolation of elemental fluorine by Henri Moissan, which Moissan did in 1886 by electrolyzing a solution of anhydrous HF. 100 years later, there was still no direct (non-electrochemical) synthesis of F_2. Christe's reaction scheme followed two steps. The first was the known synthesis of K_2MnF_6 from $KMnO_4$:

$$\mathrm{4\,{MnO_4}^-_{(aq)} + 10\,H_2O_{(l)} + 24\,F^-_{(aq)} \longrightarrow 4\,{MnF_6}^{2-}_{(aq)} = 3\,O_{2\,(g)} + 20\,OH^-_{(aq)}} \tag{6.3.2.19}$$

$$\mathrm{2\,K^+_{(aq)} + {MnF_6}^{2-}_{(aq)} \longrightarrow K_2MnF_{6\,(s)}} \tag{6.3.2.20}$$

The second step involved reacting K_2MnF_6 with the powerful Lewis acid SbF_5, to make metastable MnF_4, which decomposes spontaneously to MnF_3 and fluorine gas:

$$\mathrm{K_2MnF_{6\,(s)} + 2\,SbF_{5\,(l)} \longrightarrow 2\,KSbF_{6\,(s)} + MnF_{4\,(s)}} \tag{6.3.2.21}$$

$$\mathrm{MnF_{4\,(s)} \longrightarrow MnF_{3\,(s)} + \frac{1}{2}F_{2\,(g)}} \tag{6.3.2.22}$$

This reaction teaches us something interesting and important about the connection between acid-base and redox chemistry. Acids tend to stabilize low oxidation states, and bases stabilize high oxidation states (We will see this again soon in Chapter 4, in the context of Pourbaix diagrams). Mn is stable in the +4 oxidation state in K_2MnF_6, where it is surrounded by six basic F^- anions. However, the highest stable neutral fluoride of Mn is MnF_3, and MnF_4 (transiently formed from K_2MnF_6) spontaneously decomposes to generate fluorine.

Oxide is a better base than fluoride. Interestingly, Mn can lose all its valence electrons to form Mn^{7+} in the permanganate ion, MnO_4^-. Here the 7+ oxidation state is stabilized electrostatically by coordination to four O^{2-} ions, and by the overall -1 charge on the MnO_4^- anion. Because of its 2- charge, O^{2-} is a stronger base and a better ion for stabilizing high oxidation states than F^-. This is a general trend among transition metals: the highest oxidation state is usually reached in the oxide, not in the fluoride, despite the fact that F is a more electronegative element than O. For example, Cr^{6+} is stable in the CrO_4^{2-} and $Cr_2O_7^{2-}$ anions, but not in any neutral fluoride or fluoroanion. The +8 oxidation state occurs in RuO_4 and OsO_4, but not in any fluoride of Ru or Os.

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6.3.3: Hard and Soft Acids and Bases

Lewis acids and bases can be classified by designating them as hard or soft.

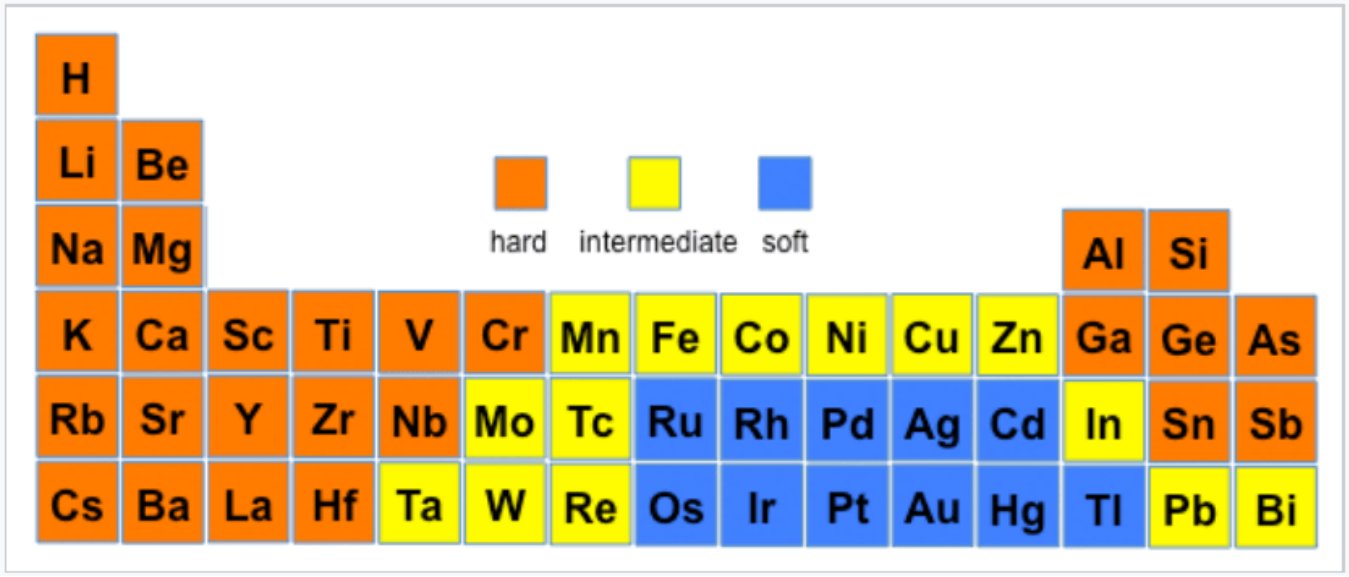
Hard Acids/Bases:

"Hard" acids and bases have a high charge (positive for acids, negative for bases) to ionic radius ratio along with higher oxidation states. Hard acids are not very polarizable and have high charge densities. Thus metal ions with high positive charges and smaller ionic sizes tend to be hard acids. Early transition metal ions in the 3d series tend to be hard Lewis acids. Hard bases are typically small anions and neutral molecules. Some examples of hard acids and bases include: H^+, O^{2-}, OH^-, F^-, Fe^{3+}, and Al^{3+}.

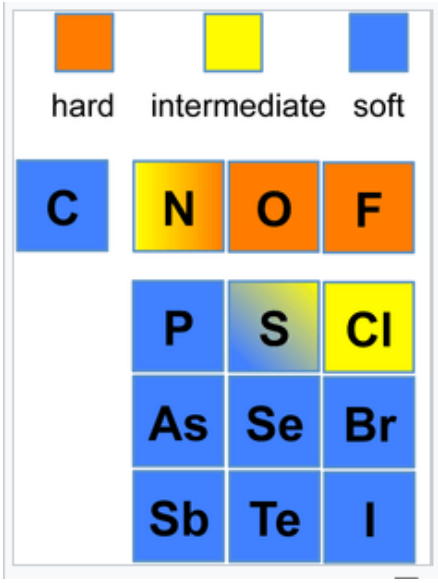
Soft Acids/Bases:

"Soft" acids or bases have a low charge to radius ratio, with low oxidation states. They are normally larger ions that are polarizable. For example, I^- and S^{2-} are soft bases and low charge density transition metals, such as Ag^+, are considered soft acids. Soft acids often include transition metals in the second and third row of the periodic table that have a +1 or +2 charge, as well as late transition metals (especially those in the 4d and 5d series) with filled or almost completely filled *d* orbitals.

Acids and bases are not strictly hard or soft, with many ions and compounds being classified as intermediate. For example, trimethylborane, Fe^{2+}, and Pb^{2+} cations are intermediate acids, and pyridine and aniline are examples of intermediate bases. An element can also change its hard/soft character depending on its oxidation state. The most extreme example is hydrogen, where H^+ is a hard acid and H^- is a soft base. Ni^{3+} (as in the layered compound NiOOH) is a hard acid, but Ni^0 (as in $Ni(CO)_4$) is a soft acid. The figures below show hard/soft trends for acids (left) and bases (right) in the periodic table. For bases, the major hard/soft discontinuity is between the 2nd row (N,O,F) and the rows below.



Hard-soft trends for acids



Hard-soft trends for bases

Like binds with Like

Hard acids interact more strongly with hard bases than they do with soft bases, and soft acids interact more strongly with soft bases than hard bases. Thus, the most stable complexes are those with hard-hard and soft-soft interactions. This tendency is illustrated in the table below, which shows the trend in formation constants for hard and soft acids. Hard acids bind halides in the order $F^- > Cl^- > Br^- > I^-$, whereas soft acids follow the opposite trend.

Log K_1	fluoride	chloride	bromide	iodide	acid classification
Fe^{3+}	6.0	1.4	0.5	-	Hard
Pb^{2+}	1.3	0.9	1.1	1.3	Intermediate
Ag^+	0.4	3.3	4.7	6.6	Soft
Hg^{2+}	1.0	6.7	8.9	12.9	Soft

The softest metal ion in the periodic table is $Au^+(aq)$. It forms stable complexes with soft bases such as phosphines and CN^-, but not with hard bases such as O^{2-} or F^-. The affinity of Au^+ for the soft base CN^- is high, and the resulting $[Au(CN)_2]^-$ complex is so stable that gold (which is normally very difficult to oxidize) can be oxidized by oxygen in the air:

$$4\,Au_{(s)} + 8\,CN^-{}_{(aq)} + O_{2\,(g)} + 2\,H_2O = 4\,[Au(CN)_2]^-{}_{(aq)} + 4\,OH^- \tag{6.3.3.1}$$

This reaction is used in gold mining to separate small flakes of Au from large volumes of sand and other oxides. Ag is similarly dissolved by air oxidation in cyanide solutions. The precious metals are then isolated from the solution using chemical reducing agents or by electroplating. The use of cyanide ion on a large scale in mining, however, creates a potentially serious environmental hazard. In 2000, a spill at Baia Mare, Romania resulted in the worst environmental disaster in Europe since Chernobyl. Cyanide, which is highly toxic, is gradually oxidized by air to the less toxic cyanate (OCN^-) ion. On the laboratory scale, cyanide plating solutions are typically disposed of by using bleach to oxidize CN^- to OCN^-, and the metal is recovered as an insoluble chloride salt.



Netted solution pond next to cyanide heap leaching of gold ore near Elko, Nevada (1992).

The Au^{3+} ion, because of its higher positive charge, is a harder acid than Au^{+} and can form complexes with harder bases such as H_2O and amines. In keeping with the "like binds like" principle, the compound AuI (soft-soft) is stable, but AuI_3 (hard-soft) is unknown. Conversely, AuF has never been isolated but AuF_3 (hard-hard) is stable.

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6.3.4: The Electrostatic-Covalent (ECW) Model for Acid-Base Reactions

The classification of Lewis acids and bases as hard and soft is a useful qualitative approach to rationalize their behavior. The ECW Model is a more quantitative model that describes and predicts the strength of Lewis acid – Lewis base interactions. The strength of the acid-base interaction is measured as the enthalpy of adduct formation, $\triangle$H . Each acid is characterized by an E_A and a C_A. Each base is likewise characterized by its own E_B and C_B. The E and C parameters refer, respectively, to the electrostatic and covalent contributions to the strength of the bonds that the acid and base will form. These parameters have been empirically obtained by using enthalpies for adducts that *form only σ bonds between the acid and base as well as adducts that have no steric repulsion between the acid and base.*

$$-\Delta H = E_A E_B + C_A C_B + W$$

This equation reproduces and predicts the enthalpy change, $\triangle$H, of a reaction between many acids and a bases. $\triangle$H is a measure of strength of the bond between the acid and the base, both in the gas phase and in weakly solvating media. The W term represents a constant energy for cleavage of a dimeric acid or base. For example, the enthalpy of cleavage of $[Rh(CO)_2Cl]_2$ by base B involves two steps. The first step is cleavage of the dimer, which is W:

$$\frac{1}{2}[\mathrm{Rh(CO)_2Cl}]_2 \longrightarrow \mathrm{Rh(CO)_2Cl}\ \ W = -43.5 kJ/mol \tag{6.3.4.1}$$

The second step is the binding of B to the $RhCl(CO)_2$ monomer. In another case, W is the enthalpy needed to cleave the internal hydrogen bonding of the H-bonding acid $(CF_3)_3COH$.

The calculation of the enthalpy of adduct formation for the reaction of pyridine, C_5H_5N and bis(hexafloroacetyacetonato)copper (II), $Cu(HFacac)_2$, shows how these parameters are used. In this case W =0 since neither the acid nor the base is a dimer. Selected parameters can be found at the Wikipedia page for the **ECW Model**

$$-\Delta H = E_A E_B + C_A C_B = (1.82)(1.78) + (2.86)(3.54) = 13.4 kcal/mol = -56.1 kJ/mol$$

$$\Delta H = -56.1 kJ/mol, \qquad \Delta H_{measured} = -56.1 kJ/mol$$

However, the ◈H calculated for the reaction of Me_3B with Me_3N is less negative than that observed. This discrepancy is attributed to steric repulsion between the methyl groups on the B and N atoms. The difference between the calculated and observed values can then be taken as the amount of the steric effect, a value otherwise not attainable. Steric effects have also been identified with $(CH_3)_3SnCl$ and with $Cu(HFacac)_2$. When π bonding contributes to the measured enthalpy, the enthalpy calculated from the E and C parameters will be less than the measured enthalpy and the difference provides a measure of the extent of the π bonding contribution.

A graphical presentation of this model clearly shows that *there is no single ranking order of Lewis acid or Lewis base strengths*, a point often overlooked, and emphasizes that the magnitude of acid and base interactions requires two parameters (E & C) to account for the interactions. A **Cramer-Bopp plot**[7]using the three Lewis bases: acetonitrile, ammonia, and dimethyl sulfide illustrates that there is no unique ordering of Lewis base strengths. The Cramer-Bopp plot is a visual tool for comparing Lewis base strengths with the range of possible Lewis acid partners, and similar plots can be constructed to examine selected Lewis acids against the range of possible Lewis bases. These plots show that two properties are needed to completely define acid and base strength and that any attempt to define strength with one property or parameter is limited in its utility. For Drago's quantitative ECW model the two properties are electrostatic and covalent while for Pearson's qualitative HSAB theory the two properties are hardness and strength.

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7: CHEM 2101 TOPIC 7 - OXIDATION AND REDUCTION

7.1: Reduction and Oxidation

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7.1.1: Introduction

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7.1.1A: Oxidation and Reduction

The simplest possible chemical reaction involves the transfer of one or more electrons between two atoms. In the simple reaction:

$$2\,\mathrm{Na} + \mathrm{Cl_2} \longrightarrow 2\,\mathrm{NaCl} \tag{7.1.1A.1}$$

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:

$$\mathrm{Na} \longrightarrow \mathrm{Na_1^+} + \mathrm{e\text{-}1} \tag{7.1.1A.2}$$

and

$$\mathrm{Cl_2} + 2\,\mathrm{e\text{-}1} > 2\,\mathrm{Cl\text{-}1} \tag{7.1.1A.3}$$

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 goes Ger" or Loss of electrons - oxidation; Gain of electrons - reduction has been used by several generations of students to remember these definitions. (OK! This is Simba, my apologies to Lion King aficionados.) 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. (You might want to think about this. The body didn't invent ethanol to compensate for the consumption of fermented beverages like beer and wine since there are relatively recent on an evolutionary time scale. Ethanol oxidase is present in the body because it had to be there to compensate for the background ethanol. I would suspect that all mammals have this enzyme, not just people. Other things that are ingested by people for their psychotropic effects do not necessarily have enzymes for their detoxification, thus they stay in the tissues longer and have a greater potential for doing damage. If you follow my dictum of not consuming anything for which you don't have an enzyme, you'll be relatively safe.) Redox chemistry also forms the basis of corrosion chemistry and battery chemistry (electrochemistry). Simple electrochemical 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:

$$Zn + 2H + 1 - - - - - - > Zn + 2 + H2 \tag{7.1.1A.4}$$

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:

$$Zn + Cu + 2 - - - - - > Cu + Zn + 2 \tag{7.1.1A.5}$$

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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7.1.1B: Oxidation States

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. K2CO3 The sum of all the oxidation numbers in this formula equal 0. Multiply the subscript by the oxidation number for each element. To calculate O.N. of C K = (2) (+ 1) = + 2 O = (3) (- 2) = - 6 therefore, C = (1) (+ 4) = + 4 HSO4 - To calculate O.N. of S The sum of all the oxidation numbers in this formula equal -1. Multiply the subscript by the oxidation number for each element. H = (1) (+ 1) = + 1 O = (4) (- 2) = - 8 therefore, S = (1) (+ 6) = + 6 Calculate O.N. in following compounds: 1. Sb in Sb2O5 2. N in Al(NO3)3 3. P in Mg3(PO4)2 4. S in (NH4)2SO4 5. Cr in CrO4 -2 6. Hg in Hg(ClO4)2 7. B in NaBO3 8. Si in MgSiF6 9. I in IO3 - 10. N in (NH4)2S 11. Mn in MnO4 - 12. Br in BrO3 - 13. Cl in ClO - 14. Cr in Cr2O7 -2 15. Se in H2SeO3 Reducing Agents and Oxidizing Agents Reducing agent - the reactant that gives up electrons. The reducing agent contains the element that is oxidized (looses electrons). If a substance gives up electrons easily, it is said to be a strong reducing agent. Oxidizing agent - the reactant that gains electrons. The oxidizing agent contains the element that is reduced (gains electrons). If a substance gains electrons easily, it is said to be a strong oxidizing agent. Example: Fe2O3 (cr) + 3CO(g) 2Fe(l) + 3CO2 (g) Notice that the oxidation number of C goes from +2 on the left to +4 on the right. The reducing agent is CO, because it contains C, which loses e - . Notice that the oxidation number of Fe goes from +3 on the left to 0 on the right. The oxidizing agent is Fe2O3, because it contains the Fe, which gains e - . Practice Problems: In any Redox equation, at least one particle will gain electrons and at least one particle will lose electrons. This is indicated by a change in the particle's oxidation number from one side of the equation to the other. For each reaction below, draw arrows and show electron numbers as in the example here. The top arrow indicates the element that gains electrons, reduction, and the bottom arrow indicates the element that looses electrons, oxidation. An arrow shows what one atom of each of these elements gaines or looses. 1. Mg + O2 MgO 2. Cl2 + I - Cl - + I2 3. MnO4 - + C2O4 -2 Mn+2 + CO2 4. Cr + NO2 - CrO2 - + N2O2 -2 5. BrO3 - + MnO2 Br - + MnO4 - 6. Fe+2 + MnO4 - Mn+2 + Fe+3 7. Cr + Sn+4 Cr+3 + Sn+2 8. NO3 - + S NO2 + H2SO4 9. IO4 - + II2 10. NO2 + ClO - NO3 - + Cl - Balancing Redox Equations by the Half-reaction Method 1. Decide what is reduced (oxidizing agent) and what is oxidized (reducing agent). Do this by drawing arrows as in the practice problems. 2. Write the reduction half-reaction. The top arrow in step #1 indicates the reduction half-reaction. Show the electrons gained on the reactant side. Balance with respect to atoms / ions. To balance oxygen, add H2O to the side with the least amount of oxygen. THEN: add H + to the other side to balance hydrogen. 3. Write the oxidation half-reaction. The bottom arrow in step #1 indicates the oxidation half-reaction. Show the electrons lost on the product side. Balance with respect to atoms / ions. To balance oxygen, add H2O to the side with the least amount of oxygen. THEN: add H + to the other side to balance hydrogen. 4. The number of electrons gained must equal the number of electrons lost. Find the least common multiple of the electrons gained and lost. In each half-reaction, multiply the electron coefficient by a number to reach the common multiple. Multiply all of the coefficients in the half-reaction by this same number. 5. Add the two half-reactions. Write one equation with all the reactants from the half-reactions on the left and all the products on the right. The order in which you write the particles in the combined equation does not matter. 6. Simplify the equation. Cancel things that are found on both sides of the equation as you did in net ionic equations. Rewrite the final balanced equation. Check to see that electrons, elements, and total charge are balanced. There should be no electrons in the equation at this time. The number of each element should be the same on both sides. It doesn't matter what the charge is as long as it is the same on both sides. Practice Problems: 1. Identify the oxidizing agent and reducing agent in each equation: H2SO4 + 8HI H2S + 4I2 + 4H2O CaC2 + 2H2O C2H2 + Ca(OH)2 Au2S3 + 3H2 2Au + 3H2S Zn + 2HCl H2 + ZnCl2 2. To make working with redox equations easier, we will omit all physical state symbols. However, remember that they should be there. An unbalanced redox equation looks like this: MnO4 - + H2SO3 + H + Mn+2 + HSO4 - + H2O Study how this equation is balanced using the half-reaction method. It is important that you understand what happens in each step. Be prepared to ask questions about this process in class tomorrow.

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7.1.1C: Stock Nomenclature

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7.1.2: STANDARD REDUCTION POTENTIALS, E°, AND THE RELATIONSHIP BETWEEN E°, ΔG°, AND K

7.1.2A: Half-Cells and Galvanic Cells

7.1.2B: Defining and Using Standard Reduction Potentials - E°

7.1.2C: Dependence of Reduction Potentials on Cell Conditions

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7.1.2A: Half-Cells and Galvanic Cells

4.2: Electrochemical potentials

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7.1.2B: Defining and Using Standard Reduction Potentials - E°

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7.1.2C: Dependence of Reduction Potentials on Cell Conditions

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7.1.3: THE EFFECT OF COMPLEX FORMATION OR PRECIPITATION ON REDUCTION POTENTIALS



- Topic hierarchy

7.1.3A: Half-Cells Involving Silver Halides

7.1.3B: Modifying the Relative Stabilities of Different Oxidation States of a Metal

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7.1.3A: Half-Cells Involving Silver Halides

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7.1.4: Disproportionation Reactions

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7.1.4A: Disproportionation

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7.1.4B: Stabilizing Species Against Disproportionation

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7.1.5: Potential Diagrams

4.5: Pourbaix diagrams

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7.1.6: FROST-EBSWORTH DIAGRAMS

- Topic hierarchy

7.1.6A: Frost-Ebsworth Diagrams and their Relationship to Potential Diagrams

7.1.6B: Interpretation of Frost-Ebsworth Diagrams

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7.1.6A: Frost-Ebsworth Diagrams and their Relationship to Potential Diagrams

4.3: Latimer and Frost diagrams

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7.1.7: The Relationships Between Standard Reduction Potentials and Some Other Quantities

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7.1.7A: Factors Influencing the Magnitudes of Standard Reduction Potentials

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7.1.8: Applications of Redox Reactions to the Extraction of Elements from their Ores

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7.1.8A: Ellingham Diagrams

It is possible to use plots of the free energy of formation of metal oxides vs. temperature to predict the temperatures at which a metal is stable and the temperatures at which it will spontaneously oxidize. For temperatures at which the free energy of formation of the oxide is positive, the reverse reaction is favored and the oxide will spontaneously decompose to the metal. From evaluation of the thermodynamic data presented in this figure, it can be seen that at 1100oC, Al will oxidize in an environment that has an oxygen partial pressure of 10-32 atm or greater, while chromium will oxidize in an oxygen partial pressure of 10-19 atm or higher. In general, a vacuum environment will be oxidizing to these elements unless a reducing species such as hydrogen is present. If inadequate oxygen is present, a nonprotective oxide film may be formed which could promote alloy depletion and loss of strength.

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7.2: REDOX STABILITY AND REDOX REACTIONS

Learning Objectives

- Balance complex oxidation-reduction reactions by the ion-electron method.
- Understand periodic trends in the activity series and electrochemical series.
- Use the Nernst equation to determine half-cell and cell potentials.
- Derive the stability field of water and use this to rationalize aqueous redox chemistry.
- Construct and be proficient with Latimer diagrams, using them to determine unknown reduction potential values and to quickly identify stable and unstable species.
- Construct and be proficient with Frost diagrams, using them to identify stable and unstable species, as well as those that are strong oxidizers.
- Construct and be proficient with Pourbaix diagrams, using them to identify redox and non-redox reactions, reactions that are and are not pH-dependent, and ultimately to predict and rationalize stability, reactivity, corrosion, and passivation.

In redox reactions, one element or compound is reduced (gains electrons) and another is oxidized (loses electrons). In terms of everyday life, redox reactions occur all of the time around us. For example, the metabolism of sugars to CO_2, which stores energy in the form of ATP, is a redox reaction. Another example of redox is fire or combustion, such as in a car engine. In a car engine, hydrocarbons in the fuel are oxidized to carbon dioxide and water, while oxygen is reduced to water. Corrosion (i.e. the formation of rust on iron) is a redox reaction involving oxidation of a metal.

7.2.1: Prelude to Redox Stability and Redox Reactions

7.2.2: Balancing Redox Reactions

7.2.3: Electrochemical Potentials

7.2.4: Latimer and Frost Diagrams

7.2.5: Redox Reactions with Coupled Equilibria

7.2.6: Pourbaix Diagrams

7.2.7: Discussion Questions

7.2.8: Problems

7.2.9: References

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7.2.1: Prelude to Redox Stability and Redox Reactions

In redox reactions, one element or compound is reduced (gains electrons) and another is oxidized (loses electrons). In terms of everyday life, redox reactions occur all of the time around us. For example, the metabolism of sugars to CO_2, which stores energy in the form of ATP, is a redox reaction. Another example of redox is fire or combustion, such as in a car engine. In a car engine, hydrocarbons in the fuel are oxidized to carbon dioxide and water, while oxygen is reduced to water. Corrosion (i.e. the formation of rust on iron) is a redox reaction involving oxidation of a metal.



Oxidation states of vanadium in acidic solution. From left to right the oxidation state goes from +5 to +2. These four oxidation states form the basis of the vanadium flow battery, a storage device for electricity generated from sunlight and wind.[1]

Oxidation-reduction reactions are important to understanding inorganic chemistry for several reasons:

- Transition metals can have multiple oxidation states
- Main group elements (N, halogens, O, S...) also have multiple oxidation states and important redox chemistry
- Many inorganic compounds catalyze redox reactions (which are especially useful in industrial and biological applications)
- Energy conversion and storage technologies (solar water splitting, batteries, electrolyzers, fuel cells) rely on inorganic redox reactions and catalysis
- Electrochemistry provides a way to measure equilibrium constants for dissolution/precipitation, complexation, and other reactions.
- Reaction mechanisms in organometallic chemistry (oxidative addition, reductive elimination) involve changes in the oxidation states of metals.

Not all oxidizers and reducers are created equal. The electrochemical series ranks substances according to their oxidizing and reducing power, i.e., their standard electrode potential. Strong oxidizing agents are typically compounds with elements in high oxidation states or with high electronegativity, which gain electrons in the redox reaction. Examples of strong oxidizers include hydrogen peroxide, permanganate, and osmium tetroxide. Reducing agents are typically electropositive elements such as hydrogen, lithium, sodium, iron, and aluminum, which lose electrons in redox reactions. Hydrides (compounds that contain hydrogen in the formal -1 oxidation state), such as sodium hydride, sodium borohydride and lithium aluminum hydride, are often used as reducing agents in organic and organometallic reactions.

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7.2.2: Balancing Redox Reactions

In studying redox chemistry, it is important to begin by learning to balance electrochemical reactions. Simple redox reactions (for example, $H_2 + I_2 \rightarrow 2\ HI$) can be balanced by inspection, but for more complex reactions it is helpful to have a foolproof, systematic method. The **ion-electron method** allows one to balance redox reactions regardless of their complexity. We illustrate this method with two examples.

Example 1:

I^- is oxidized to **IO_3^-** by **MnO_4^-**, which is reduced to **Mn^{2+}**.

How can this reaction be balanced? In the ion-electron method we follow a series of four steps:

Step 1A: Write out the (unbalanced) reaction and identify the elements that are undergoing redox.

$$\mathbf{Mn}O_4^- + \mathbf{I}^- \rightarrow \mathbf{I}O_3^- + \mathbf{Mn}^{2+}$$ (The elements undergoing redox are **Mn** and **I**)

Step 1B: Separate the reaction into two **half reactions**, balancing the element undergoing redox in each.

$$\mathbf{Mn}O_4^- \rightarrow \mathbf{Mn}^{2+}$$

$$\mathbf{I}^- \rightarrow \mathbf{I}O_3^-$$

Step 2A: Balance the **oxygen** atoms by adding water to one side of each half reaction.

$$Mn\mathbf{O_4^-} \rightarrow Mn^{2+} + \mathbf{4}H_2\mathbf{O}$$

$$\mathbf{3}H_2\mathbf{O} + I^- \rightarrow \mathbf{I}O_3^-$$

Step 2B: Balance the **hydrogen** atoms by adding H^+ ions.

$$\mathbf{8H^+} + MnO_4^- \rightarrow Mn^{2+} + \mathbf{4H_2}O$$

The left side has a net charge of **+7** and the right side has a net charge of **+2**

$$\mathbf{3H_2}O + I^- \rightarrow IO_3^- + \mathbf{6H^+}$$

The left side has a net charge of **-1** and the right side has a net charge of **+5**

Step 2C: Balance the overall charge by adding **electrons**

$$8H^+ + \mathbf{5e^-} + MnO_4^- \rightarrow Mn^{2+} + 4H_2O$$

The left side has a charge of **+2** while the right side has a charge of **+2**. They are balanced.

$$3H_2O + I^- \rightarrow IO_3^- + 6H^+ + \mathbf{6e^-}$$

The left side has a charge of **-1** while the right side has a charge of **-1**. They are balanced.
Note: We did not need to explicitly determine the oxidation states of Mn or I to arrive at the correct number of electrons in each half reaction.

Step 3: Combine the half reactions so that there are equal numbers of electrons on the left and right sides

6 $(8H^+ + \mathbf{5e^-} + MnO_4^- \rightarrow Mn^{2+} + 4H_2O)$

5 $(3H_2O + I^- \rightarrow IO_3^- + 6H^+ + \mathbf{6e^-})$

$48H^+ + \mathbf{30e^-} + 15H_2O + 6MnO_4^- + 5I^- \rightarrow 5IO_3^- + 6Mn^{2+} + 24H_2O + \mathbf{30e^-} + 30H^+$

Cancel the **H^+**, **electrons**, and **water**:

~~$48H^+$~~ + ~~$30e^-$~~ + ~~$15H_2O$~~ + $6MnO_4^- + 5I^- \rightarrow 5IO_3^- + 6Mn^{2+}$ + ~~$24H_2O$~~ + ~~$30e^-$~~ + ~~$30H^+$~~

The overall balanced reaction is therefore:

$18H^+ + 6MnO_4^- + 5I^- \rightarrow 5IO_3^- + 6Mn^{2+} + 9H_2O$

Check your work by making sure that all **elements** and **charges** are balanced.

Step 4: If the reaction occurs under basic conditions, we add **OH^-** to each side to cancel **H^+**

$18H^+$ + **$18OH^-$** + $6MnO_4^- + 5I^- \rightarrow 5IO_3^- + 6Mn^{2+}$ + **$9H_2O$** + **$18OH^-$**

The **$18H^+$** + **$18OH^-$** will become **$18H_2O$** so the overall balanced reaction is:

$9H_2O + 6MnO_4^- + 5I^- \rightarrow 5IO_3^- + 6Mn^{2+} + 18OH^-$

Again, it is a good idea to check and make sure that all of the elements are balanced, and that the charge is the same on both sides. If this is not the case, you need to find the error in one of the earlier steps.

Example 2:

Redox reaction of **$S_2O_3^{2-}$** and **H_2O_2**

$S_2O_3^{2-}$ + **H_2O_2** → **$S_4O_6^{2-}$** + **H_2O**

Which elements are undergoing redox? **S** and **O**

Step 1: Write out half reactions, balancing the element undergoing redox

$2S_2O_3^{2-} \rightarrow S_4O_6^{2-}$

$H_2O_2 \rightarrow 2H_2O$

Step 2A: Balance oxygen (already balanced)

Step 2B: Balance hydrogen:

$2S_2O_3^{2-} \rightarrow S_4O_6^{2-}$

$H_2O_2 + 2H^+ \rightarrow 2H_2O$

Step 2C: Balance charge by adding electrons:

$2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2e^-$

$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$

Step 3: Combine the half reactions so that there are equal numbers of electrons on the left and right sides (already equal)
Overall balanced reaction:

$2S_2O_3^{2-} + H_2O_2 + 2H^+ \rightarrow S_4O_6^{2-} + 2H_2O$

Note that again, we did not need to know the formal oxidation states of S or O in the reactants and products in order to balance

the reaction. In this case, assigning the oxidation states would be rather complex, because $S_2O_3^{2-}$ and $S_4O_6^{2-}$ both contain sulfur in more than one oxidation state.

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7.2.3: Electrochemical Potentials

In electrochemical cells, or in redox reactions that happen in solution, the thermodynamic driving force can be measured as the **cell potential**. Chemical reactions are spontaneous in the direction of -ΔG, which is also the direction in which the cell potential (defined as $E_{cathode}$ - E_{anode}) is positive. A cell operating in the **spontaneous** direction (for example, a battery that is discharging) is called a **galvanic cell**. A cell that is being driven in the **non-spontaneous** direction is called an **electrolytic cell**. For example, let us consider the reaction of hydrogen and oxygen to make water:

$$2\,H_{2\,(g)} + O_{2\,(g)} = 2\,H_2O_{(l)} \tag{7.2.3.1}$$

Thermodynamically, this reaction is spontaneous in the direction shown and has an overall standard free energy change (ΔG°) of -237 kJ per mole of water produced.

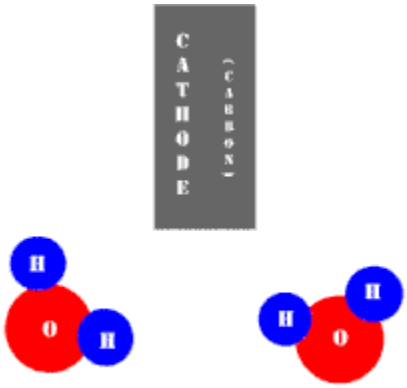
When this reaction occurs electrochemically in the spontaneous direction (e.g., in a hydrogen-air fuel cell), the two half cell reactions that occur are:

Anode: $H_{2\,(g)} \longrightarrow 2\,H^+{}_{(aq)} + 2\,e^-$

Cathode: $O_{2\,(g)} + 4\,H^+{}_{(aq)} + 4\,e^- \longrightarrow 2\,H_2O_{(l)}$

Here the anode is the negative electrode and the cathode is the positive electrode; under conditions of very low current density (where there are minimal resistive losses and kinetic overpotentials), the potential difference we would measure between the two electrodes would be 1.229 V.

In an **electrolytic cell**, this reaction is run in reverse. That is, we put in electrical energy to split water into hydrogen and oxygen molecules. In this case, the half reactions (and their standard potentials) reverse. O_2(g) bubbles form at the anode and H_2(g) is formed at the cathode. Now the **anode** is the **positive** electrode and the **cathode** is **negative**. Electrons are extracted from the substance at the anode (water) and pumped into the solution at the cathode to make hydrogen. An animation of the cathode half reaction is shown below.

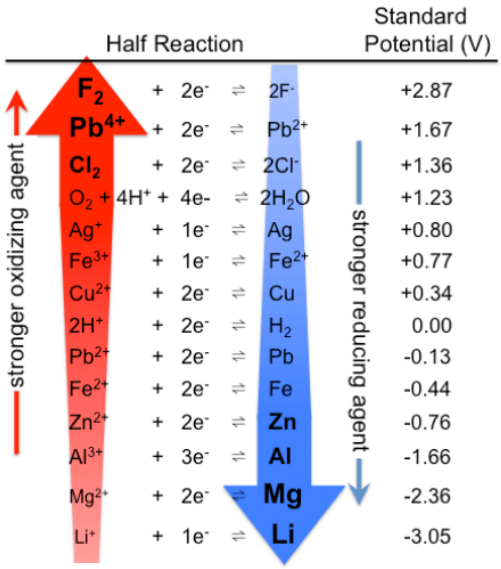


In both galvanic and electrolytic cells, **oxidation** occurs at the **anode** and **reduction** occurs at the **cathode**.

Half-cell potentials

As noted above, the equilibrium voltage of an electrochemical cell is proportional to the free energy change of the reaction. Because electrochemical reactions can be broken up into two half-reactions, it follows that the potentials of half reactions (like free energies) can be added and subtracted to give an overall value for the reaction. If we take the **standard hydrogen electrode** as our reference, i.e., if we assign it a value of zero volts, we can measure all the other half cells against it and thus obtain the voltage of each one. This allows us to rank redox couples according to their **standard reduction potentials** (or more simply their

standard potentials), as shown in the table below.



Note that when we construct an electrochemical cell and calculate the voltage, we simply take the difference between the half cell potentials and do not worry about the number of electrons in the reaction. For example, for the displacement reaction in which silver ions are reduced by copper metal, the reaction is:

$$2\,\mathrm{Ag^+}_{(aq)} + \mathrm{Cu}_{(s)} = 2\,\mathrm{Ag}_{(s)} + \mathrm{Cu^{2+}}_{(aq)}$$

The two half-cell reactions are:

$$Ag^+_{(aq)} + e^- = Ag_{(s)} \quad +0.80V$$

$$Cu^{2+}_{(aq)} + 2e^- = Cu_{(s)} \quad +0.34V$$

and the standard potential $E^o = +0.80 - 0.34V = +0.46V$

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 (see below) makes E^o an **intensive property** (like pressure, temperature, etc.).

Relationship between E and ΔG. For systems that are in equilibrium, $\Delta G^o = -nFE^o_{cell}$, where *n* is number of moles of electrons per mole of products and *F* is the Faraday constant, ~96485 C/mol. Here the ^{o} symbol indicates that the substances involved in the reaction are in their standard states. For example, for the water electrolysis reaction, the standard states would be pure liquid water, H^+ at 1M concentration (or more precisely, at unit activity), and O_2 and H_2(g) at 1 atmosphere pressure.

More generally (at any concentration or pressure), $\Delta G = -nFE$, where

$$E = E^o - \frac{RT}{nF} * lnQ \tag{7.2.3.2}$$

,

or at 298 K

$$E = E^o - \frac{0.0592}{n} * \log Q \tag{7.2.3.3}$$

where Q is the concentration ratio of products over reactants, raised to the powers of their coefficients in the reaction. This equation (in either form) is called the Nernst equation. The second term in the equation, when multiplied by -nF, is RT*lnQ. This is the free energy difference between ΔG and ΔG°. We can think of this as an entropic term that takes into account the positive

entropy change of dilution, or the negative entropy change of concentrating a reactant or product, relative to its standard state.

Using the Nernst equation

Example 1:

For the half reaction $2\,\mathrm{H^+} + 2\,\mathrm{e^-} = \mathrm{H_2}$, $E°_{1/2}$ = 0.000 V (by definition)

What is $E_{1/2}$ at pH 5 and P_{H_2} = 1 atm?

$pH = -\log[H^+] = 5$, so $[H^+] = 10^{-5}$ M

$$E = E^o - \frac{0.0592}{2} * \log\frac{P_{H2}}{(H^+)^2} = E^o - \frac{0.0592}{2} * \log\,(10^5)^2 = E^o - \frac{0.0592}{2}(10) = 0.000 - 0.296 = -0.296V \qquad (7.2.3.4)$$

Example 2:

What is the potential of a fuel cell (a galvanic H_2/O_2 cell) operating at pH 5?

Overall reaction: $2\,\mathrm{H_{2\,(g)}} + \mathrm{O_{2\,(g)}} = 2\,\mathrm{H_2O_{(l)}}$

In this reaction, H_2 is oxidized to H^+ and O_2 is reduced to H_2O. According to our convention, we write out and balance both half-cell reactions as reductions. For convenience, we do this in acid. (It is left as an exercise to the interested reader to try to work the problem in base)

Half cell reactions:

$2\,\mathrm{H_{2\,(g)}} = 4\,\mathrm{H^+} + 4\,\mathrm{e^-}$

$\mathrm{O_{2\,(g)}} + 4\,\mathrm{H^+_{(aq)}} + 4\,\mathrm{e^-} = 2\,\mathrm{H_2O_{(l)}}$



Toyota fuel cell hybrid bus. The bus runs on electrical energy obtained directly from the H_2/O_2 reaction. Individual fuel cells are connected in series to make a power train that charges a battery pack and drives an electric motor. Although the standard potential of the reaction is 1.23 V, because of kinetic overpotentials each fuel cell in the power train operates at a voltage of about 0.70 V. Despite this energy loss, the fuel cell system is still about twice as efficient as a combustion engine performing the same reaction.

To solve this problem we need to find the difference between the H_2/ H^+ and O_2/H_2O half cell potentials at pH 5.

$2\,\mathrm{H^+} + 2\,\mathrm{e^-} \longrightarrow \mathrm{H_2}$ $E°_{1/2}$ = 0.000 V

Like all standard potentials, this is written as a reduction. We need to reverse it and change the sign of E^o since H_2 is being oxidized:

$\mathrm{H_2} \longrightarrow 2\,\mathrm{H^+} + 2\,\mathrm{e^-}$ $E°_{1/2}$ = -0.000 V

and add the standard potential of the substance being reduced at the cathode:

$\mathrm{O_2} + 4\,\mathrm{H^+} + 4\,\mathrm{e^-} \longrightarrow 2\,\mathrm{H_2O}$ $E°_{1/2}$ = +1.229 V

The difference between the two standard half cell potentials is +1.229 - 0.000 = +1.229 V

$E°_{cell}$ = +1.229 Volts

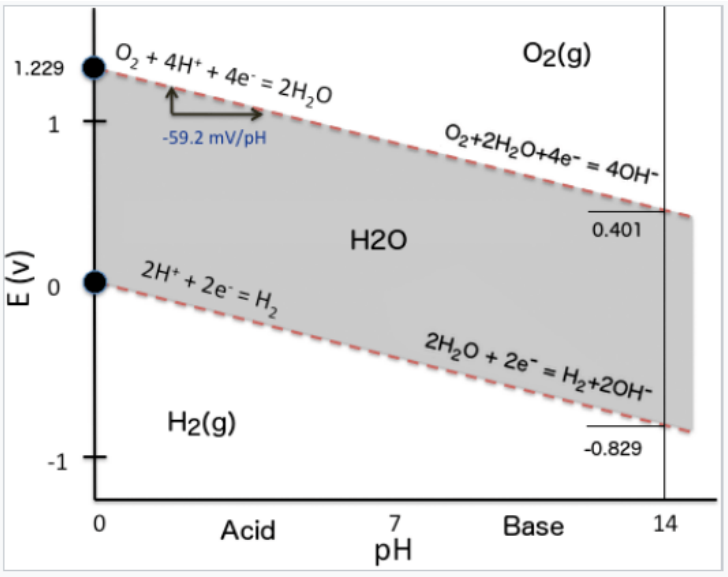
We now use the Nernst equation to account for the fact that H^+ is not in its standard state:

$$E_{cell} = E^o - \frac{0.0592}{4} * log\frac{[H^+]^4}{P_{O2}P_{H2}^2[H^+]^4} = E^o - \frac{0.0592}{4} * log(1) = E^o = +1.229V \tag{7.2.3.5}$$

Note that the value of E_{cell} **does not change** with pH since **both couples shift -59.2 mV/pH** according to the Nernst equation. This is the consequence of the fact that the number of electrons equals the number of protons in each of the half cell reactions. Another way to rationalize this result is to remember that the overall reaction ($2H_2 + O_2 = 2H_2O$) does not involve H^+ as a reactant or product, so ΔG and E should be independent of pH.

We can plot the shift in the H_2/H^+ and O_2/H_2O half-cell potentials with pH on a potential-pH diagram (also called a Pourbaix diagram) as shown below. The pH-dependent potentials of the H_2 and O_2 couples are shown as dotted lines. Notice that the

potential difference between them is always 1.23 V. The dark circles represent the standard potentials.



Pourbaix diagram for water.

Pourbaix diagrams are essentially electrochemical **phase diagrams**, which plot regions of thermodynamic stability for redox-active substances. As in other kinds of phase diagrams, the lines represent conditions under which two phases coexist in equilibrium. The shaded area in the water Pourbaix diagram represents the conditions of potential and pH where liquid water is stable relative to hydrogen or oxygen. Outside the shaded region, water is thermodynamically unstable and is reduced to H_2(g) or oxidized to O_2(g). Although these processes are spontaneous in the thermodynamic sense (for example, water is unstable in the presence of Pb^{4+}, Cl_2, Fe, Zn, or Al), they are kinetically slow and require catalysis to proceed.

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7.2.4: Latimer and Frost Diagrams

In addition to Pourbaix diagrams, there are two other kinds of redox stability diagrams known as Latimer and Frost diagrams. Each of these diagrams contains similar information, but one representation may be more useful in a given situation than the others.

Latimer and Frost diagrams help predict stability relative to higher and lower oxidation states, usually at one fixed pH. Pourbaix diagrams help understand pH-dependent equilibria, which are often coupled to solubility equilibria and corrosion (which will be talked about more later).



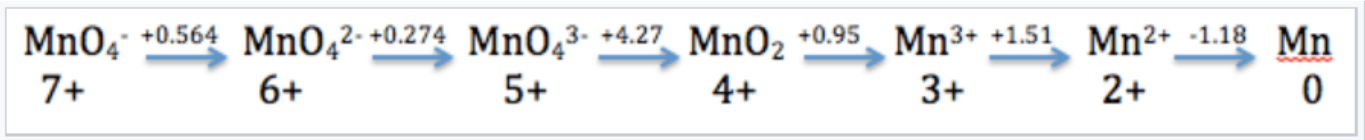
Manganese nodules on the sea floor contain Mn in oxidation states 2+, 3+, and 4+.

Latimer diagrams:

Latimer diagrams are the oldest and most compact way to represent electrochemical equilibria for substances that have multiple oxidation states. Electrochemical potential values are written for successive redox reactions (from highest to lowest oxidation state), typically under standard conditions in either strong acid ($[H^+]$ = 1 M, pH 0) or strong base ($[OH^-]$ = 1 M, pH 14). The oxidation states of successive substances in a Latimer diagram can differ by one or more electrons. Oxidation states for the element undergoing redox are typically determined by difference; we assign the oxygen atoms an oxidation state of -2 and the hydrogen atoms an oxidation state of +1.

Example:

Mn in Acid



The Latimer diagram for Mn illustrates its standard reduction potentials (in 1 M acid) in oxidation states from +7 to 0.

The Latimer diagram compresses into shorthand notation all the standard potentials for redox reactions of the element Mn. For example, the entry that connects Mn^{2+} and Mn gives the potential for the half-cell reaction:

$\mathrm{Mn^{2+}_{(aq)} + 2\,e^- \longrightarrow Mn_{(s)}}$ $E_{1/2}°$ = -1.18V

and the entry connecting Mn^{4+} and Mn^{3+} represents the reaction:

$\mathrm{MnO_{2\,(s)} + 4\,H^+_{(aq)} + e^- \longrightarrow Mn^{3+}_{(aq)} + 2\,H_2O_{(l)}}$, :$E_{1/2}°$ = +0.95V

We can also calculate values for **multi-electron reactions** by first adding ΔG°(=-nFE°) values and then dividing by the total number of electrons

For example, for the 5-electron reduction of MnO_4^- to Mn^{2+}, we write

$$E^o = \frac{1(0.564) + 1(0.274) + 1(4.27) + 1(0.95) + 1(1.51)}{5} = +1.51V \tag{7.2.4.1}$$

and for the three-electron reduction of MnO_4^-(aq) to MnO_2(s),

$$E^o = \frac{1(0.564) + 1(0.274) + 1(4.27)}{3} = +1.70V \tag{7.2.4.2}$$

Remember to divide by the number of electrons involved in the oxidation number change (5 and 3 for the above equations).

Thermodynamically stable and unstable oxidation states

An unstable species on a Latimer diagram will have a lower standard potential to the left than to the right.

Example:

\(\ce{2MnO4^{3-} -> MnO2 + MnO4^{2-}}\ ) the MnO_4^{3-} species is unstable

$E^o = +4.27 - 0.274 = 3.997V$ (spontaneous disproportionation)

Which Mn species are unstable with respect to disproportionation?

MnO_4^{3-} 5+ → 6+,4+

Mn^{3+} 3+ → 4+,2+

So stable species are: MnO_4^-, MnO_4^{2-}, MnO_2, Mn^{2+}, and Mn^0.

But **MnO_4^{2-}** is also unstable - why?

$\mathrm{MnO_4^{2-} \longrightarrow MnO_2}$

$\mathrm{2\,MnO_4^{2-} \longrightarrow 2\,MnO_4^- + MnO_2}$ E° = 2.272 - 0.564 = +1.708 V

Moral: All possible disproportionation reactions must be considered in order to determine stability (this is often more convenient with a Frost diagram).

Note

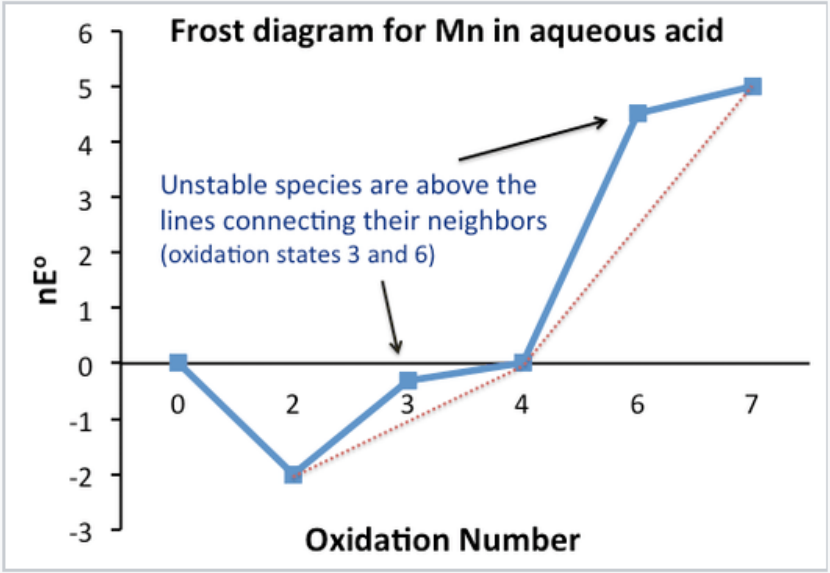
Thermodynamically unstable ions can be quite stable kinetically. For example, most N-containing molecules (NO_2, NO, N_2H_4) are unstable relative to the elements (O_2, N_2, H_2), but they are still quite stable kinetically.

Frost diagrams:

In a Frost diagram, we plot $\Delta G°/F$ (= nE°) vs. oxidation number. The zero oxidation state is assigned a nE° value of zero.[2]

Stable and **unstable oxidation states** can be easily identified in the plot. Unstable compounds are higher on the plot than the line connecting their neighbors. Note that this is simply a graphical representation of what we did with the Latimer diagram to determine which oxidation states were stable and unstable.

The **standard potential** for any electrochemical reaction is given by the **slope** of the line connecting the two species on a Frost diagram. For example, the line connecting Mn^{3+} and MnO_2 on the Frost diagram has a slope of +0.95, the standard potential of MnO_2 reduction to Mn^{3+}. This is the number that is written above the arrow in the Latimer diagram for Mn. Multielectron potentials can be calculated easily by connecting the dots in a Frost diagram.



A Frost diagram:

Contains the same information as in a Latimer diagram, but graphically shows stability and oxidizing power.

The lowest species on the diagram are the most stable (Mn^{2+}, MnO_2)

The highest species on diagram are the strongest oxidizers (MnO_4^-)

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7.2.5: Redox Reactions with Coupled Equilibria

Redox Reactions with Coupled Equilibria

Coupled equilibria (solubility, complexation, acid-base, and other reactions) change the value of E°, effectively by changing the concentrations of free metal ions. We can use the Nernst equation to calculate the value of E° from the equilibrium constant for the coupled reaction. Alternatively, we can measure the half-cell potential with and without the coupled reaction to get the value of the equilibrium constant. This is one of the best ways to measure K_{sp}, K_a, and K_d values.

As an example, we consider the complexation of Fe^{2+} and Fe^{3+} by CN^- ions:

$$\mathrm{Fe^{2+}{}_{(aq)} + 6\,CN^-{}_{(aq)} \longrightarrow [Fe(CN)_6]^{4-}} \tag{7.2.5.1}$$

$$\mathrm{Fe^{3+}{}_{(aq)} + 6\,CN^-{}_{(aq)} \longrightarrow [Fe(CN)_6]^{3-}} \tag{7.2.5.2}$$

Which oxidation state of Fe is more strongly complexed by CN^-? We can answer this question by measuring the standard half-cell potential of the $[Fe(CN)_6]^{3-/4-}$ couple and comparing it to that of the $Fe^{3+/2+}$couple:

$\mathrm{Fe^{3+}{}_{(aq)} + e^- = Fe^{2+}{}_{(aq)}}$ E° = +0.77 V (3)

$\mathrm{[Fe(CN)_6]^{3-} + 3^- = [Fe(CN)_6]^{4-}}$ E° = +0.42 V (4)

Iron(III) is ***harder to reduce*** (i.e., **E° is less positive**) when it is complexed to $\mathrm{CN^-}$

This implies that the equilibrium constant for complexation reaction (Equation 7.2.5.1) should be **smaller** than that for reaction (Equation 7.2.5.2). How much smaller?
We can calculate the ratio of equilibrium constants by adding and subtracting reactions:

$\mathrm{Fe^{3+} + 6\,CN^- \longrightarrow [Fe(CN)_6]^{3-}} \quad K = K_1$

$\mathrm{[Fe(CN)_6]^{4-} \longrightarrow Fe^{2+} + 6\,CN^-} \quad K = \frac{1}{K_2}$

$\mathrm{Fe^{3+} + Fe(CN)_6{}^{4-} \longleftrightarrow Fe^{2+} + Fe(CN)_6{}^{3-}}$

The equilibrium constant for this reaction is the product of the two reactions we added, i.e., $K = K_1/K_2$.

But we can make the same overall reaction by combining reactions (3) and (4)

$\mathrm{Fe^{3+}{}_{(aq)} + e^- = Fe^{2+}{}_{(aq)}} \quad E^o = +0.77V$

$\mathrm{[Fe(CN)_6]^{4-} = [Fe(CN)_6]^{3-} + e^-} \quad E^o = -0.42V$

$\mathrm{Fe^{3+} + Fe(CN)_6{}^{4-} \longleftrightarrow Fe^{2+} + Fe(CN)_6{}^{3-}}$

In this case, we can calculate E° = 0.77 - 0.42 = +0.35 V

It follows from $nFE° = -\Delta G° = RTlnK$ that

$E^o = \frac{RT}{nF} ln \frac{K_1}{K_2}$

$\frac{K_1}{K_2} = exp\frac{(nFE^o}{RT} = exp[(1\ \ equiv/mol)(96,500C/equiv)(0.35J/C)(8.314J/molK)(298)] = exp(13.63) = 8 \times 10^5$

Thus we find that $Fe(CN)_6^{3-}$ is about a million times more stable as a complex than $Fe(CN)_6^{4-}$.

Solubility Equlibria

We can use a similar procedure to measure K_{sp} values electrochemically.
For example, the silver halides (AgCl, AgBr, AgI) are sparingly soluble. We can calculate the K_{sp} of AgCl by measuring the standard potential of the AgCl/Ag couple. This can be done very simply by measuring the potential of a silver wire, which is in contact with solid AgCl and 1 M Cl^-(aq), against a hydrogen reference electrode. That value is then compared to the standard potential of the Ag^+/Ag couple:

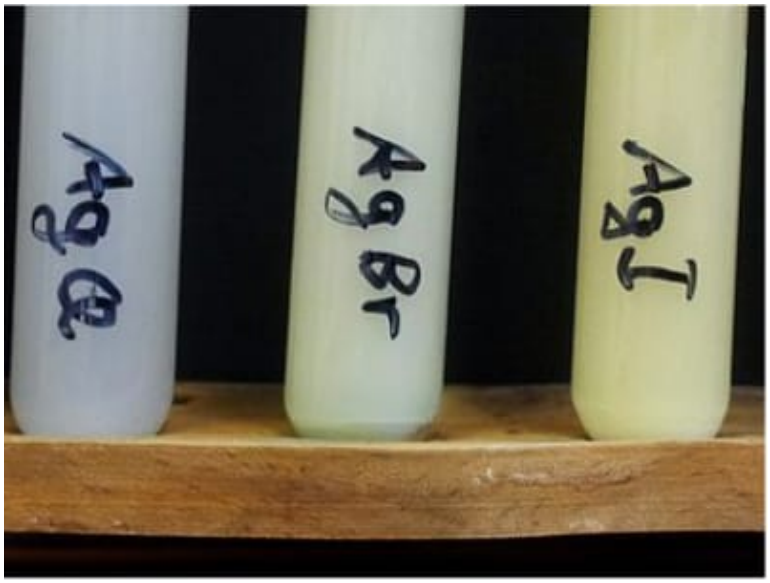
$$\mathrm{AgCl_{(s)} + e^- \longrightarrow Ag_{(s)} + Cl^-{}_{(aq)} \quad } E^o + .207V$$

$$\mathrm{Ag^+{}_{(aq)} + e^- \longrightarrow Ag_{(s)} \quad } E^o = +0.799V$$

Subtracting the second reaction from the first one we obtain:

$$\mathrm{AgCl_{(s)} = Ag^+{}_{(aq)} + Cl^-{}_{(aq)} \quad } E^o = +0.207 - 0.799 = -0.592V$$

and again using nFE° = RTlnK, we obtain K = K_{sp} = **9.7 x 10^{-11} M^2**.



Because the solubility of the silver halides is so low, this would be a very difficult number to measure by other methods, e.g., by measuring the concentration of Ag+ spectroscopically, or by gravimetry. In practice almost all K_{sp} values involving electroactive substances are measured potentiometrically.

Acid-Base Equilibria

Many electrochemical reactions involve H^+ or OH^-. For these reactions, the half-cell potentials are **pH-dependent**.

Example: Recall that the disproportionation reaction $\mathrm{3\,MnO_4{}^{2-}{}_{(a)} \longrightarrow 2\,MnO_4{}^-{}_{(aq)} + MnO_{2\,(s)}}$ is **spontaneous** at pH=0 ([H^+] = 1M), from the Latimer diagram or Frost plot.

However, when we properly balance this half reaction we see that it involves **protons as a reactant**:

$$\mathrm{3\,MnO_4{}^{2-}\,(aq) + 4\,H^+\,(aq) \rightleftharpoons 2\,MnO_4{}^-\,(aq) + MnO_2\,(s) + 2\,H_2O\,(l)} \tag{7.2.5.3}$$

By Le Chatelier's principle, it follows that **removing protons** (increasing the pH) should **stabilize** the reactant, $\mathbf{MnO_4^{2-}}$. Thus we would expect the +6 oxidation state of Mn, which is unstable in acid, to be stabilized in basic media. We will examine these proton-coupled redox equilibria more thoroughly in the context of Pourbaix diagrams below.



Acid mine drainage occurs when sulfide rocks such as pyrite (FeS_2) are exposed to the air and oxidized. The reaction produces aqueous Fe^{3+} and H_2SO_4. When the acidic effluent of the mine meets a stream or lake at higher pH, solid $Fe(OH)_3$ precipitates, resulting in the characteristic orange muddy color downstream of the mine. The acidic effluent is toxic to plants and animals.

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7.2.6: Pourbaix Diagrams

Pourbaix Diagrams plot electrochemical stability for different redox states of an element as a function of pH.[3] As noted above, these diagrams are essentially phase diagrams that map the conditions of potential and pH (most typically in aqueous solutions) where different redox species are stable. We saw a simple example of such a diagram in section 4.2 for H_2O. Typically, the water redox reactions are plotted as dotted lines on these more complicated diagrams for other elements.

The lines in Pourbaix diagrams represent redox and acid-base reactions, and are the parts of the diagram where two species can exist in equilibrium. For example, in the Pourbaix diagram for Fe below, the horizontal line between the Fe^{3+} and Fe^{2+} regions represents the reaction $\mathrm{Fe^{3+}_{(aq)} + e^- = Fe^{2+}_{(aq)}}$, which has a standard potential of +0.77 V. 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.

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^-)

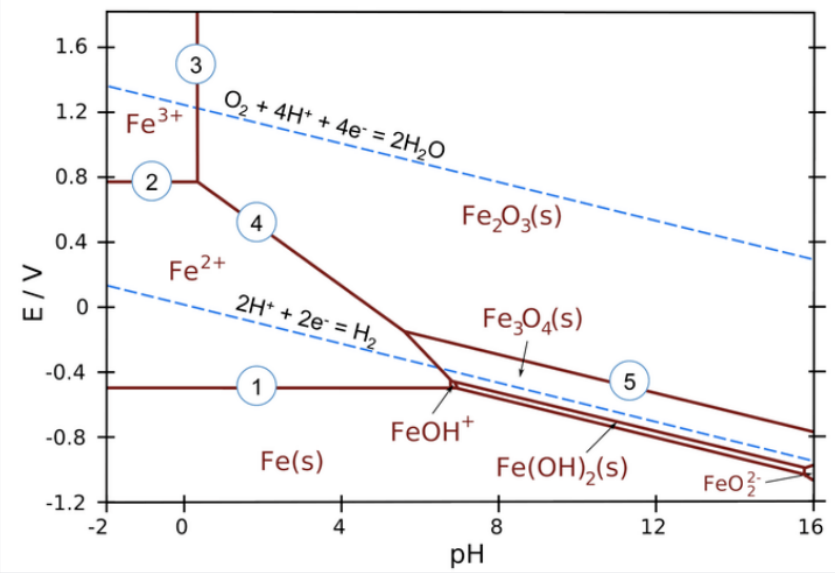


Figure 7.2.6.1: Pourbaix diagram for iron at ionic concentrations of 1.0 mM. (CC BY-SA 3.0 Unported; Metallos via Wikipedia)

Examples of equilibria in the iron Pourbaix diagram (numbered on the plot):

1. $\mathrm{Fe^{2+} + 2\,e^- \longrightarrow Fe_{(s)}}$ (pure redox reaction - no pH dependence)
2. $\mathrm{Fe^{3+} + e^- \longrightarrow Fe^{2+}}$ (pure redox reaction - no pH dependence)
3. $\mathrm{2\,Fe^{3+} + 3\,H_2O \longrightarrow Fe_2O_{3\,(s)} + 6\,H^+}$ (pure acid-base, no redox)
4. $\mathrm{2\,Fe^{2+} + 3\,H_2O \longrightarrow Fe_2O_{3\,(s)} + 6\,H^+ + 2\,e^-}$ (slope = -59.2 x 6/2 = -178 mV/pH)
5. $\mathrm{2\,Fe_3O_{4\,(s)} + H_2O \longrightarrow 2\,H^+ + 2\,e^-}$ (slope = -59.2 x 2/2 = -59.2 mV/pH)

The water redox lines have special significance on a Pourbaix diagram for an element such as iron. Recall that liquid water is stable *only* in the region between the dotted lines. Below the H_2 line, water is unstable relative to hydrogen gas, and above the

O_2 line, water is unstable with respect to oxygen. 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:

$\mathrm{Fe_{(s)} + 2\,H^+ \longrightarrow Fe^{2+}{}_{(aq)} + H_2}$ (in acid)

$\mathrm{fe_{(s)} + 2\,H_2O \longrightarrow Fe(OH)_{2\,(s)} + H_2}$ (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:

$\mathrm{4\,Fe_{(s)} + 3\,O_2 + 12\,H^+ \longrightarrow 4\,Fe^{3+} + 6\,H_2O}$ (in acid)

\(\ce{4Fe_{(s)} + 3O2 -> 2Fe2O3_{(s)} (in base)

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:

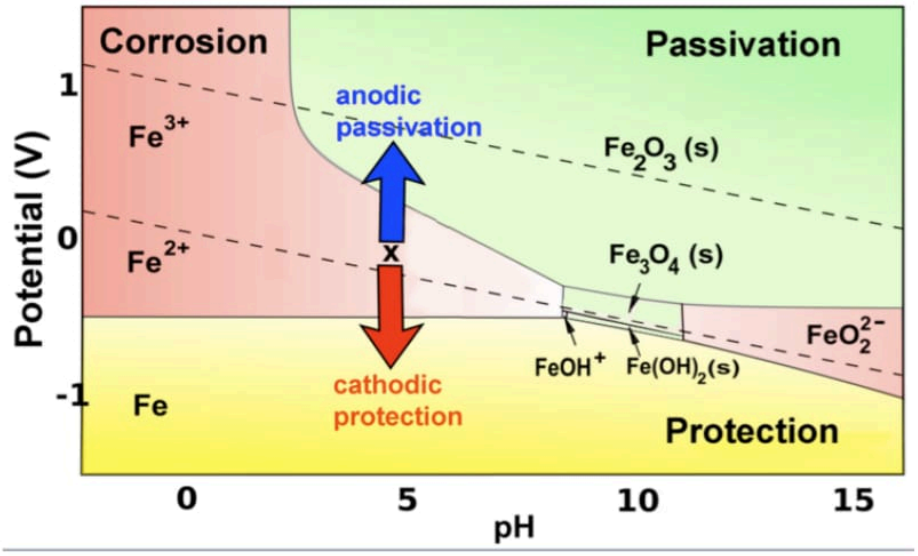
$$\mathrm{Fe_{(s)} + 2\,H^+ \longrightarrow Fe^{2+}{}_{(aq)} + H_2} \tag{7.2.6.1}$$

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:

$$\mathrm{4\,Fe_{(s)} + 3\,O_2 \longrightarrow 2\,Fe_2O_{3\,(s)}} \tag{7.2.6.2}$$

This oxidation reaction is orders of magnitude slower because the oxide that is formed *passivate*s 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

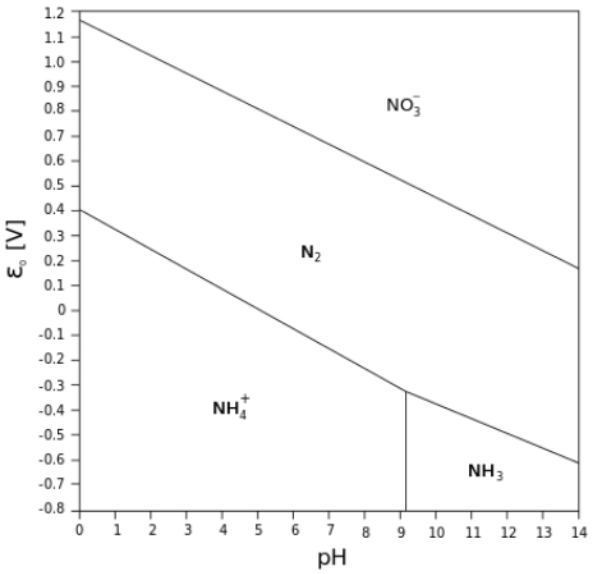
Differential aeration is involved in the formation of a rust ring around wet areas of cast iron, e.g., an iron frying pan left partially submerged in water for a day or more. (You may have seen this mechanism of corrosion in action when you did not get to the dirty dishes right away). Under the water, 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.

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7.2.7: Discussion Questions

- Explain the simplified Pourbaix diagram for nitrogen, shown below. Discuss the reactions that are implied by the lines, and explain why they have the slopes they do.



- Use the information in the Pourbaix diagram to construct a Frost diagram for nitrogen at pH 7.

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7.2.8: Problems

1. Balance the following redox reactions, adding H_2O and H^+ (or OH^-) as needed. Predict for each one whether the reaction would become more or less spontaneous at higher pH.

(a) $\mathrm{MnO_4^-_{(aq)} + N_2O_{(g)} = Mn^{2+}_{(aq)} + NO_3^-_{(aq)}}$ (in acid)

(b) $\mathrm{Cr_2O_7^{2-}_{(aq)} + S_2O_3^{2-}_{(aq)} = Cr_2O_{3\,(s)} + SO_4^{2-}_{(aq)}}$ (in base)

(c) $\mathrm{H_2O_{2\,(aq)} + HI_{(aq)} = I_3^-_{(aq)}}$ (in acid)

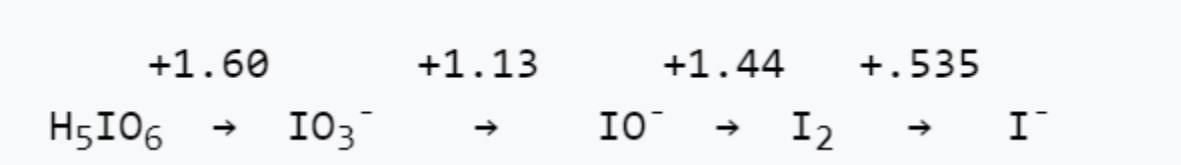
(d) $\mathrm{HOBr_{(aq)} = HBr_{(aq)} + HBrO_{2\,(aq)}}$ (in acid)

(e) $\mathrm{C_{12}H_{22}O_{11}\ (sucrose, aq) + ClO_3^-_{(aq)} = HCO_3^-_{(aq)} + Cl^-_{(aq)}}$ (in base)

2. Silver metal is not easily oxidized, and does not react with oxygen-saturated water. However, when excess NaCN is added to a suspension of silver particles, some silver dissolves. If oxygen is removed (e.g., by bubbling nitrogen through the solution), the dissolution reaction stops. Write a balanced equation for the dissolution reaction (hint: it is a redox reaction).

3. The standard potentials for the Fe^{3+}/Fe^{2+} and Cl^-/Cl_2 couples are +0.77 and +1.36 V. Calculate the cell potential of a redox flow battery that has Fe^{3+}/Fe^{2+} and Cl^-/Cl_2 solutions on the two sides (both containing 1.0 M HCl as the electrolyte). The pressure of Cl_2 gas on the chlorine side is 0.2 atm, and the concentrations of Fe^{2+} and Fe^{3+} on the iron side are both 0.10 M.

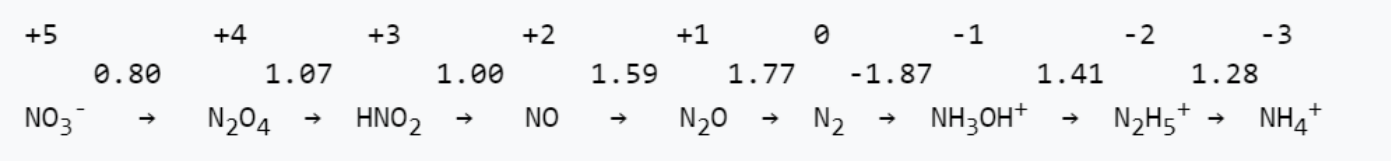
4. The Latimer potential diagram for iodine (in acidic solutions) is given below.



(a) What is the potential for the IO_3^-/I^- redox couple?

(b) Construct a Frost diagram and identify any species that are unstable with respect to disproportionation.

5. The Latimer diagram for nitrogen in acidic solutions is shown below:



(a) Write a balanced half reaction for reduction of NO to NH_4^+ in acid.

(b) What is the value of E^o for the half reaction in part (a)?

(c) Is this half reaction more thermodynamically favorable in acid or in base? Explain.

(d) All the nitrogen-containing molecules and ions listed above are kinetically stable, but only three are *thermodynamically* stable with respect to disproportionation in acid. Which ones are they?

6. Referring to the Pourbaix diagram for Mn below:

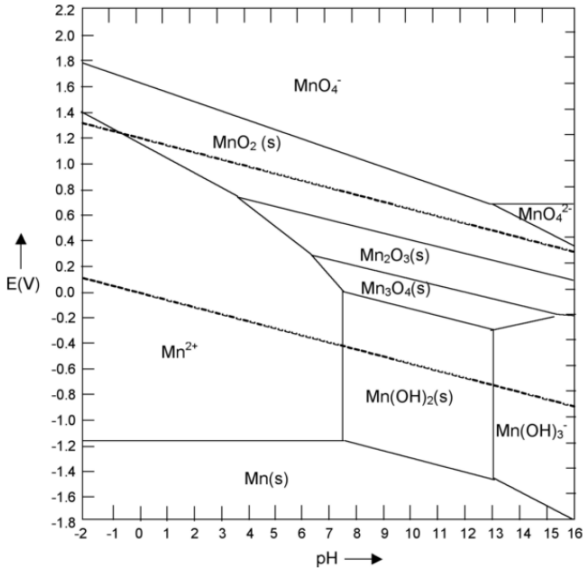
(a) Write out the balanced half reaction corresponding to the line separating Mn^{2+} and Mn_2O_3. Use your answer to calculate the slope of the line (give units).

(b) Is Mn metal stable in water at any pH? If so, in what range of pH?

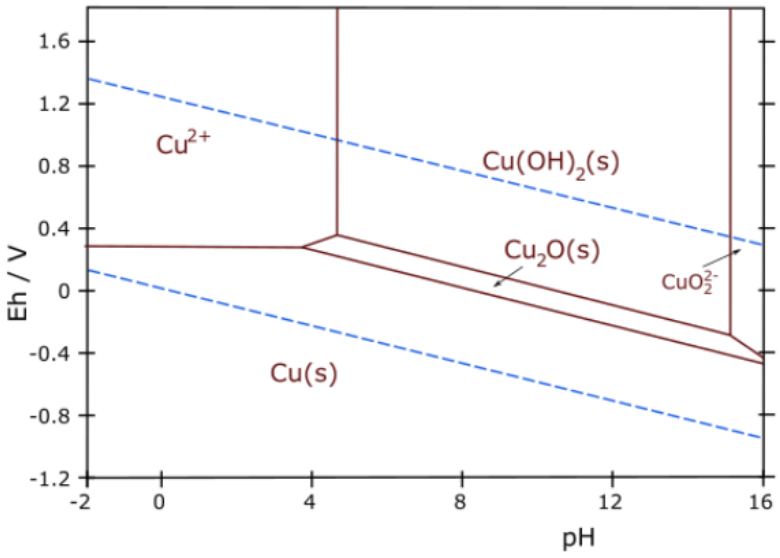
(c) What spontaneous reaction would you expect for an aqueous solution of MnO_4^- at pH 6?

(d) Describe an electrochemical procedure (specifying pH and potential) for making $Mn_3O_4(s)$ from aqueous Mn^{2+}.

(e) Label the regions of the diagram that correspond to corrosion and passivation of Mn metal.



7. The Pourbaix diagram for copper is shown below.



(a) Write a balanced half-reaction that corresponds to the boundary between the $Cu_2O(s)$ and $Cu(OH)_2(s)$ regions of the diagram.

(b) What is the slope of the line (do not try to measure it from the graph!) that connects the $Cu^{2+}(aq)$ and $Cu_2O(s)$ regions? Explain your reasoning.

(c) Over what pH range (if any) is copper metal stable in contact with pure water?

(d) Thermodynamically, the reaction between coppper and oxygen is spontaneous at pH 7. Would you expect copper to corrode or to be passivated against corrosion in aerated water at neutral pH? Explain your reasoning.

(e) Some recent studies have suggested the use of Cu_2O as a water splitting photocatalyst. Would you expect Cu_2O to be stable in the presence of the oxygen formed in the reaction? Explain your reasoning.

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