Chapter 1

General Concepts and Trends

1.1 Fundamental Properties

1.1.1 Oxidation State[1]

The oxidation state of an element is defined as *the formal charge on the atom if all bonds were assumed to be fully ionic*.

In an ionic compound the oxidation state is equal to the charge on the ion, e.g., in NaCl the charge on the sodium is +1 and the oxidation state is also +1. In contrast, the charge on an atom in a covalent compound never approaches the charge implied from the oxidation number, e.g., in CCl_4, the oxidation state of carbon is +4 but the charge on the carbon atom is significantly less.

Thus, while oxidation state is a simple formulism it is very useful in a number of ways:

1) Classification of compounds of elements, especially those of the transition metals.
2) Enables the balance of reduction-oxidation (redox) reactions.

To determine the oxidation state of an element within a particular compound the following steps act as a guideline.

Step 1) The oxidation state of any atom of any element in its elemental form is zero.
Step 2) The oxidation state of a monatomic ion is equal to its charge.
Step 3) Any homoleptic X-X bonds (e.g., the C-C bond in H_3C-CH_3) are assumed to be non-ionic and do not contribute to the oxidation state of X.
Step 4) Fluorine always has oxidation state of –1.
Step 5) Elements of Group 1 (IA) (except hydrogen) have an oxidation state of +1 in compounds.
Step 6) Elements of Group 2 (IIA) have an oxidation state of +2 in compounds.
Step 7) Elements of Group 17 (VIIA) have an oxidation state of -1 when they combine with elements below or to the left of their position in the periodic table.
Step 8) Oxygen is usually assigned the oxidation state of –2, except in compounds with fluorine, oxygen has a positive oxidation number.
Step 9) Hydrogen is assigned the oxidation state of +1 with non-metals and –1 with metals.
Step 10) In any compound the sum of the oxidation states (oxidation numbers) is equal to the overall charge.

Exercise 1.1.1.1 ***(Solution on p. 63.)***

What is the oxidation state of sulfur in Na_2SO_4?

Exercise 1.1.1.2 ***(Solution on p. 63.)***

What is the oxidation state of sulfur in Na_2SO_3?

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[1] This content is available online at <http://cnx.org/content/m31475/1.2/>.

Exercise 1.1.1.3 ***(Solution on p. 63.)***

What is the oxidation state of sulfur in H_2S?

In writing the oxidation state of an element within a compound it is common to use a Roman numeral, rather than the *charge*, i.e., Al(III) rather than Al^{3+}.

1.1.2 Ionization Energy[2]

The ionization energy (IE), or more properly the ionization enthalpy, is defined as the energy required to loose an electron from a gaseous atom or ion.

$$M^{n+}_{(g)} \rightarrow M^{(n+1)+}_{(g)} + e^{-} \tag{1.1}$$

Each subsequent ionization energy is greater than the previous one because of the increase in charge on the ion. For example, for any given atom or ion the 1st ionization energy is less than the 2nd ionization energy, and so on. This is shown in Table 1.1.

Ionization	**Ionization energy (kJ/mol)**
$Al^0 \rightarrow Al^+ + e^-$	548
$Al^+ \rightarrow Al^{2+} + e^-$	1823
$Al^{2+} \rightarrow Al^{3+} + e^-$	2751

Table 1.1: The first three ionization energies for aluminum.

How does the ionization energy vary with elements in the periodic table? If we consider the 1st ionization potential of the elements in a particular group of the periodic table we note that there is a decrease in ionization potential as you go down the Group. The reason for this trend is due to the increased shielding of the outer shell electrons (ns^1) by the completed (filled) inner shells. The ns^1 electron thus exhibits a lower effective nuclear charge and makes it easier to remove. For example, Table 1.2 shows the 1st ionization potential for the Group 1 alkali metals.

Element	**Ionization energy (kJ/mol)**
Li	526
Na	502
K	425
Rb	409
Cs	382

Table 1.2: Variation of the first ionization potential ($M^0 \rightarrow M^+$) for the Group 1 (IA) elements.

In contrast, to individual Groups, moving across a particular Period results in a general increase in the ionization potential as is shown in Figure 1.1. The lack of additional screening of filled shells across the Period means that the ionization energy for the outer shell electrons is dominated by the increase in nuclear charge (number of protons) with increased atomic number.

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[2] This content is available online at <http://cnx.org/content/m31450/1.4/>.

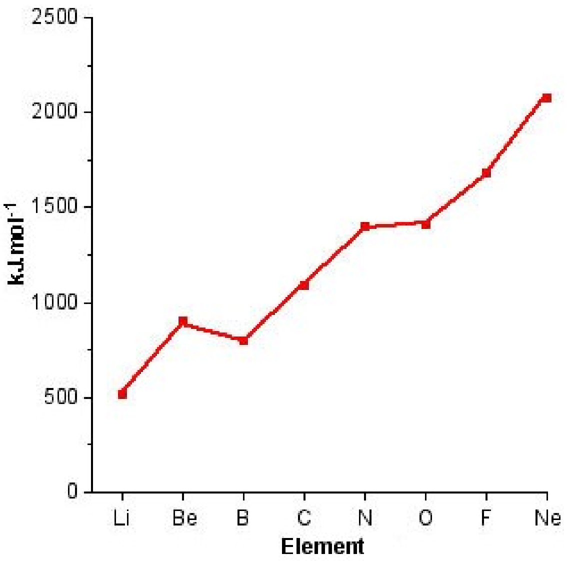

Figure 1.1: Plot of the first ionization potential for the elements Li to Ne.

From Figure 1.1 it can be seen that the Periodic trend is not linear, there are significant steps in the plot. Boron, for example, has a lower first ionization potential than beryllium, why? A consideration of the electron configuration for the elements provides in answer (Figure 1.2). Beryllium has a $2s^2$ outer shell configuration, while boron has a $2s^2$ $2p^1$ configuration. The $2p^1$ electron is easy to remove because it exhibits increased shielding from the nucleus due to the filled 2s orbital.

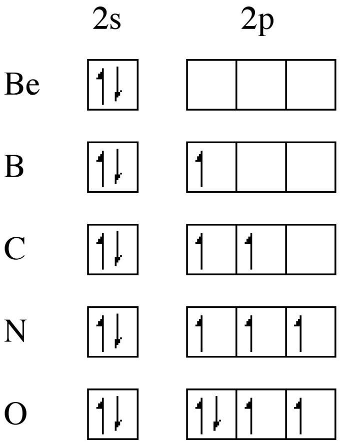

Figure 1.2: Outer shell electron configuration of beryllium through oxygen.

As we move from, boron to nitrogen, the 2p shell is filled (Figure 1.2) without additional shielding and the effect of the increased nuclear charge dominates. Finally, the $2p^4$ configuration for oxygen (Figure 1.2) results in an electron pair, which repel each other, thus making it easier to remove an electron (lower ionization potential) that expected from the increased nuclear charge. From Figure 1 we can see that the effect of electron pairing is less than that of a filled shell.

The trend for the 2nd ionization potential is similar, but different, to that of the 1st ionization potential. As may be seen in Figure 1.3 the steps observed for the 1st ionization energy plot (i.e., between Be/B and N/O have moved one element to the right. A view of the electron configuration for the E^+ ions (Figure 1.4) shows that the rational for the trend in the 1st ionization potential trends still applies but to the ion of the lement to the right in the Periodic table. Now B^+ has a $2s^2$ outer shell configuration, while C^+ has a $2s^2$ $2p^1$ configuration. A similar plot for the 3rd ionization energy would move the steps another element to the right.

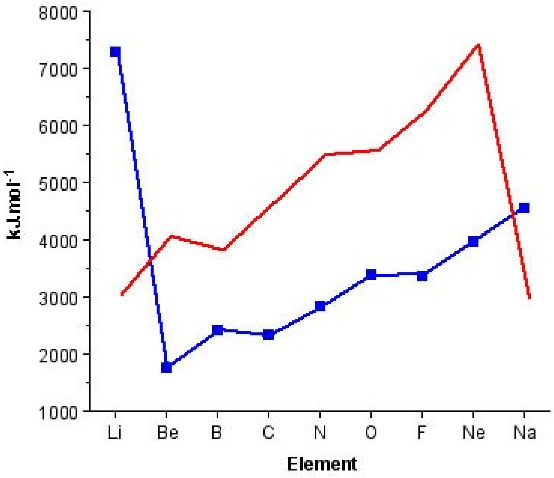

Figure 1.3: A plot of 2nd ionization energy (enthalpy) for elements Li to Na (blue with square data points) showing the relative trend to the 1st ionization potential (red line – not to scale).

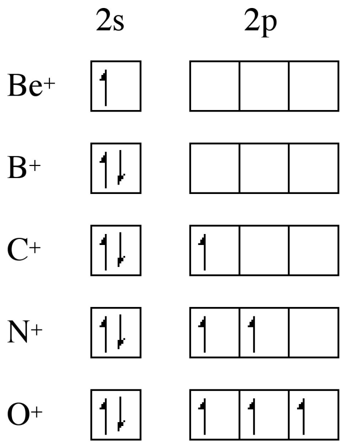

Figure 1.4: Outer shell electron configuration of E^{+} for beryllium through oxygen.

The other observation to be made from Figure 1.3 is the very large 2nd ionization potential for lithium associated with the ionization of Li^{+} to Li^{2+}. The large increase is due to the removal of an electron from the filled $1s^2$ shell.

1.1.3 Electron Affinity[3]

The electron affinity (EA) of an element is defined as the energy given off when a neutral atom in the gas phase gains an extra electron to form a negatively charged ion.

$$X^{n-}{}_{(g)} + e^{-} \rightarrow X^{(n+1)-}{}_{(g)} \tag{1.2}$$

Electron affinities are more difficult to measure than ionization energies and are usually less accurately known. Electron affinities are large and negative for elements such as fluorine and oxygen, and small and positive for metals.

Electron affinities generally become smaller as you go down a Group of the periodic table (Table 1.3). This is because the electron being added to the atom is placed in a larger orbital, where it spends less time near the nucleus of the atom, and also the number of electrons on an atom increases as we go down a column, so the force of repulsion between the electron being added and the electrons already present on a neutral atom becomes larger. Electron affinities are further complicated since the repulsion between the electron being added to the atom and the electrons already present on the atom depends on the volume of the atom. Thus, for the nonmetals in Groups 6 (VIA) and 7 (VIIA), this force of repulsion is largest for the very smallest atoms in these columns: oxygen and fluorine. As a result, these elements have a smaller electron affinity than the elements below them in these columns as shown in Table 1.3.

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[3] This content is available online at <http://cnx.org/content/m31451/1.3/>.

Element	Electron affinity (kJ/mol)
F	-322
Cl	-349
Br	-325
I	-295

Table 1.3: The electron affinity for the non-metallic halogens.

Although there is a general trend that for Group 1 (IA) to Group 17 (VIIA) elements the electron affinity increases across the Periodic table from left to right, the details of the trend are more complex. As may be seen from Figure 1.5, there is a cyclic trend. The explanation of this is a consequence of the unusually stable electron configurations exhibited by atoms with filled or half filled shells, i.e., helium, beryllium, nitrogen and neon (see Table 1.4). These configurations are so stable that it actually takes energy to force one of these elements to pick up an extra electron to form a negative ion.

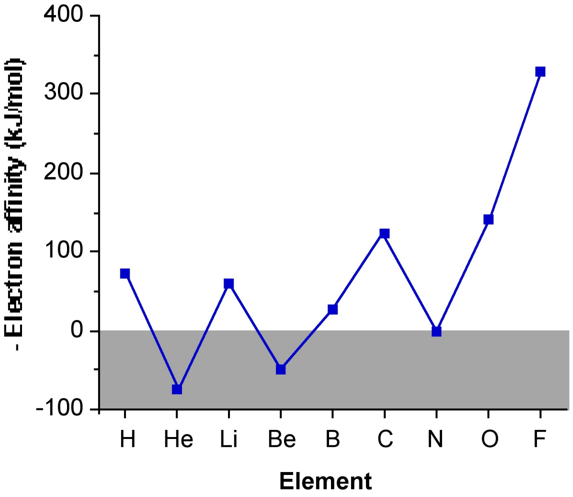

Figure 1.5: Plot of the electron affinity for the elements hydrogen to fluorine. N.B. Values for helium, beryllium, nitrogen, and neon are not known with any accuracy but are all positive.

Element	**Electron affinity (kJ/mol)**	**Electron configuration**
H	-72.8	$1s^1$
He	+ve	$1s^2$
Li	-59.8	[He] $2s^1$
Be	+ve	[He] $2s^2$
B	-27	[He] $2s^2$ $2p^1$
C	-122.3	[He] $2s^2$ $2p^2$
N	+ve	[He] $2s^2$ $2p^3$
O	-141.1	[He] $2s^2$ $2p^4$
F	-328.0	[He] $2s^2$ $2p^5$
Ne	+ve	[He] $2s^2$ $2p^6$

Table 1.4: Electron affinities of the elements hydrogen to neon. N.B. Values for helium, beryllium, nitrogen, and neon are not known with any accuracy but are all positive.

1.1.4 Electronegativity[4]

An issue with ionization potential and electron affinity is that they are defined and measured as reactions in the gas phase. Although values have been determined for molecular fragments it is still difficult to correlate with reaction trends in solution. To overcome this issue the concept of electronegativity was developed.

Electronegativity is defined as the *tendency of an atom in a molecule to attract electrons to itself*. Although several electronegativity scales have been developed, that by Linus Pauling (Figure 1.6) is the most often used. Table 1.5 provides selected Pauling electronegativity values (unit less).

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[4] This content is available online at <http://cnx.org/content/m31452/1.2/>.

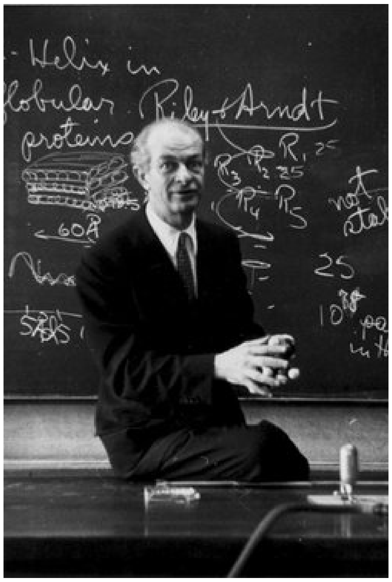

Figure 1.6: American chemist Linus Carl Pauling (1901 –1994).

Element	**Pauling scale**
F	4.0
O	3.5
Cl	3.0
N	3.0
S	2.5
C	2.5
H	2.1
B	2.0
Na	0.9

Table 1.5: Selected Pauling electronegativity values.

The advantage of the Pauling electronegativity scale is that it allows the prediction of general behavior. For example, the larger the difference in electronegativity between two elements the more ionic character or more polar the bonding interaction. Thus, a H-O bond (3.5 - 2.1 = 1.4) is more polar than a H-S bond (2.5 – 2.1 = 0.4).

1.2 Structure and Bonding

1.2.1 Valence Shell Electron Pair Repulsion (VSEPR) Theory[5]

The idea of a correlation between molecular geometry and the number of valence electrons was first presented in 1940 by Sidgwick and Powell; however, in 1957, Ronald Gillespie (Figure 1.7) and Sir Ronald Nyholm (Figure 1.8) refined this concept to build a more detailed theory. It is their work that provides the basis of the *valence shell electron pair repulsion* (VSEPR) theory, and as such it is also known as the Gillespie-Nyholm theory.

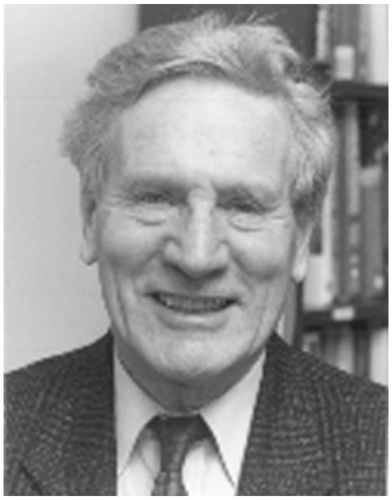

Figure 1.7: Chemist Ronald J. Gillespie (1924 -).

Figure 1.8: Australian chemist Sir Ronald Sydney Nyholm (1917 -).

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[5] This content is available online at <http://cnx.org/content/m31949/1.3/>.

One attribute of VSEPR is that with the ability to predict the shape of a molecule for a compound comes the ability to predict some of the physical and chemical properties of that compound.

The formal definition that is the basis for VSEPR is as follows: *Pairs of electrons in the valence shell of a central atom of a molecule repel each other and take up positions as far apart as possible.*

Within this definition it is implicitly assumed that the core shells are not polarized and therefore take no part in bonding, and therefore can be ignored. Since the maximum repulsion of the electron pairs (be they associated with a bonding interaction or a lone pair) control the shape of a molecule, for each number of electron pairs we can define the geometric optimum position that maximizes the distance between the electron pairs (Table 1.6). The number of electron pairs surrounding an atom, both bonding and nonbonding, is called its steric number.

Number of central atom electron pairs	**Bonding pairs**	**Non-bonding pairs**	**Shape**	**Example**
2	2	0	Linear	$BeCl_2$
3	3	0	Triangular	BF_3
3	2	1	Bent	$SnCl_2$
4	4	0	Tetrahedral	CCl_4
4	3	1	Pyramidal	NH_3
4	2	2	Bent	H_2O
5	5	0	Trigonal bipyramidal (tbp)	PF_5
5	4	1	Pseudo-tdp	BrF_4^-
5	3	2	T-shaped	BrF_3
5	2	3	Linear	XeF_2
6	6	0	Octahedral	SF_6,PF_6^-
6	5	1	Square pyramidal	IF_5
6	4	2	Square planar	XeF_4,IF_4^-

Table 1.6: Shapes of molecules and ions

The steps for defining the molecular shape are as follows:

Step 1. Draw a simple Lewis structure including single, double, and triple bonds where appropriate.
Step 2. Count the number of electrons on the central atom assuming it is neutral.
Step 3. Add one electron for each σ-bond.
Step 4. Subtract one electron for each π-bond.
Step 5. Subtract one electron for each positive (+) charge.
Step 6. Add one electron for each negative (-) charge.
Step 7. Divide the number of electrons by two to give the number of electron pairs.
Step 8. Use the list in Table 1.6 to predict the structure of the molecule.

Example 1.1
What is the shape of NH_4^+?

Step 1. Nitrogen has 5 valence electrons
Step 2. Add 4 electrons for the four σ-bonds: $5 + 4 = 9$

Step 3. Subtract one electron for the positive (+) charge: 9 – 1 = 8
Step 4. Divide the number of electrons by two to give the number of electron pairs: 8/2 = 4
Step 5. Four bonding pairs and no lone pairs = tetrahedral geometry

Exercise 1.2.1.1 ***(Solution on p. 63.)***
What is the shape of $HgCl_2$?

Exercise 1.2.1.2 ***(Solution on p. 63.)***
What is the shape of H_2CO?

1.2.1.1 Lone pairs versus bonding pairs

The prediction of the detailed molecular structure (including bond angles) is not as simple as shown in Table 1.6. In molecules with either lone pair electrons or multiple (double or triple) bonds the angles about the central atom are distorted due to the increased electron repulsion (Figure 1.9). The differences in repulsion caused by a lone pair or a bonding pair may be rationalized in a simple manner by a lone pair taking up more space than a bonding pair (Figure 1.10).

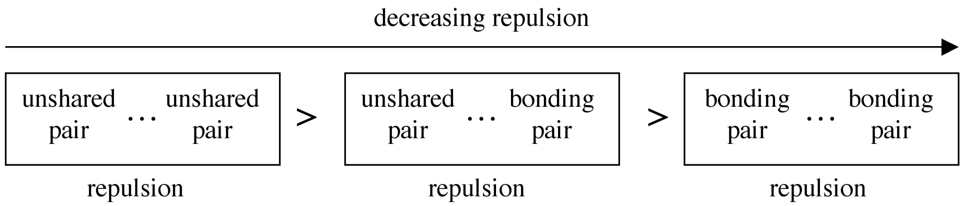

Figure 1.9: The order of decreasing repulsion between non-bonding (unshared) and bonding electron pairs.

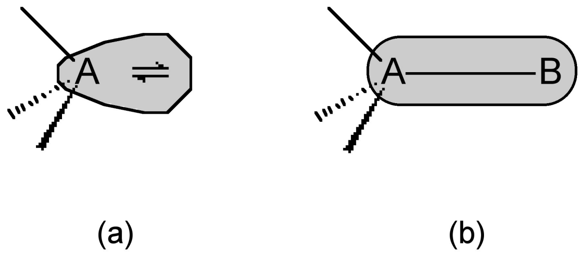

Figure 1.10: Representation of the relative space taken up by (a) a lone pair of electrons and (b) a bonding pair of electrons.

Water is one of the classic cases in considering the issue of non-bonding (unshared) electron pairs.

Step 1. Oxygen has 6 valence electrons
Step 2. Add 2 electrons for the two σ-bonds: $6 + 2 = 8$
Step 3. Divide the number of electrons by two to give the number of electron pairs: $8/2 = 4$
Step 4. Two bonding pairs and two lone pairs = tetrahedral geometry

From this an idealized tetrahedral geometry would give the H-O-H angle as 109.5 °, however, from Figure 1.9 we know that the lone pair···lone pair repulsion is greater than the lone pair···bonding pair repulsion which is greater than the bonding pair···bonding pair repulsion, and thus, the H-O-H angle should be decreased from the ideal tetrahedral. The experimentally determined H-O-H angle in water is in fact 104.5 °.

Ethylene is a good case in considering the issue of multiple bonds. Ethylene contains both σ-bond and π-bond between the carbon atoms. This combination can be thought of as a *super bond*, and as such its effect is similar to a lone pair.

Step 1. Carbon has 4 valence electrons
Step 2. Add 3 electrons for the two σ-bonds: $4 + 3 = 7$
Step 3. Subtract one electron for each π-bond: $7 - 1 = 6$
Step 4. Divide the number of electrons by two to give the number of electron pairs: $6/2 = 3$
Step 5. Three bonding pairs and no lone pairs = triangular geometry

From this an idealized tetrahedral geometry would give the H-C-H angle as 120 °, however, the π-bond repulsion is greater than the σ-bond repulsion, and thus, the H-C-H angle should be decreased from the ideal tetrahedral. The experimentally determined H-O-H angle in water is in fact 118.3 °.

1.2.1.2 Resonance structures

If a molecule or ion has two or more resonance forms it is necessary to consider each form before angles are predicted. For example, the carbonate anion, CO_3^-, can be drawn as a single structure from which it would be predicted that two groups of O-C-O angles would result (Figure 1.11).

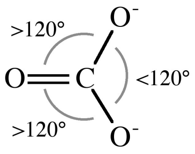

Figure 1.11: VSEPR predicted structure of a single resonance form of CO_3^{2-}.

However, CO_3^- should actually be drawn in each of its resonance forms as in Figure 1.12.

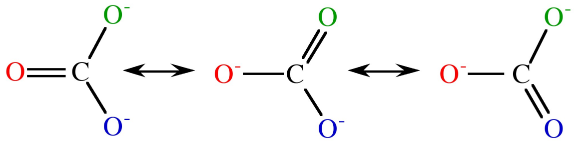

Figure 1.12: Resonance forms of CO_3^{2-}.

From Figure 1.12 it is clear that the real structure will be an average of the three resonance forms, and hence there will be a single O-C-O angle = 120 ° (Figure 1.13).

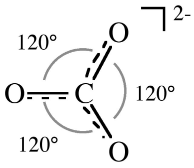

Figure 1.13: Structure of CO_3^{2-}.

1.2.1.3 Atom electronegativities

In an A-X bond where the atom electronegativities are very different the bonding pair is assumed to occupy less space than in bond between two atoms of similar electronegativities. As the bonding pair occupies less space it will repel neighboring electron pairs less.

For example, based on the above, a comparison of the tetrahedral compounds H_2O and F_2O would suggest that the F-O-F angle be smaller than the H-O-H angle since fluorine has a higher electronegativity than hydrogen (4.0 and 2.1, respectively). This is indeed observed (Figure 1.14).

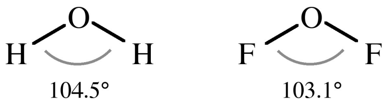

Figure 1.14: Structures of H_2O and F_2O.

In many cases, inter-ligand steric interactions can also be used to explain the difference in angle. For example, while fluorine is more electronegative than chlorine (4.0 versus 3.0, respectively) it is also significantly smaller (Table 1.7). Thus, a larger Cl-X-Cl angle than a F-X-F angle in the homologous compound, can be attributed to a greater steric interactions, rather than difference in electronegativities.

Ligand	Covalent radius (Å)	Van der Waal radius (Å)
F	0.57	1.35
Cl	1.02	1.80

Table 1.7: Comparison of size between fluoride and chloride ligands.

1.2.1.4 Bent's rule

There is the potential for more than one isomer for molecules that adopt structures in which there is a symmetry difference between at least two of the ligand positions. For example a trigional bipyramidal compound of the formula PXY_4 has two possible structures. One where the X occupies an axial position (Figure 1.15a) and the other where it occupies an equatorial position (Figure 1.15b).

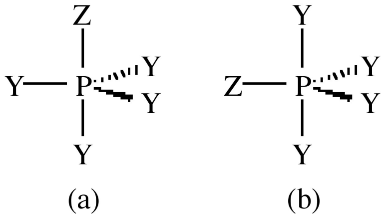

Figure 1.15: The two possible structures of PXY_4.

Through the consideration of structures Henry Bent suggested a rule: *More electronegative substituents prefer hybrid orbitals with less s character, and conversely, more electropositive substituents prefer hybrid orbitals with greater s character.*

For example, in $PFCl_5$ the fluorine is the most electronegative substituent and will therefore occupy the axial (p-character only) position.

1.2.1.5 Bibliography

- H. A. Bent, *J. Chem. Educ.*, 1960, **37**, 616.
- H. A. Bent, *Chem. Rev.*, 1961, **61**, 275.
- R. J. Gillespie, *J. Chem. Educ.*, 1970, **47**, 18.
- R. J. Gillespie, *Chem. Soc. Rev.*, 1992, **21**, 59.
- R. J. Gillespie and R. S. Nyholm, *Quart. Rev.*, 1957, **11**, 339.

1.2.2 Crystal Structure[6]

1.2.2.1 Introduction

In any sort of discussion of crystalline materials, it is useful to begin with a discussion of crystallography: the study of the formation, structure, and properties of crystals. A crystal structure is defined as the particular repeating arrangement of atoms (molecules or ions) throughout a crystal. Structure refers to the internal

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[6] This content is available online at <http://cnx.org/content/m16927/1.10/>.

arrangement of particles and not the external appearance of the crystal. However, these are not entirely independent since the external appearance of a crystal is often related to the internal arrangement. For example, crystals of cubic rock salt (NaCl) are physically cubic in appearance. Only a few of the possible crystal structures are of concern with respect to simple inorganic salts and these will be discussed in detail, however, it is important to understand the nomenclature of crystallography.

1.2.2.2 Crystallography

1.2.2.2.1 Bravais lattice

The Bravais lattice is the basic building block from which all crystals can be constructed. The concept originated as a topological problem of finding the number of different ways to arrange points in space where each point would have an identical "atmosphere". That is each point would be surrounded by an identical set of points as any other point, so that all points would be indistinguishable from each other. Mathematician Auguste Bravais discovered that there were 14 different collections of the groups of points, which are known as Bravais lattices. These lattices fall into seven different "crystal systems", as differentiated by the relationship between the angles between sides of the "unit cell" and the distance between points in the unit cell. The unit cell is the smallest group of atoms, ions or molecules that, when repeated at regular intervals in three dimensions, will produce the lattice of a crystal system. The "lattice parameter" is the length between two points on the corners of a unit cell. Each of the various lattice parameters are designated by the letters *a*, *b*, and *c*. If two sides are equal, such as in a tetragonal lattice, then the lengths of the two lattice parameters are designated *a* and *c*, with *b* omitted. The angles are designated by the Greek letters α, β, and γ, such that an angle with a specific Greek letter is not subtended by the axis with its Roman equivalent. For example, α is the included angle between the *b* and *c* axis.

Table 1.8 shows the various crystal systems, while Figure 1.16 shows the 14 Bravais lattices. It is important to distinguish the characteristics of each of the individual systems. An example of a material that takes on each of the Bravais lattices is shown in Table 1.9.

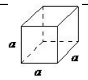
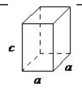
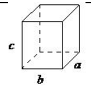
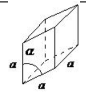
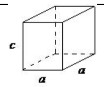
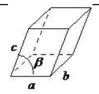
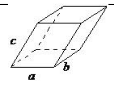
System	**Axial lengths and angles**	**Unit cell geometry**
cubic	$a = b = c$, $\alpha = \beta = \gamma = 90\,^\circ$	
tetragonal	$a = b \neq c$, $\alpha = \beta = \gamma = 90\,^\circ$	
orthorhombic	$a \neq b \neq c$, $\alpha = \beta = \gamma = 90\,^\circ$	
rhombohedral	$a = b = c$, $\alpha = \beta = \gamma \neq 90\,^\circ$	
hexagonal	$a = b \neq c$, $\alpha = \beta = 90\,^\circ$, $\gamma = 120\,^\circ$	
monoclinic	$a \neq b \neq c$, $\alpha = \gamma = 90\,^\circ$, $\beta \neq 90\,^\circ$	
triclinic	$a \neq b \neq c$, $\alpha \neq \beta \neq \gamma$	

Table 1.8: Geometrical characteristics of the seven crystal systems.

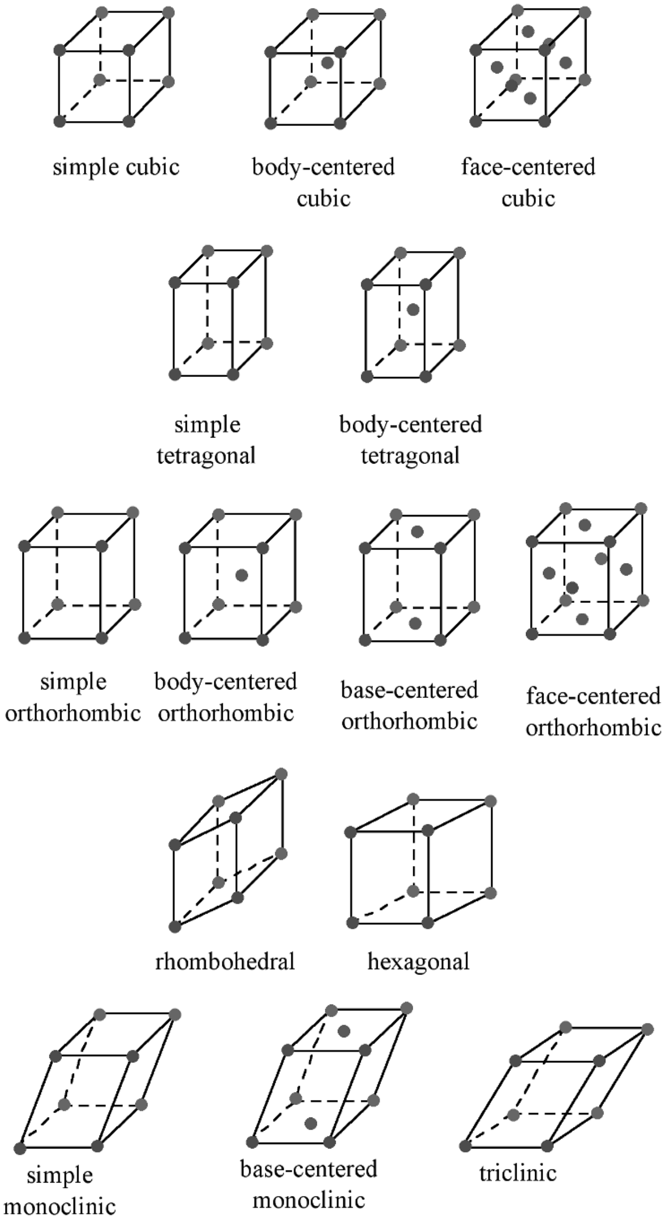


Figure 1.16: Bravais lattices.

Crystal system	**Example**
triclinic	$K_2S_2O_8$
monoclinic	As_4S_4, KNO_2
rhombohedral	Hg, Sb
hexagonal	Zn, Co, NiAs
orthorhombic	Ga, Fe_3C
tetragonal	In, TiO_2
cubic	Au, Si, NaCl

Table 1.9: Examples of elements and compounds that adopt each of the crystal systems.

The cubic lattice is the most symmetrical of the systems. All the angles are equal to 90 °, and all the sides are of the same length ($a = b = c$). Only the length of one of the sides (a) is required to describe this system completely. In addition to simple cubic, the cubic lattice also includes body-centered cubic and face-centered cubic (Figure 1.16). Body-centered cubic results from the presence of an atom (or ion) in the center of a cube, in addition to the atoms (ions) positioned at the vertices of the cube. In a similar manner, a face-centered cubic requires, in addition to the atoms (ions) positioned at the vertices of the cube, the presence of atoms (ions) in the center of each of the cubes face.

The tetragonal lattice has all of its angles equal to 90 °, and has two out of the three sides of equal length ($a = b$). The system also includes body-centered tetragonal (Figure 1.16).

In an orthorhombic lattice all of the angles are equal to 90 °, while all of its sides are of unequal length. The system needs only to be described by three lattice parameters. This system also includes body-centered orthorhombic, base-centered orthorhombic, and face-centered orthorhombic (Figure 1.16). A base-centered lattice has, in addition to the atoms (ions) positioned at the vertices of the orthorhombic lattice, atoms (ions) positioned on just two opposing faces.

The rhombohedral lattice is also known as trigonal, and has no angles equal to 90 °, but all sides are of equal length ($a = b = c$), thus requiring only by one lattice parameter, and all three angles are equal ($\alpha = \beta = \gamma$).

A hexagonal crystal structure has two angles equal to 90 °, with the other angle (γ) equal to 120 °. For this to happen, the two sides surrounding the 120 ° angle must be equal ($a = b$), while the third side (c) is at 90 ° to the other sides and can be of any length.

The monoclinic lattice has no sides of equal length, but two of the angles are equal to 90 °, with the other angle (usually defined as β) being something other than 90 °. It is a tilted parallelogram prism with rectangular bases. This system also includes base-centered monoclinic (Figure 1.16).

In the triclinic lattice none of the sides of the unit cell are equal, and none of the angles within the unit cell are equal to 90 °. The triclinic lattice is chosen such that all the internal angles are either acute or obtuse. This crystal system has the lowest symmetry and must be described by 3 lattice parameters (a, b, and c) and the 3 angles (α, β, and γ).

1.2.2.2.2 Atom positions, crystal directions and Miller indices

1.2.2.2.2.1 Atom positions and crystal axes

The structure of a crystal is defined with respect to a unit cell. As the entire crystal consists of repeating unit cells, this definition is sufficient to represent the entire crystal. Within the unit cell, the atomic arrangement is expressed using coordinates. There are two systems of coordinates commonly in use, which can cause some confusion. Both use a corner of the unit cell as their origin. The first, less-commonly seen system is that of Cartesian or orthogonal coordinates (X, Y, Z). These usually have the units of Angstroms and relate to the distance in each direction between the origin of the cell and the atom. These coordinates may be manipulated in the same fashion are used with two- or three-dimensional graphs. It is very simple, therefore, to calculate inter-atomic distances and angles given the Cartesian coordinates of the atoms. Unfortunately, the repeating nature of a crystal cannot be expressed easily using such coordinates. For example, consider a cubic cell of dimension 3.52 Å. Pretend that this cell contains an atom that has the coordinates (1.5, 2.1, 2.4). That is, the atom is 1.5 Å away from the origin in the x direction (which coincides with the *a* cell axis), 2.1 Å in the y (which coincides with the *b* cell axis) and 2.4 Å in the z (which coincides with the *c* cell axis). There will be an equivalent atom in the next unit cell along the x-direction, which will have the coordinates (1.5 + 3.52, 2.1, 2.4) or (5.02, 2.1, 2.4). This was a rather simple calculation, as the cell has very high symmetry and so the cell axes, *a*, *b* and *c*, coincide with the Cartesian axes, X, Y and Z. However, consider lower symmetry cells such as triclinic or monoclinic in which the cell axes are not mutually orthogonal. In such cases, expressing the repeating nature of the crystal is much more difficult to accomplish.

Accordingly, atomic coordinates are usually expressed in terms of fractional coordinates, (x, y, z). This coordinate system is coincident with the cell axes (*a*, *b*, *c*) and relates to the position of the atom in terms of the fraction along each axis. Consider the atom in the cubic cell discussion above. The atom was 1.5 Å in the *a* direction away from the origin. As the *a* axis is 3.52 Å long, the atom is ($^{1.5}/_{3.52}$) or 0.43 of the axis away from the origin. Similarly, it is ($^{2.1}/_{3.52}$) or 0.60 of the *b* axis and ($^{2.4}/_{3.5}$) or 0.68 of the *c* axis. The fractional coordinates of this atom are, therefore, (0.43, 0.60, 0.68). The coordinates of the equivalent atom in the next cell over in the *a* direction, however, are easily calculated as this atom is simply 1 unit cell away in *a*. Thus, all one has to do is add 1 to the x coordinate: (1.43, 0.60, 0.68). Such transformations can be performed regardless of the shape of the unit cell. Fractional coordinates, therefore, are used to retain and manipulate crystal information.

1.2.2.2.2.2 Crystal directions

The designation of the individual vectors within any given crystal lattice is accomplished by the use of whole number multipliers of the lattice parameter of the point at which the vector exits the unit cell. The vector is indicated by the notation [*hkl*], where *h*, *k*, and *l* are reciprocals of the point at which the vector exits the unit cell. The origination of all vectors is assumed defined as [000]. For example, the direction along the *a*-axis according to this scheme would be [100] because this has a component only in the *a*-direction and no component along either the *b* or *c* axial direction. A vector diagonally along the face defined by the *a* and *b* axis would be [110], while going from one corner of the unit cell to the opposite corner would be in the [111] direction. Figure 1.17 shows some examples of the various directions in the unit cell. The crystal direction notation is made up of the lowest combination of integers and represents unit distances rather than actual distances. A [222] direction is identical to a [111], so [111] is used. Fractions are not used. For example, a vector that intercepts the center of the top face of the unit cell has the coordinates x = 1/2, y = 1/2, z = 1. All have to be inversed to convert to the lowest combination of integers (whole numbers); i.e., [221] in Figure 1.17. Finally, all parallel vectors have the same crystal direction, e.g., the four vertical edges of the cell shown in Figure 1.17 all have the crystal direction [*hkl*] = [001].

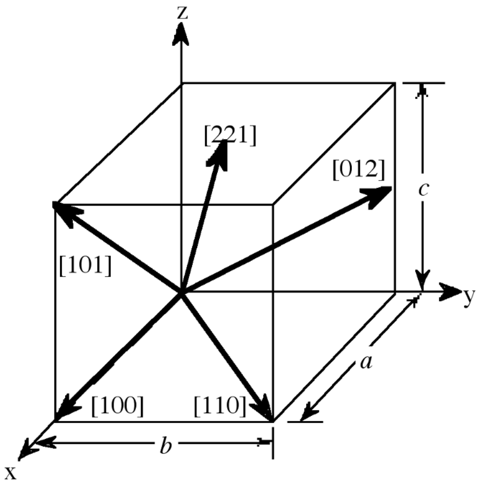


Figure 1.17: Some common directions in a cubic unit cell.

Crystal directions may be grouped in families. To avoid confusion there exists a convention in the choice of brackets surrounding the three numbers to differentiate a crystal direction from a family of direction. For a direction, square brackets [*hkl*] are used to indicate an individual direction. Angle brackets <*hkl*> indicate a family of directions. A family of directions includes any directions that are equivalent in length and types of atoms encountered. For example, in a cubic lattice, the [100], [010], and [001] directions all belong to the <100> family of planes because they are equivalent. If the cubic lattice were rotated 90 °, the *a*, *b*, and *c* directions would remain indistinguishable, and there would be no way of telling on which crystallographic positions the atoms are situated, so the family of directions is the same. In a hexagonal crystal, however, this is not the case, so the [100] and [010] would both be <100> directions, but the [001] direction would be distinct. Finally, negative directions are identified with a bar over the negative number instead of a minus sign.

1.2.2.2.2.3 Crystal planes

Planes in a crystal can be specified using a notation called Miller indices. The Miller index is indicated by the notation [*hkl*] where *h*, *k*, and *l* are reciprocals of the plane with the *x*, *y*, and *z* axes. To obtain the Miller indices of a given plane requires the following steps:

Step 1. The plane in question is placed on a unit cell.
Step 2. Its intercepts with each of the crystal axes are then found.
Step 3. The reciprocal of the intercepts are taken.
Step 4. These are multiplied by a scalar to insure that is in the simple ratio of whole numbers.

For example, the face of a lattice that does not intersect the y or z axis would be (100), while a plane along the body diagonal would be the (111) plane. An illustration of this along with the (111) and (110) planes is given in Figure 1.18.

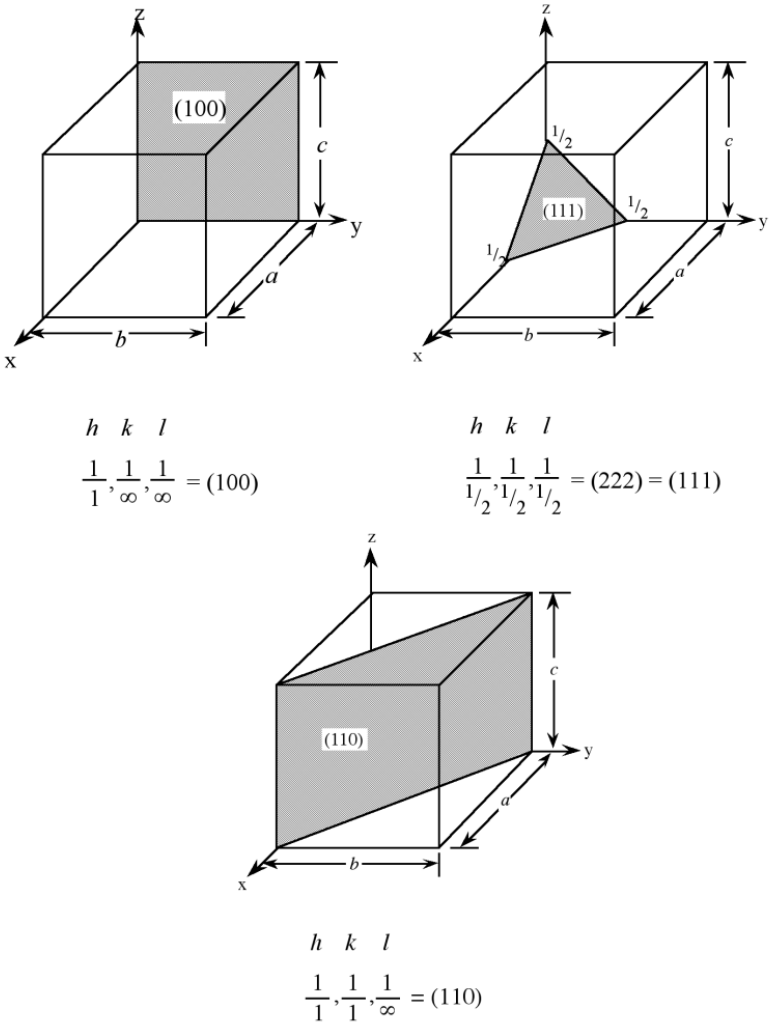


Figure 1.18: Examples of Miller indices notation for crystal planes.

As with crystal directions, Miller indices directions may be grouped in families. Individual Miller indices are given in parentheses (*hkl*), while braces {*hkl*} are placed around the indices of a family of planes. For example, (001), (100), and (010) are all in the {100} family of planes, for a cubic lattice.

1.2.2.3 Description of crystal structures

Crystal structures may be described in a number of ways. The most common manner is to refer to the size and shape of the unit cell and the positions of the atoms (or ions) within the cell. However, this information is sometimes insufficient to allow for an understanding of the true structure in three dimensions. Consideration of several unit cells, the arrangement of the atoms with respect to each other, the number of other atoms they in contact with, and the distances to neighboring atoms, often will provide a better understanding. A number of methods are available to describe extended solid-state structures. The most applicable with regard to elemental and compound semiconductor, metals and the majority of insulators is the close packing approach.

1.2.2.3.1 Close packed structures: hexagonal close packing and cubic close packing

Many crystal structures can be described using the concept of close packing. This concept requires that the atoms (ions) are arranged so as to have the maximum density. In order to understand close packing in three dimensions, the most efficient way for equal sized spheres to be packed in two dimensions must be considered.

The most efficient way for equal sized spheres to be packed in two dimensions is shown in Figure 1.19, in which it can be seen that each sphere (the dark gray shaded sphere) is surrounded by, and is in contact with, six other spheres (the light gray spheres in Figure 1.19). It should be noted that contact with six other spheres the maximum possible is the spheres are the same size, although lower density packing is possible. Close packed layers are formed by repetition to an infinite sheet. Within these close packed layers, three close packed rows are present, shown by the dashed lines in Figure 1.19.

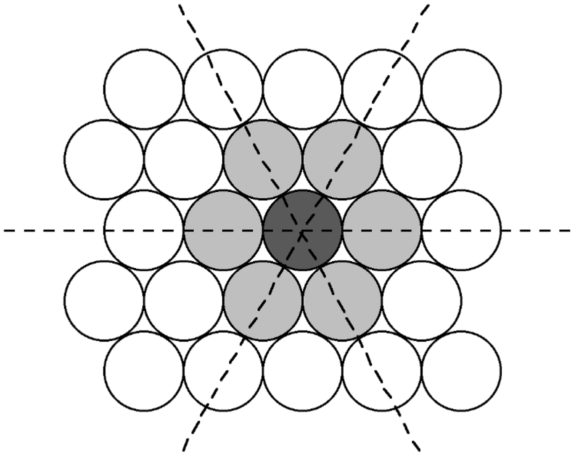


Figure 1.19: Schematic representation of a close packed layer of equal sized spheres. The close packed rows (directions) are shown by the dashed lines.

The most efficient way for equal sized spheres to be packed in three dimensions is to stack close packed layers on top of each other to give a close packed structure. There are two simple ways in which this can be done, resulting in either a hexagonal or cubic close packed structures.

1.2.2.3.1.1 Hexagonal close packed

If two close packed layers A and B are placed in contact with each other so as to maximize the density, then the spheres of layer B will rest in the hollow (vacancy) between three of the spheres in layer A. This is demonstrated in Figure 1.20. Atoms in the second layer, B (shaded light gray), may occupy one of two possible positions (Figure 1.20a or b) but not both together or a mixture of each. If a third layer is placed on top of layer B such that it exactly covers layer A, subsequent placement of layers will result in the following sequence ...ABABAB.... This is known as hexagonal close packing or *hcp*.

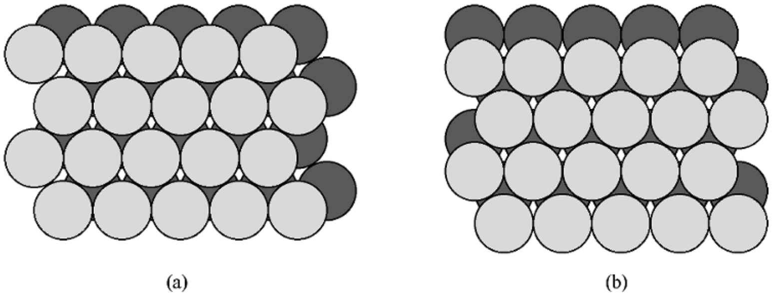


Figure 1.20: Schematic representation of two close packed layers arranged in A (dark grey) and B (light grey) positions. The alternative stacking of the B layer is shown in (a) and (b).

The hexagonal close packed cell is a derivative of the hexagonal Bravais lattice system (Figure 1.16) with the addition of an atom inside the unit cell at the coordinates ($^1/_3$,$^2/_3$,$^1/_2$). The basal plane of the unit cell coincides with the close packed layers (Figure 1.21). In other words the close packed layer makes-up the {001} family of crystal planes.

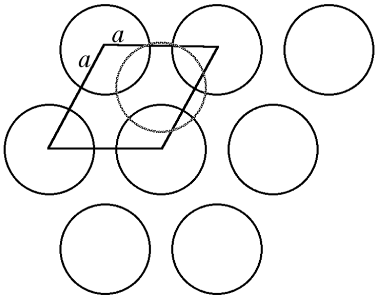


Figure 1.21: A schematic projection of the basal plane of the hcp unit cell on the close packed layers.

The "packing fraction" in a hexagonal close packed cell is 74.05%; that is 74.05% of the total volume is occupied. The packing fraction or density is derived by assuming that each atom is a hard sphere in contact with its nearest neighbors. Determination of the packing fraction is accomplished by calculating the number of whole spheres per unit cell (2 in hcp), the volume occupied by these spheres, and a comparison with the total volume of a unit cell. The number gives an idea of how "open" or filled a structure is. By comparison, the packing fraction for body-centered cubic (Figure 1.16) is 68% and for diamond cubic (an important semiconductor structure to be described later) is it 34%.

1.2.2.3.1.2 Cubic close packed: face-centered cubic

In a similar manner to the generation of the hexagonal close packed structure, two close packed layers are stacked (Figure 1.19) however, the third layer (C) is placed such that it does not exactly cover layer A, while sitting in a set of troughs in layer B (Figure 1.22), then upon repetition the packing sequence will be ...ABCABCABC.... This is known as cubic close packing or *ccp*.

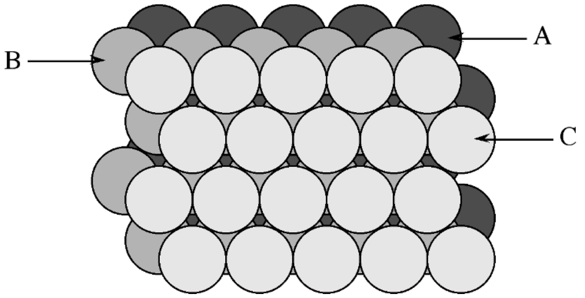


Figure 1.22: Schematic representation of the three close packed layers in a cubic close packed arrangement: A (dark grey), B (medium grey), and C (light grey).

The unit cell of cubic close packed structure is actually that of a face-centered cubic (*fcc*) Bravais lattice. In the *fcc* lattice the close packed layers constitute the {111} planes. As with the *hcp* lattice packing fraction in a cubic close packed (*fcc*) cell is 74.05%. Since face centered cubic or *fcc* is more commonly used in preference to cubic close packed (*ccp*) in describing the structures, the former will be used throughout this text.

1.2.2.3.2 Coordination number

The coordination number of an atom or ion within an extended structure is defined as the number of nearest neighbor atoms (ions of opposite charge) that are in contact with it. A slightly different definition is often used for atoms within individual molecules: the number of donor atoms associated with the central atom or ion. However, this distinction is rather artificial, and both can be employed.

The coordination numbers for metal atoms in a molecule or complex are commonly 4, 5, and 6, but all values from 2 to 9 are known and a few examples of higher coordination numbers have been reported. In contrast, common coordination numbers in the solid state are 3, 4, 6, 8, and 12. For example, the atom in the center of body-centered cubic lattice has a coordination number of 8, because it touches the eight atoms at the corners of the unit cell, while an atom in a simple cubic structure would have a coordination number of 6. In both *fcc* and *hcp* lattices each of the atoms have a coordination number of 12.

1.2.2.3.3 Octahedral and tetrahedral vacancies

As was mentioned above, the packing fraction in both *fcc* and *hcp* cells is 74.05%, leaving 25.95% of the volume unfilled. The unfilled lattice sites (interstices) between the atoms in a cell are called interstitial sites or vacancies. The shape and relative size of these sites is important in controlling the position of additional atoms. In both *fcc* and *hcp* cells most of the space within these atoms lies within two different sites known as octahedral sites and tetrahedral sites. The difference between the two lies in their “coordination number”, or the number of atoms surrounding each site. Tetrahedral sites (vacancies) are surrounded by four atoms arranged at the corners of a tetrahedron. Similarly, octahedral sites are surrounded by six atoms which make-up the apices of an octahedron. For a given close packed lattice an octahedral vacancy will be larger than a tetrahedral vacancy.

Within a face centered cubic lattice, the eight tetrahedral sites are positioned within the cell, at the general fractional coordinate of $(^n/_4,^n/_4,^n/_4)$ where n = 1 or 3, e.g., $(^1/_4,^1/_4,^1/_4)$, $(^1/_4,^1/_4,^3/_4)$, etc. The octahedral sites are located at the center of the unit cell ($^1/_2$,$^1/_2$,$^1/_2$), as well as at each of the edges of the cell, e.g., ($^1/_2$,0,0). In the hexagonal close packed system, the tetrahedral sites are at (0,0,$^3/_8$) and ($^1/_3$,$^2/_3$,$^7/_8$), and the octahedral sites are at ($^1/_3$,$^1/_3$,$^1/_4$) and all symmetry equivalent positions.

1.2.2.3.4 Important structure types

The majority of crystalline materials do not have a structure that fits into the one atom per site simple Bravais lattice. A number of other important crystal structures are found, however, only a few of these crystal structures are those of which occur for the elemental and compound semiconductors and the majority of these are derived from *fcc* or *hcp* lattices. Each structural type is generally defined by an archetype, a material (often a naturally occurring mineral) which has the structure in question and to which all the similar materials are related. With regard to commonly used elemental and compound semiconductors the important structures are diamond, zinc blende, Wurtzite, and to a lesser extent chalcopyrite. However, rock salt, β-tin, cinnabar and cesium chloride are observed as high pressure or high temperature phases and are therefore also discussed. The following provides a summary of these structures. Details of the full range of solid-state structures are given elsewhere.

1.2.2.3.4.1 Diamond Cubic

The diamond cubic structure consists of two interpenetrating face-centered cubic lattices, with one offset $^1/_4$ of a cube along the cube diagonal. It may also be described as face centered cubic lattice in which half of the tetrahedral sites are filled while all the octahedral sites remain vacant. The diamond cubic unit cell is shown in Figure 1.23. Each of the atoms (e.g., C) is four coordinate, and the shortest interatomic distance (C-C) may be determined from the unit cell parameter (a).

$$\text{C-C} = \frac{a\sqrt{3}}{4} \approx 0.422\,a \tag{1.3}$$

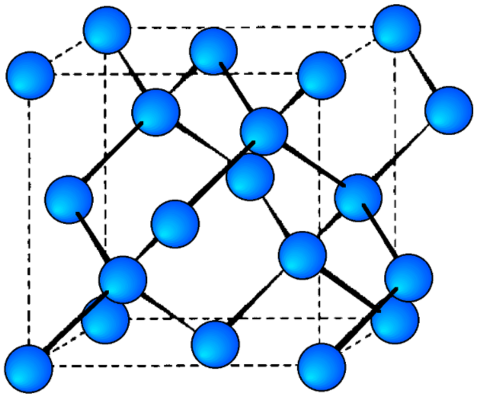


Figure 1.23: Unit cell structure of a diamond cubic lattice showing the two interpenetrating face-centered cubic lattices.

1.2.2.3.4.2 Zinc blende

This is a binary phase (ME) and is named after its archetype, a common mineral form of zinc sulfide (ZnS). As with the diamond lattice, zinc blende consists of the two interpenetrating *fcc* lattices. However, in zinc blende one lattice consists of one of the types of atoms (Zn in ZnS), and the other lattice is of the second type of atom (S in ZnS). It may also be described as face centered cubic lattice of S atoms in which half of the tetrahedral sites are filled with Zn atoms. All the atoms in a zinc blende structure are 4-coordinate. The zinc blende unit cell is shown in Figure 1.24. A number of inter-atomic distances may be calculated for any material with a zinc blende unit cell using the lattice parameter (a).

$$\text{Zn-S} = \frac{a\sqrt{3}}{4} \approx 0.422\,a \tag{1.4}$$

$$\text{Zn-Zn} = \text{S-S} = \frac{a}{\sqrt{2}} \approx 0.707\,a \tag{1.5}$$

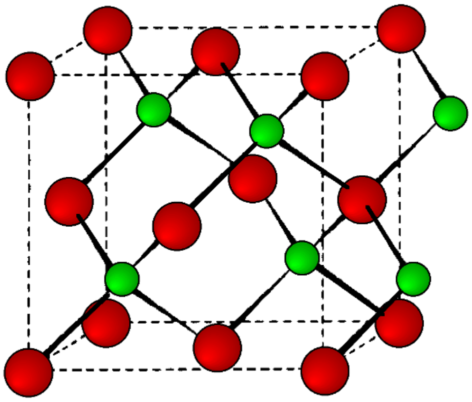


Figure 1.24: Unit cell structure of a zinc blende (ZnS) lattice. Zinc atoms are shown in green (small), sulfur atoms shown in red (large), and the dashed lines show the unit cell.

1.2.2.3.4.3 Chalcopyrite

The mineral chalcopyrite $CuFeS_2$ is the archetype of this structure. The structure is tetragonal ($a = b \neq c$, $\alpha = \beta = \gamma = 90°$, and is essentially a superlattice on that of zinc blende. Thus, is easiest to imagine that the chalcopyrite lattice is made-up of a lattice of sulfur atoms in which the tetrahedral sites are filled in layers, ...FeCuCuFe..., etc. (Figure 1.25). In such an idealized structure $c = 2a$, however, this is not true of all materials with chalcopyrite structures.

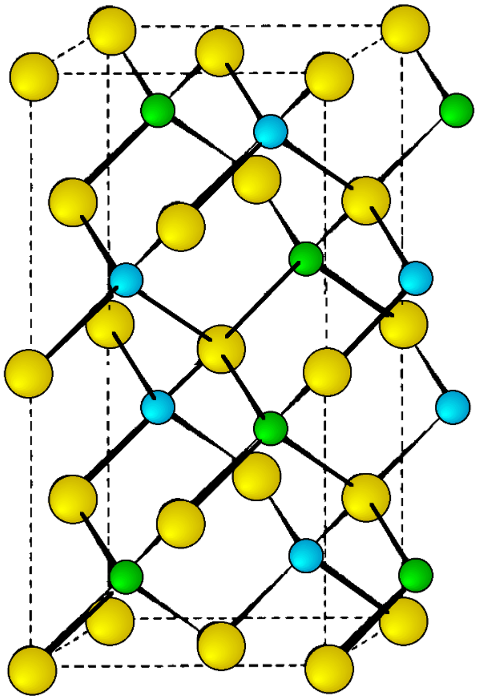


Figure 1.25: Unit cell structure of a chalcopyrite lattice. Copper atoms are shown in blue, iron atoms are shown in green and sulfur atoms are shown in yellow. The dashed lines show the unit cell.

1.2.2.3.4.4 Rock salt

As its name implies the archetypal rock salt structure is NaCl (table salt). In common with the zinc blende structure, rock salt consists of two interpenetrating face-centered cubic lattices. However, the second lattice is offset 1/2a along the unit cell axis. It may also be described as face centered cubic lattice in which all of the octahedral sites are filled, while all the tetrahedral sites remain vacant, and thus each of the atoms in the rock salt structure are 6-coordinate. The rock salt unit cell is shown in Figure 1.26. A number of inter-atomic distances may be calculated for any material with a rock salt structure using the lattice parameter (a).

$$\text{Na-Cl} = \frac{a}{2} \approx 0.5\,a \tag{1.6}$$

$$\text{Na-Na} = \text{Cl-Cl} = \frac{a}{\sqrt{2}} \approx 0.707\,a \tag{1.7}$$

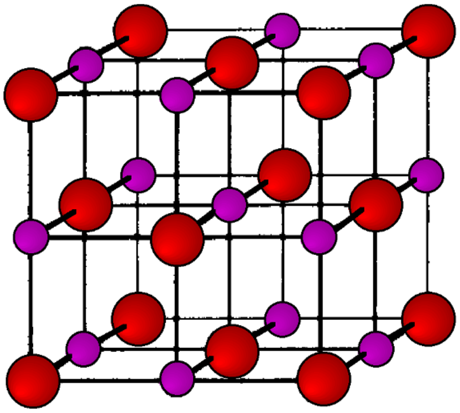


Figure 1.26: Unit cell structure of a rock salt lattice. Sodium ions are shown in purple (small spheres) and chloride ions are shown in red (large spheres).

1.2.2.3.4.5 Cinnabar

Cinnabar, named after the archetype mercury sulfide, HgS, is a distorted rock salt structure in which the resulting cell is rhombohedral (trigonal) with each atom having a coordination number of six.

1.2.2.3.4.6 Wurtzite

This is a hexagonal form of the zinc sulfide. It is identical in the number of and types of atoms, but it is built from two interpenetrating *hcp* lattices as opposed to the *fcc* lattices in zinc blende. As with zinc blende all the atoms in a wurtzite structure are 4-coordinate. The wurtzite unit cell is shown in Figure 1.27. A number of inter atomic distances may be calculated for any material with a wurtzite cell using the lattice parameter (a).

$$\text{Zn-S} = a\sqrt{3/8} = 0.612\,a = \frac{3\,c}{8} = 0.375\,c \tag{1.8}$$

$$\text{Zn-Zn} = \text{S-S} = a = 1.632\,c \tag{1.9}$$

However, it should be noted that these formulae do not necessarily apply when the ratio a/c is different from the ideal value of 1.632.

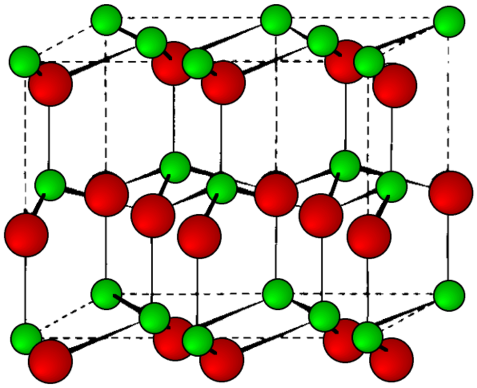


Figure 1.27: Unit cell structure of a wurtzite lattice. Zinc atoms are shown in green (small spheres), sulfur atoms shown in red (large spheres), and the dashed lines show the unit cell.

1.2.2.3.4.7 Cesium Chloride

The cesium chloride structure is found in materials with large cations and relatively small anions. It has a simple (primitive) cubic cell (Figure 1.16) with a chloride ion at the corners of the cube and the cesium ion at the body center. The coordination numbers of both Cs^+ and Cl^-, with the inner atomic distances determined from the cell lattice constant (a).

$$\text{Cs-Cl} = \frac{a\sqrt{3}}{2} \approx 0.866\,a \tag{1.10}$$

$$\text{Cs-Cs} = \text{Cl-Cl} = a \tag{1.11}$$

1.2.2.3.4.8 β-Tin.

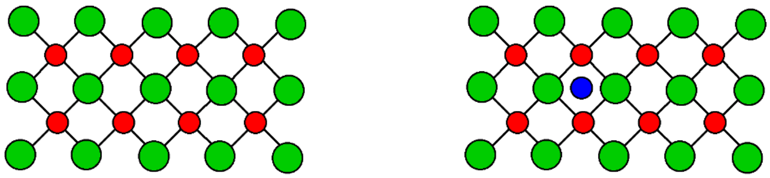
The room temperature allotrope of tin is β-tin or white tin. It has a tetragonal structure, in which each tin atom has four nearest neighbors (Sn-Sn = 3.016 Å) arranged in a very flattened tetrahedron, and two next nearest neighbors (Sn-Sn = 3.175 Å). The overall structure of β-tin consists of fused hexagons, each being linked to its neighbor via a four-membered Sn_4 ring.

1.2.2.4 Defects in crystalline solids

Up to this point we have only been concerned with ideal structures for crystalline solids in which each atom occupies a designated point in the crystal lattice. Unfortunately, defects ordinarily exist in equilibrium between the crystal lattice and its environment. These defects are of two general types: point defects and extended defects. As their names imply, point defects are associated with a single crystal lattice site, while extended defects occur over a greater range.

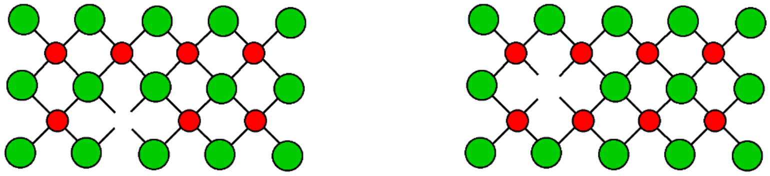
1.2.2.4.1 Point defects: "too many or too few" or "just plain wrong"

Point defects have a significant effect on the properties of a semiconductor, so it is important to understand the classes of point defects and the characteristics of each type. Figure 1.28 summarizes various classes of native point defects, however, they may be divided into two general classes; defects with the wrong number of atoms (deficiency or surplus) and defects where the identity of the atoms is incorrect.



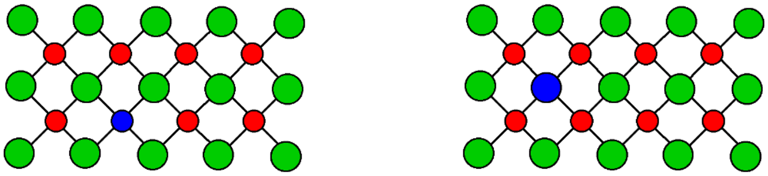
(a) perfect lattice

(b) interstitial impurity



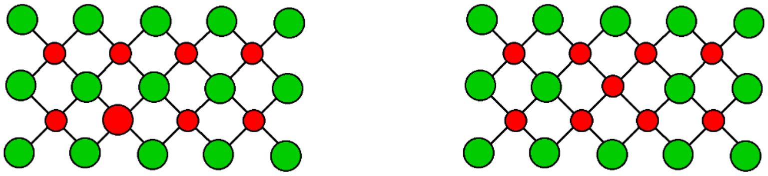
(c) cation vacancy

(d) anion vacancy



(e) substitution of cation

(f) substitution of anion



(g) B_A antisite defect

(h) A_B antisite defect

Figure 1.28: Point defects in a crystal lattice.

1.2.2.4.1.1 Interstitial Impurity

An interstitial impurity occurs when an extra atom is positioned in a lattice site that should be vacant in an ideal structure (Figure 1.28b). Since all the adjacent lattice sites are filled the additional atom will have to squeeze itself into the interstitial site, resulting in distortion of the lattice and alteration in the local electronic behavior of the structure. Small atoms, such as carbon, will prefer to occupy these interstitial sites. Interstitial impurities readily diffuse through the lattice via interstitial diffusion, which can result in a change of the properties of a material as a function of time. Oxygen impurities in silicon generally are located as interstitials.

1.2.2.4.1.2 Vacancies

The converse of an interstitial impurity is when there are not enough atoms in a particular area of the lattice. These are called vacancies. Vacancies exist in any material above absolute zero and increase in concentration with temperature. In the case of compound semiconductors, vacancies can be either cation vacancies (Figure 1.28c) or anion vacancies (Figure 1.28d), depending on what type of atom are "missing".

1.2.2.4.1.3 Substitution

Substitution of various atoms into the normal lattice structure is common, and used to change the electronic properties of both compound and elemental semiconductors. Any impurity element that is incorporated during crystal growth can occupy a lattice site. Depending on the impurity, substitution defects can greatly distort the lattice and/or alter the electronic structure. In general, cations will try to occupy cation lattice sites (Figure 1.28e), and anion will occupy the anion site (Figure 1.28f). For example, a zinc impurity in GaAs will occupy a gallium site, if possible, while a sulfur, selenium and tellurium atoms would all try to substitute for an arsenic. Some impurities will occupy either site indiscriminately, e.g., Si and Sn occupy both Ga and As sites in GaAs.

1.2.2.4.1.4 Antisite Defects

Antisite defects are a particular form of substitution defect, and are unique to compound semiconductors. An antisite defect occurs when a cation is misplaced on an anion lattice site or vice versa (Figure 1.28g and h). Dependant on the arrangement these are designated as either $\mathrm{A_B}$ antisite defects or $\mathrm{B_A}$ antisite defects. For example, if an arsenic atom is on a gallium lattice site the defect would be an $\mathrm{As_{Ga}}$ defect. Antisite defects involve fitting into a lattice site atoms of a different size than the rest of the lattice, and therefore this often results in a localized distortion of the lattice. In addition, cations and anions will have a different number of electrons in their valence shells, so this substitution will alter the local electron concentration and the electronic properties of this area of the semiconductor.

1.2.2.4.2 Extended Defects: Dislocations in a Crystal Lattice

Extended defects may be created either during crystal growth or as a consequence of stress in the crystal lattice. The plastic deformation of crystalline solids does not occur such that all bonds along a plane are broken and reformed simultaneously. Instead, the deformation occurs through a dislocation in the crystal lattice. Figure 1.29 shows a schematic representation of a dislocation in a crystal lattice. Two features of this type of dislocation are the presence of an extra crystal plane, and a large void at the dislocation core. Impurities tend to segregate to the dislocation core in order to relieve strain from their presence.

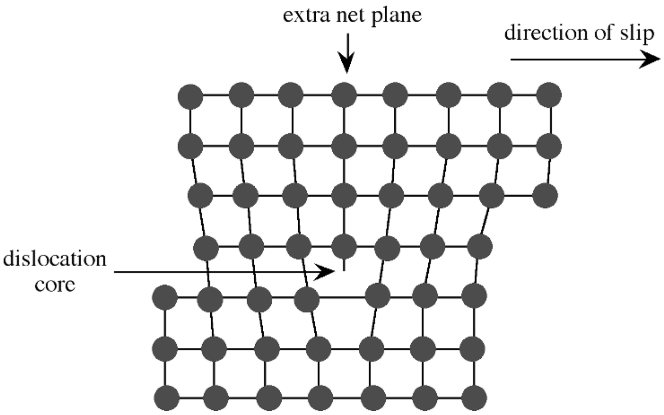


Figure 1.29: Dislocation in a crystal lattice.

1.2.2.5 Epitaxy

Epitaxy, is a transliteration of two Greek words *epi*, meaning "upon", and *taxis*, meaning "ordered". With respect to crystal growth it applies to the process of growing thin crystalline layers on a crystal substrate. In epitaxial growth, there is a precise crystal orientation of the film in relation to the substrate. The growth of epitaxial films can be done by a number of methods including molecular beam epitaxy, atomic layer epitaxy, and chemical vapor deposition, all of which will be described later.

Epitaxy of the same material, such as a gallium arsenide film on a gallium arsenide substrate, is called homoepitaxy, while epitaxy where the film and substrate material are different is called heteroepitaxy. Clearly, in homoepitaxy, the substrate and film will have the identical structure, however, in heteroepitaxy, it is important to employ where possible a substrate with the same structure and similar lattice parameters. For example, zinc selenide (zinc blende, $a = 5.668$ Å) is readily grown on gallium arsenide (zinc blende, $a = 5.653$ Å). Alternatively, epitaxial crystal growth can occur where there exists a simple relationship between the structures of the substrate and crystal layer, such as is observed between Al_2O_3 (100) on Si (100). Whichever route is chosen a close match in the lattice parameters is required, otherwise, the strains induced by the lattice mismatch results in distortion of the film and formation of dislocations. If the mismatch is significant epitaxial growth is not energetically favorable, causing a textured film or polycrystalline untextured film to be grown. As a general rule of thumb, epitaxy can be achieved if the lattice parameters of the two materials are within about 5% of each other. For good quality epitaxy, this should be less than 1%. The larger the mismatch, the larger the strain in the film. As the film gets thicker and thicker, it will try to relieve the strain in the film, which could include the loss of epitaxy of the growth of dislocations. It is important to note that the <100> directions of a film must be parallel to the <100> direction of the substrate. In some cases, such as Fe on MgO, the [111] direction is parallel to the substrate [100]. The epitaxial relationship is specified by giving first the plane in the film that is parallel to the substrate [100].

1.2.2.6 Bibliography

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1.2.3 Stereochemistry[7]

1.2.3.1 Stereo isomers

Stereo isomers have the same empirical formula or molecular formula but different structural formulas. A typical example is butane, C_4H_{10}, which can have two different possible structures: *n*-butane (Figure 1.30a) and *iso*-butane also known as 1-methylpropane (Figure 1.30b).

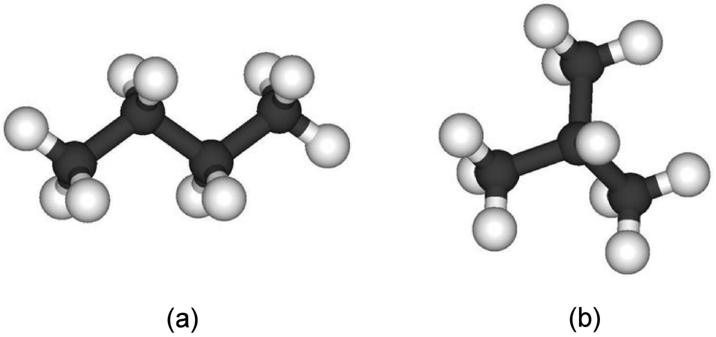

Figure 1.30: The two stereo isomers of butane: (a) *n*-butane and (b) *iso*-butane.

1.2.3.2 Geometric isomers

Geometric isomers have the same empirical formula or molecular formula and also the same structural formula, but have a different relative arrangement of the substituent groups. For example, the two geometric isomers of 1,2-dichloroethene (Figure 1.31) have the molecular formula of $C_2H_2Cl_2$, and the same structural formula of Cl(H)C=C(H)Cl, but the relative position of the two chlorine atoms can either be the same side of the C=C double bond (i.e., *cis*, see Figure 1.31a) or on opposite sides of the C=C double bond (i.e., *trans*, see Figure 1.31b). The use of *cis* and *trans* is not limited to organic compounds such as olefins, but can also be used in metal complexes, e.g., Figure 1.32.

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[7] This content is available online at <http://cnx.org/content/m34480/1.3/>.

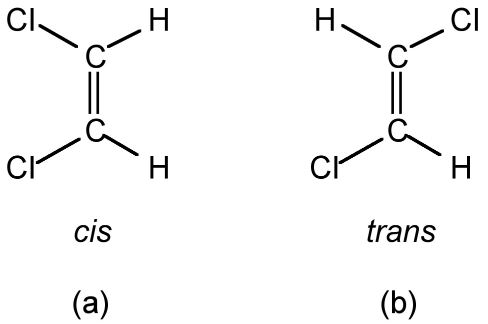


Figure 1.31: The two geometric isomers of 1,2-dichloroethene.

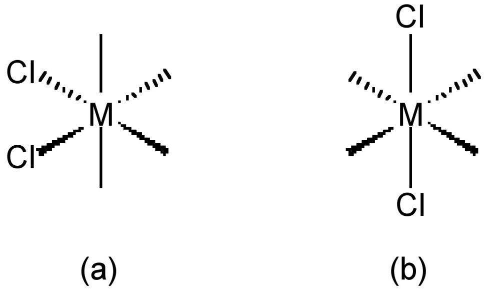


Figure 1.32: Examples of (a) *cis* and (b) *trans* geometric isomers for metal complexes.

When it is not possible to describe geometric isomers by the terms *cis* or *trans*, the terms facial (*fac*, Figure 1.33a) or meridinal (*mer*, Figure 1.33b) are commonly employed.

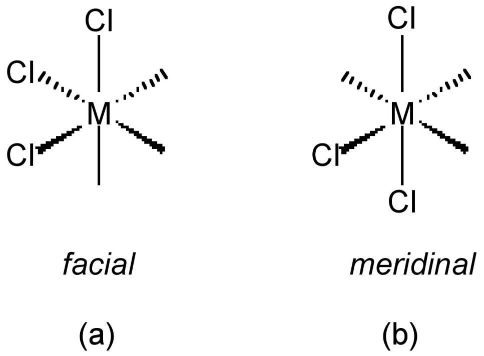


Figure 1.33: Examples of (a) *fac* and (b) *mer* geometric isomers for metal complexes.

1.2.3.3 Optical isomers

If the mirror object and mirror image of a molecule are not the same (i.e., they are not superimposable) they are known as *enantiomers*. If they also have optical activity they are called *chiral* and are described as having *chirality*. Enantiomers of a particular compound have the same general properties with two exceptions:

1. Their behavior to polarized light.
2. Their reaction with other chiral molecules.

It is possible to determine if a molecule is chiral or not from its symmetry. Chiral molecules will have no symmetry or axis of rotation. The optical activity of a chiral molecule will turn the plane of polarized light either to the right (+) or the left (-). The former is known as *dextrorotatory* (D), while the latter is known as *levorotatory* (L).

1.2.3.3.1 Configuration

The configuration of a chiral molecule may be represented in a number of ways. Lactic acid ($C_3H_6O_3$) provides a suitable and simple example. The two optical isomers of lactic acid can be represented in 3-dimensional (3D) form as shown in Figure 1.34; however, it is also possible to draw the same molecules in 2D using the Fischer projection (Figure 1.35). While the Fisher projection does not appear to define the geometry about the central carbon atom, the convention is that the side chains are out of the plane of the page (towards the observer), while the top and bottom groups are into the plane of the page (away from the observer). Thus, Figure 1.35a is a representation of Figure 1.34a, and Figure 1.35b is a representation of Figure 1.34b.

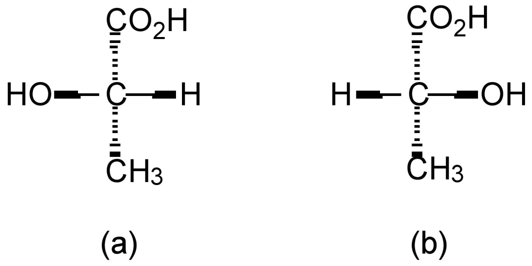


Figure 1.34: 3D representations of lactic acid.

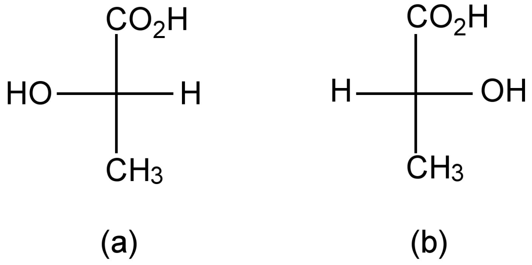


Figure 1.35: 2D Fischer representations of lactic acid.

1.2.3.3.2 Fischer-Rosenoff convention

The Fischer-Rosenoff convention defines chirality of a molecule using the Fischer projection. The convention is based upon *D*-(+)-glyceraldehydes (Figure 1.36).

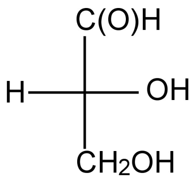


Figure 1.36: The Fischer projection of *D*-(+)-glyceraldehyde.

To determine the chiral label for a molecule, the Fischer projection is drawn with the longest carbon chain pointing away from the observer, i.e., into the plain of the page. The number 1 carbon (that of the highest substitution) is positioned at the top of the diagram. If the functional group is on the right of the diagram the isomer is given the label *D* (from the dextrorotatory enantiomer of glyceraldehydes rather than the molecule being dextrorotatory per se), i.e., Figure 1.36. On the other hand if the functional group is on the left of the diagram the isomer is given the label *L* (from the levorotatory enantiomer of glyceraldehyde rather than the molecule being levorotatory per se).

1.2.3.3.2.1 Rules

Where molecules are large and complex a number of additional rules are useful:

1. Make any alcohol substituent to be nearest to the top, e.g., a butan-2-ol (Figure 1.37a) rather than a butan-3-ol (Figure 1.37b).
2. Aldehydes and ketones are the number 1 carbon atom.
3. If there are both sets of substituents, rule 1 has precedence over rule 2.

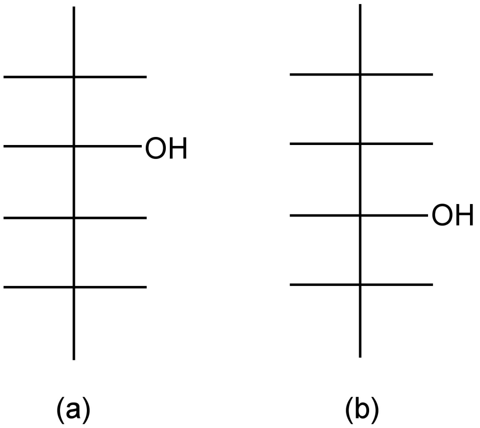


Figure 1.37: Preferred positioning of an alcohol substituent to be nearest the top (a) rather than at the bottom (b), according to the rules of the Fischer-Rosenoff convention.

1.2.3.3.3 Nomenclature in terms of *R* and *S*

The *R*/*S* nomenclature is a more widely used alternative to the *D*/*L* nomenclature, and is based upon the hierarchical order of the substituents. From the Fischer projection, the groups are ordered with the largest atom first, as shown in Figure 1.38. The lowest numbered substituent is then oriented away from the observer (i.e., H in Figure 1.38). The order of the remaining substituents 1, 2, 3 is then traced: if it goes clockwise the molecule is labeled *R*, if it goes anti-clockwise (counter-clockwise) the molecule is labeled *S*.

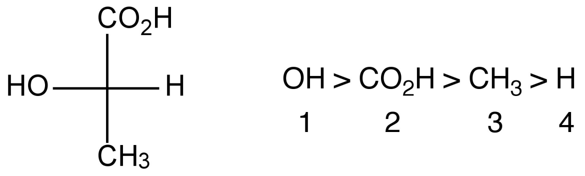


Figure 1.38: The structure of *S*–lactic acid, and the ordering of the substituents.

The advantage of the *R*/*S* methodology is that it can also be used for geometric isomers. Thus, while *cis* and *trans* are useful when the groups either side of a C=C double bond are the same (e.g., *cis*-1,2-dichloroethene, Figure 1.39a); however, when four different groups are present (e.g., A, B, X, and Y as seen in Figure 1.39b) then an alternative must be used. By taking either group A/B or X/Y and placing in order of precedence, the relative order defines the isomer. Thus, if in Figure 10b A>B and X>Y the label *Z* (*zusammen* from the German for *together*) is used. Conversely, if in Figure 10b A<B and X>Y the label *E* (*entgegen* from the German for *opposite*) is used.

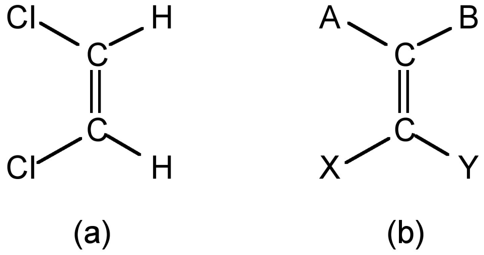


Figure 1.39: The structures of (a) *cis*-1,2-dichloroethene and (b) a generic olefin with four different substituent groups.

1.2.3.3.4 More complex molecules

As molecules become more complex with multiple functional groups and multiple chiral centers the *D*/*L* nomenclature has the potential to become confusing. Erythrose has two chiral centers, and based upon the Fischer projections it may be seen that since the alcohol substituents in the 2 and 3 positions are on the same side of the backbone in the Fischer projection irrespective if it is *D*-(-)-erythrose or *L*-(+)-erythrose (Figure 1.40a and b). Thus, the naming is simplified despite the presence of multiple side groups. However, in threose (Figure 1.40c) the substituents are on different sides of the Fischer projection raising the issue as to whether this should be *L* or *D*. However, in such cases the substituent at the bottom of the side chain takes priority, thus Figure 1.40c is *D*-(-)-threose.

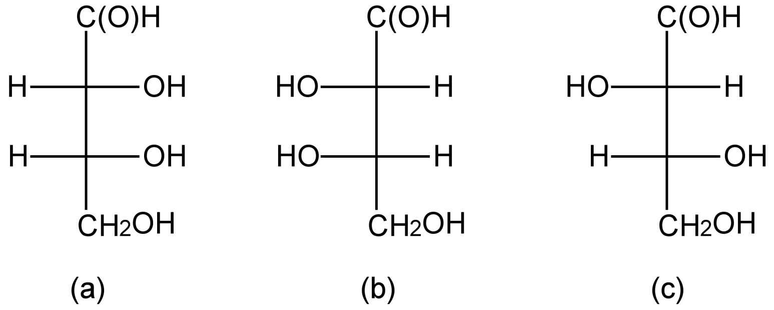


Figure 1.40: The Fischer projections of (a) *D*-(-)-erythrose, (b) *L*-(+)-erythrose, and (c) *D*-(-)-threose.

NOTE: *D*-(-)-erythrose and *L*-(+)-erythrose are *enantiomers*, and *D*-(+)-threose and *L*-(+)-threose are also *enantiomers*, but threose and erythrose are *diasteriomers*. Enantiomers have the same physical properties (just different behavior to polarized light), while diasteriomers may have different physical properties such as melting points and solubility.

1.2.3.3.4.1 Amino acids

Amino acids (or more properly α-amino acids) are compounds containing both an amine (NH_2) group and a carboxylic acid (CO_2H) attached to the same carbon atom. The presence of both acid and base groups can result in the formation of the Zwitterionic form with ammonium (NH_3^+) and carboxylate (CO_2^-) groups.

In defining the labels for amino acids, the basis is *D*-(-)-allothreonine (Figure 1.41), whereas for an amino acid such as threonine the top substituent is used for a label, e.g., Figure 1.42.

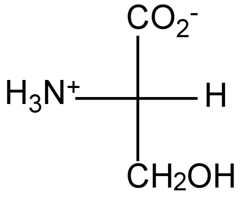


Figure 1.41: The Fischer projection of *D*-(-)-allothreonine.

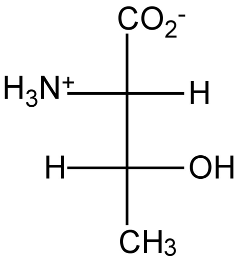


Figure 1.42: The Fischer projection of *D*-(-)-threonine.

1.2.3.3.4.2 Similar chiral centers

Just because a compound has more than one chiral center does not mean that it is optically active. A consideration of erythritol shows the presence of a mirror plane of symmetry (Figure 1.43). As such, erythritol is not optically active, i.e., there is no effect on polarized light. In contrast, while threitol has the same molecular and geometric formula, the lack of a mirror plane of symmetry (Figure 1.44) means that the *L*- and *D*+ forms are optically active.

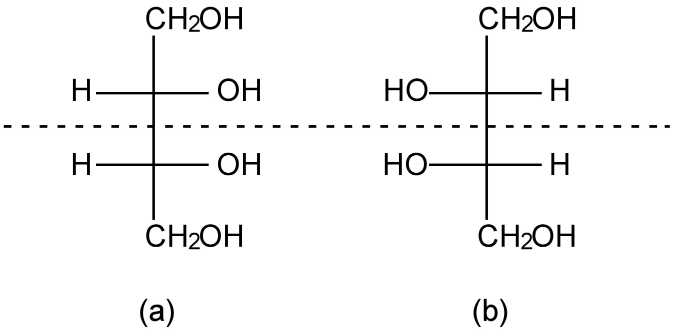


Figure 1.43: The Fischer projections of *D* and *L* erythritol showing the presence of a mirror plane of symmetry. N.B. The presence of a mirror plane means that erythritol is not optically active and hence there is no need to label with "+" or "-".

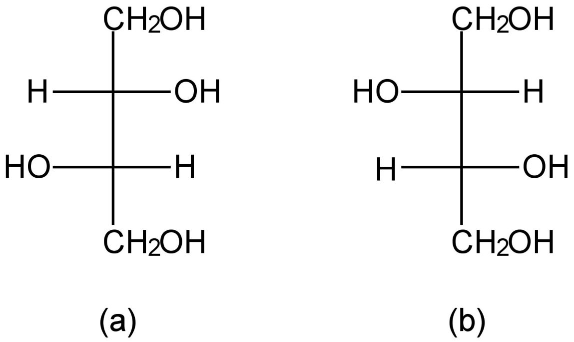


Figure 1.44: The Fischer projections of (a) *L*-(-)-threitol and (b) *D*-(+)-threitol.

Compounds with a D:L ratio of 1:1 are called racemic compounds and are totally optically inactive. However, it is also possible for a racemic solution of a compound to crystallize to form crystals of pure *D* or *L*, which may be manually separated.

1.2.3.3.5 Optical isomers that are not tetrahedral

1.2.3.3.5.1 Pyramidal molecules

Pyramidal molecules can also exhibit chirality when the three substituents are distinct, e.g., $PR_1R_2R_3$ (Figure 1.45). Unfortunately, most pyramidal compounds undergo an inversion of their isomers (in a similar manner to turning an umbrella inside out), such that the chiral forms interconvert rapidly. In such a case, it is not possible to resolve (separate) the different forms. Phosphines may generally be resolved because the barrier to their inversion is sufficiently large (ca. 132 kJ/mol).

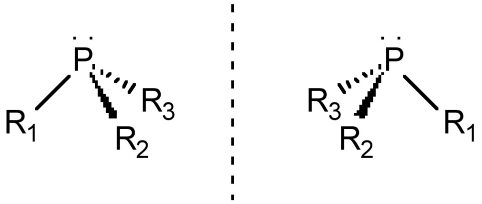


Figure 1.45: An example of a chiral phosphine where $R_1 \neq R_2 \neq R_3$.

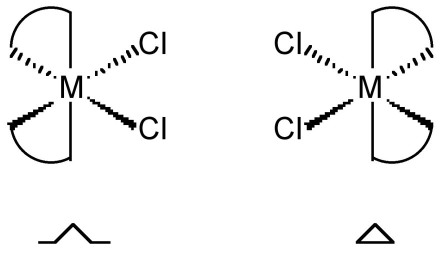
The notation used for pyramidal molecules is the same as that for tetrahedral molecules, in that the individual substituents are ordered with the largest atom first. The lone pair is defined as having the lowest numbering and thus is oriented away from the observer. The order of the remaining substituents 1, 2, and 3 is then traced: if it goes clockwise the molecule is labeled *R*, if it goes anti-clockwise (counter-clockwise) the molecule is labeled *S*.

1.2.3.3.5.2 Chirality in octahedral complexes

The presence of a chelate ligand on an octahedral complex can induce chirality in the complex.

> NOTE: A chelate ligand is a molecule or ion that is bonded to at least two points of a central atom or ion. The term *chelate* is from the Greek *chelè*, meaning *claw*.

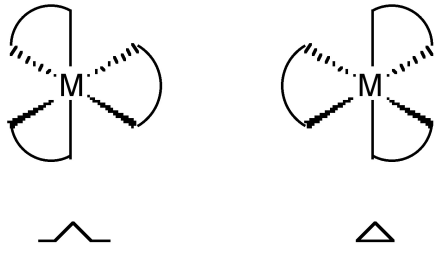
Unlike tetrahedral based compounds, chiral octahedral compounds have their nomenclature based on the structure of a helix. For example, in the case of a *bis*-chelate complex (Figure 1.46), with one of the chelate ligands pointing straight up the helix, the direction of the other defines the chirality of the helix, i.e., if it is a left or right hand helix. If the ligand points up to the left the complex is assigned the symbol shown in Figure 1.46a, while if the ligand points up to the right the complex is assigned the symbol shown in Figure 1.46b.



(a) (b)

Figure 1.46: The two optical isomers of a *bis*-chelate metal complex.

In complexes with three chelate ligands (i.e., a *tris*-chelate complex, Figure 1.47), the same methodology applies, in that any two ligands can be chosen and the same rules applied.



(a) (b)

Figure 1.47: The two optical isomers of a *tris*-chelate metal complex.

1.2.3.3.6 Methods of resolution of racemic mixtures

A racemic mixture, or racemate, is one that has equal amounts of left- and right-handed enantiomers of a chiral molecule. The first known racemic mixture was "racemic acid," which Louis Pasteur (Figure 1.48) found to be a mixture of the two enantiomeric isomers of tartaric acid (Figure 1.49).

Figure 1.48: French microbiologist and chemist Louis Pasteur who is remembered for his remarkable breakthroughs in the causes and preventions of disease (1822 – 1895).

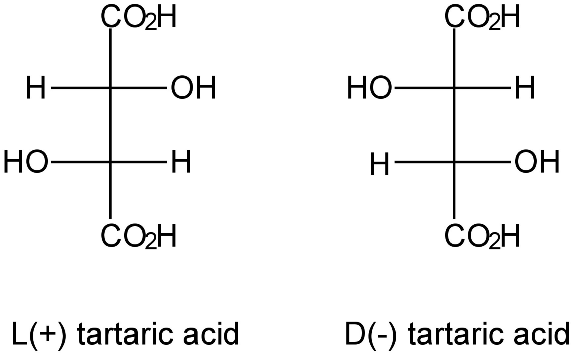


Figure 1.49: The Fischer projections of the two enantiomeric isomers of tartaric acid.

In nature, it is common that only one of an optical isomers is naturally produced, but in laboratory synthesis it is more common that both isomers are made in equal amounts. The separation of a racemate into its components (the pure enantiomers) is called a chiral resolution.

1.2.3.3.6.1 Mechanical separation

The crystals of enantiomerically pure compounds often have different appearances. Thus, just as Pasteur did in 1848, it is often possible to look under a microscope and physically separate the two different enantiomers.

1.2.3.3.6.2 Resolution by formation of diasteriomers

One of the differentiating properties of a chiral molecule is that each enantiomer reacts with another chiral molecule to form a diastereomeric pair of compounds. For example, a racemic acid, (+)HA and (-)HA, will react with a chiral base, (-)B, to form a mixture of diasteriomers, [(-)BH$^+$.(+)A$^-$] and [(-)BH$^+$.(-)A$^-$]. Because diasteriomers have different physical properties they can be separated by recrystallization. Once separated by recrystallization, the addition of excess acid will liberate the enantiomerically pure compound, i.e., (+)HA or (-)HA. A typical chiral base would be a natural alkaloid base to ensure that it is pure + or -. If it is a base that is needed to be separated, then (-)malic acid is a suitable acid.

1.2.3.3.6.3 Resolution by chromatography

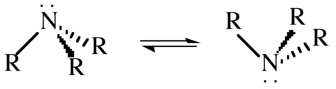
In a related method to resolution by the formation of diasteriomers, a chiral column material will allow for the chromatographic separation of an enantiomeric mixture. Thus, the retention rate for (+)X will be different from (-)X on a column in which the stationary phase is chiral, i.e., (-)A. Many common chiral stationary phases are based on oligosaccharides such as cellulose or cyclodextrin (in particular with β-cyclodextrin).

1.2.3.3.7 Labile stereo isomers and racemization

It is only possible to separate (resolve) racemic mixtures if the molecule stays as one form for a long time. In other words, if there is a mechanism by which the two forms are interconverted, then resolution cannot be achieved.

1.2.3.3.7.1 Intramolecular rearrangement

Intramolecular rearrangements involve no bonds being broken. The classic example is the inversion of an amine, (1.12), which has a low energy barrier (24.7 kJ/mol).



(1.12)

Another example of an intramolecular rearrangement is the conversion of a square-based pyramidal geometry via a trigonal bipyramidal geometry to the isomeric square-based pyramidal geometry, or the alternative isomerization of one trigonal bipyramidal geometry to another via a square-based pyramidal transition state. Such a process is known as a *Berry rotation*. The Berry mechanism is a pseudorotation process for simultaneously interchanging two equatorial groups with the two axial groups, while the third equatorial group (called the pivot group) remains an equatorial group (Figure 1.50).

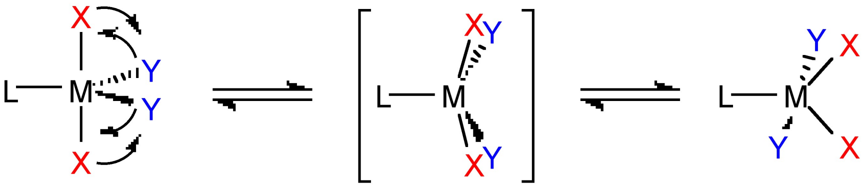


Figure 1.50: The Berry pseudorotation.

1.2.3.3.7.2 Intermolecular processes

Intermolecular processes involve bond breaking (and bond formation). For example a tetrahedral compound could loose one ligand, which creates a labile pyramidal compound. Rapid inversion of the pyramidal compound is followed by re-attachment of the ligand. Such a process is often so fast that resolution cannot be achieved.

1.2.3.3.7.3 Intramolecular processes

Intramolecular processes with bond breaking (and making) also lead to racemization. For example, in an octahedral complex with chelate ligands, if one of the ends of a chelate ligand detaches, it can reattach in the same confguration, or attach differently to change the chirality. In this manner the chirality can be changed from one form to another.

1.2.3.4 Conformation

The conformation of a molecule arises from the rotation of a single bond (Figure 1.51). However, even though there is rotation about the bond, there are energy barriers due to steric interactions of the substituents. In order to understand (and predict) these interactions, it is necessary to visualize the molecule in such a manner as to highlight the across-bond interactions; this is done by using a Newman projection.

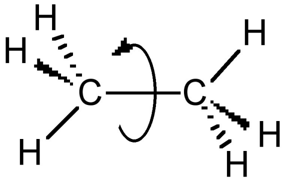


Figure 1.51: The rotation about the C-C single bond in ethane.

A Newman projection, useful in alkane stereochemistry, visualizes chemical conformations of a carbon-carbon chemical bond from front to back, with the front carbon represented by a dot and the back carbon as a circle (Figure 1.52). The front carbon atom is called proximal, while the back atom is called distal. This type of representation is useful for assessing the torsional angle between bonds. Using ethane as an example, the Newman projection along the C-C single bond results in two basic conformations: eclipsed (Figure 1.52a) and staggered (Figure 1.52b). The staggered conformation will be energetically favored since the substituents are the most distant from each other. Conversely, the staggered will be the highest in energy. The difference in energy between the two conformations will define the barrier to rotation. In the case of ethane this is very small (12.5 kJ/mol).

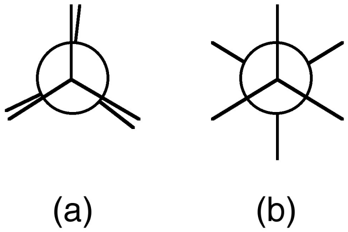


Figure 1.52: The Newman projection of ethane showing (a) eclipsed (E) and (b) staggered (S) conformations.

Although we often only consider the two extreme conformations, in reality there is a continuum around 360° rotation of the C-C bond. Figure 1.53 shows the relative energy as a function of the dihedral angle for ethane. Since each carbon in ethane has equivalent substitution (i.e., three H atoms) the energy for each staggered conformation is the same. This is not true for more complex molecules such as butane (Figure 1.54).

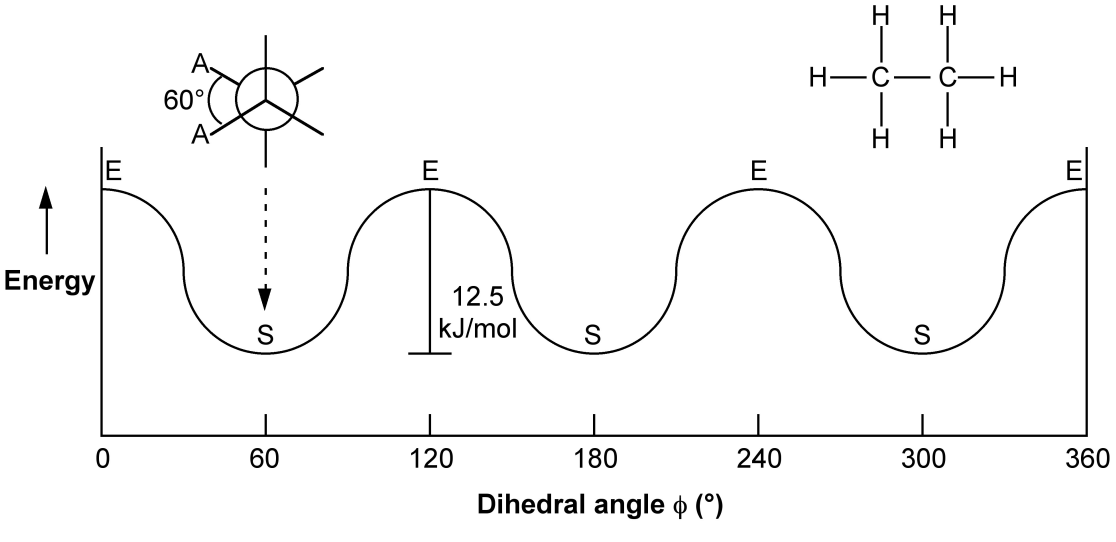


Figure 1.53: The relative energy as a function of the dihedral angle for ethane.

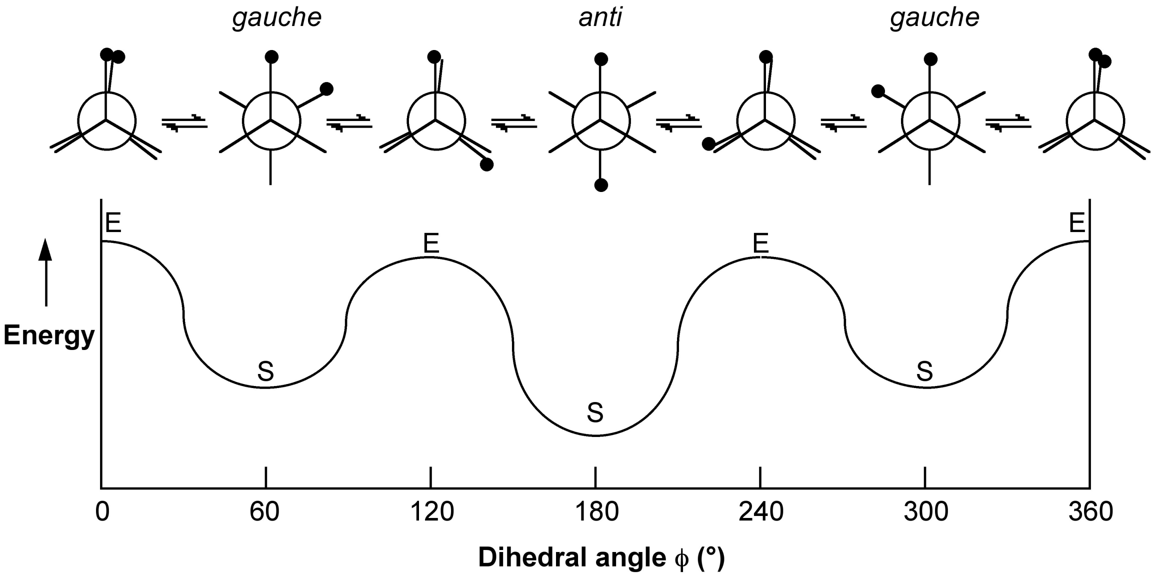


Figure 1.54: The relative energy as a function of the dihedral angle for butane.

As may be seen from Figure 1.54, the staggered conformation in which the two methyl groups (represented by the black circles) are as far away from each other (*anti*) is the most energetically favored. The other two staggered conformations (*gauche*) are mirror images of each other and are hence conformation enantiomers. It should also be noted from Figure 1.54 that the eclipsed conformations vary in energy since the presence of methyl···methyl near neighbors is clearly less energetically favorable than methyl···H near neighbors.

Generally the rotation about C-C bonds has a low barrier to rotation, however, if substituents are sufficiently bulky the molecule will not twist around the bond, e.g., substituted bi-phenyl with sterically bulky substituents (Figure 1.55).

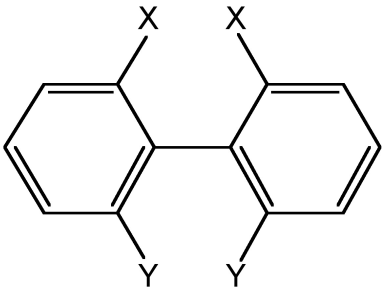


Figure 1.55: The ease of rotation about the C-C bond of a substituted bi-phenyl will depend on the steric bulk of X and Y.

Free rotation about a C-C bond is not fully possible when you have a ring system, e.g., in a cyclic compound such as cyclohexane, C_6H_{12}. The limited rotation about the C-C bonds results in the flipping of the ring conformation from the chair form (Figure 1.56a) to the boat form (Figure 1.56b). Since the boat form has steric hindrance between the hydrogen atoms, the chair form is the more stable.

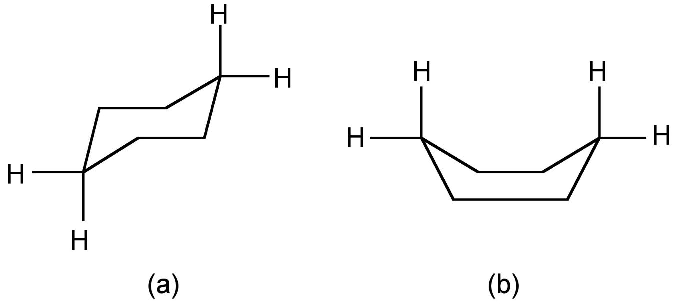


Figure 1.56: The chair (a) and boat (b) conformations of cyclohexane, C_6H_{12}.

1.2.3.4.1 Conformation of compounds with lone pairs

Lone pairs often behave in a different manner to substituents in regard to conformations. Thus, methylamine (CH_3NH_2) would be predicted to have the staggered conformation shown in Figure 1.57a. However, the lower steric bulk of the lone pair results in the nitrogen being 0.09 Å away from the true center of the CH_3 projection (Figure 1.57b).

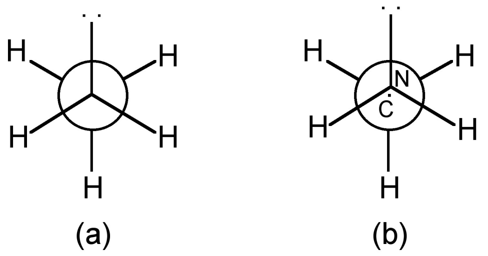


Figure 1.57: The ideal (a) and observed (b) conformations of methylamine, CH_3NH_2.

In compounds with more than one lone pair, the lowest energy form is not always the *anti* conformation. For example, at 20 °C hydrazine (H_2NNH_2) is 100% *gauche* (Figure 1.58a); but for substituted hydrazines (i.e., a diamine, R_2NNR_2) if the substituent groups are sufficiently large then the *anti* conformation will dominate (Figure 1.58b).

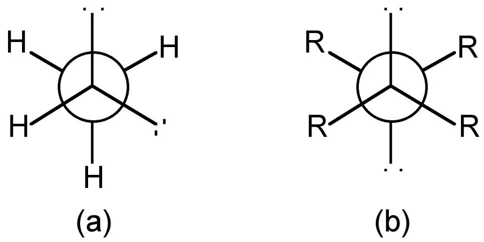


Figure 1.58: The stable conformation of hydrazine (H_2NNH_2) at 20 °C (a) as compared to the *anti* conformation (b) observed for diamines (R_2NNR_2).

The conformation of hydrogen peroxide (H_2O_2) is dominated by the lone pairs rather than the hydrogen atoms. Instead of the expected *anti* conformation (c.f., Figure 1.54 where the black circles would represent the hydrogen atoms) in the free state the dihedral angle is 94° (Figure 1.59). The conformation of hydrogen peroxide is therefore neither eclipsed nor staggered but an intermediate structure. When in the solid state hydrogen bonding will cause the shape and angles to change.

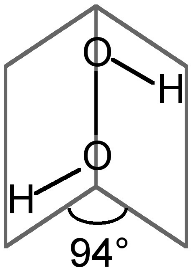


Figure 1.59: The structure of hydrogen peroxide in the free state.

1.2.3.5 Bibliography

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- A. Keys, S. G. Bott, and A. R. Barron, *J. Chem. Cryst.*, 1998, **28**, 629.

1.3 Acids, Bases, and Solvents

1.3.1 Choosing a Solvent[8]

The choice of solvent is an important parameter for any chemical reaction. The following provides a guide to some of the consideration to be made in choosing a solvent to ensure the desired reaction occurs.

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[8] This content is available online at <http://cnx.org/content/m33076/1.3/>.

1.3.1.1 Solvation

Solvation may be defined as the interaction between the solvent and the solute, however, two general classes of solvation have different consequences to the stability of either reagents or products in a chemical reaction, and hence the potential of a reaction to occur.

- **Specific solvation** is where the solvent interacts with one of the ions (or molecules) in solution via a covalent interaction. Furthermore, there will be a specific number of solvent molecules bound to each ion (or molecule), e.g., $[Cu(NH_3)_4]^{2+}$ and $[Mg(H_2O)_6]^{2+}$ (Figure 1.60a).
- **Non-specific** solvation is as a result of van der Waals or dipole-dipole forces between the solvent and an ion (or molecule). There will be no defined number of interactions and the solvent···ion interaction will be highly fluxional, e.g., while water solvates the chloride ion (Figure 1.60b) the number of water molecules around each anion is not fixed.

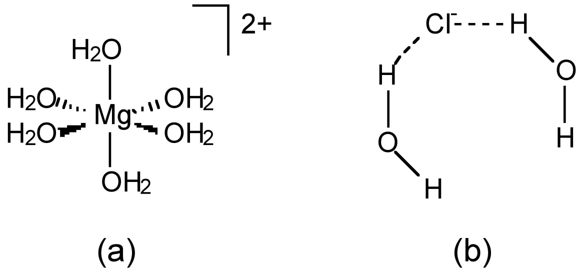


Figure 1.60: Examples of (a) specific and (b) non-specific solvation.

Table 1.10 shows the ability of three solvents to act with specific and non-specific solvation. The relative solvation ability of each solvent results in three different products from the dissolution of iron(III) chloride ($FeCl_3$).

Solvation	**DMSO (Me_2SO)**	**Pyridine (C_5H_5N)**	**Acetonitrile (MeCN)**
Specific	Good	Very good	Poor
Non-specific	Good	Poor	Moderately good

Table 1.10: The ability for specific and non-specific solvation.

Dissolution of $FeCl_3$ in DMSO results in the dissociation of a chloride ligand, (1.13), due to both the specific solvation of the "$FeCl_2{}^+$" cation and the non-specific solvation of the Cl^- anion. In fact, the good solvation properties of DMSO means that depending on the concentration (and temperature) a series of dissociations may occur, (1.14).

$$FeCl_3 \xrightleftharpoons{\text{DMSO}} [FeCl_2(DMSO)_4]^+ + Cl^-_{(solv)} \qquad (1.13)$$

$$[FeCl_2(DMSO)_4]^+ \xrightleftharpoons[-\,Cl^-_{(solv)}]{+\,\text{DMSO}} [FeCl(DMSO)_5]^{2+} \xrightleftharpoons[-\,Cl^-_{(solv)}]{+\,\text{DMSO}} [Fe(DMSO)_6]^{3+} \qquad (1.14)$$

In contrast, if $FeCl_3$ is dissolved in pyridine (py) the neutral Lewis acid-base complex is formed, (1.15), because while pyridine is a very good at specific solvation (Table 1.10), it is poor at solvating the chloride anion.

$$FeCl_3 + py \rightarrow FeCl_3(py) \tag{1.15}$$

In a similar manner, $FeCl_3(MeCN)_3$ will be formed by the dissolution in acetonitrile, because although it is not good at specific solvation, it is not sufficiently good at non-specific solvation to stabilize the chloride anion. However, since the $FeCl_4^-$ anion has a lower charge density that Cl^-, it can be supported by the non-specific solvation of acetonitrile and thus a disproportionation reaction occurs, (1.16).

$$2\,FeCl_3(MeCN)_3 \rightleftharpoons [FeCl_2(MeCN)_4]^+ + FeCl_4^- \tag{1.16}$$

1.3.1.2 Interference by the solvent

Rather than solvating a molecule or ion, the solvent can take an active and detrimental role in the synthesis of a desired compound.

1.3.1.2.1 Solvolysis

The archetypal solvolysis reaction is the reaction with water, i.e., hydrolysis, (1.17). However, solvolysis is a general reaction, involving bond breaking by the solvent. Thus, the reaction with ammonia is ammonolysis, (1.18), the reaction with acetic acid is acetolysis, (1.19), and the reaction with an alcohol is alcoholysis, (1.20) where Et = C_2H_5. In each case the same general reaction takes place yielding the cation associated with the solvent.

$$SO_2Cl_2 + 4\,H_2O \rightarrow SO_2(OH)_2 + 2\,H_3O^+ + 2\,Cl^- \tag{1.17}$$

$$SO_2Cl_2 + 4\,NH_3 \rightarrow SO_2(NH_2)_2 + 2\,NH_4^+ + 2\,Cl^- \tag{1.18}$$

$$SO_2Cl_2 + 4\,MeCO_2H \rightarrow SO_2(O_2CMe)_2 + 2\,MeCO_2H_2^+ + 2\,Cl^- \tag{1.19}$$

$$SO_2Cl_2 + 4\,EtOH \rightarrow SO_2(OEt)_2 + 2\,EtOH_2^+ + 2\,Cl^- \tag{1.20}$$

1.3.1.2.2 Competition reactions

Where more than one reaction could occur the reaction involving the solvent can often compete with the desired reaction.

If it is desired to synthesis the Lewis acid-base complex between diethylether (Et_2O) and boron trifluoride (BF_3) it is important to choose a solvent that will not compete with the complex formation. For example, pyridine is a poor choice because the nitrogen donor is a stronger Lewis base than the diethylether, (1.21), and thus no reaction would occur between diethylether and boron trifluoride. In contrast, since acetonitrile (MeCN) is a poor Lewis base, then the reaction will occur.

$$BF_3(Et_2O) + py \rightarrow BF_3(py) + Et_2O \tag{1.21}$$

If the synthesis of $GeCl_6^{2-}$ from germanium tetrachloride ($GeCl_4$) and a source of chloride anion, then water would be a poor choice of solvent since hydrolysis of $GeCl_4$ would result. Liquid hydrogen chloride would be equally poor solvent since strong $Cl^{-}\cdots H\text{-}Cl$ hydrogen bonding would stabilize the chloride anion and preclude reaction. In contrast, nitromethane (CH_3NO_2) would be a polar enough solvent to solvate the $GeCl_4$, but it will be displaced by the chloride anion, which would be only weakly solvated.

1.3.1.3 Salt formation

The formation of a salt via a double displacement reaction, (1.22), can be promoted by the choice of solvent by shifting the equilibrium by stabilization of one or more reagent/product.

$$MX + M'X' \rightleftharpoons MX' + M'X \tag{1.22}$$

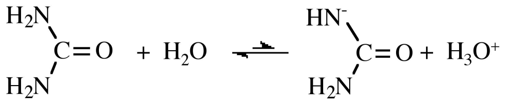
1.3.1.3.1 Salt stabilization through relative acidity

The attempted formation of nitronium perchlorate from nitric acid and perchloric acid, (1.23), in water will result in the decomposition of the NO_2^+ cation, (1.24). However, if the reaction is carried out in a stronger acid, i.e., sulfuric acid, the NO_2^+ cation is stable, and the resulting salt can be recystallized, (1.23).

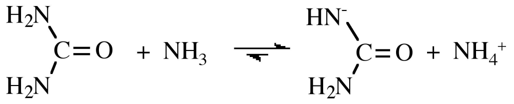
$$HNO_3 + HClO_4 \rightarrow NO_2^+ + ClO_4^- + H_2O \tag{1.23}$$

$$NO_2^+ + 2\,H_2O \rightarrow HNO_3 + H_3O^+ \tag{1.24}$$

In a similar manner, the weak basic character of water means the equilibrium reaction, (1.25), has a very small equilibrium constant, K. However, if the reaction is carried out in a strongly basic solvent such as ammonia the uride anion is stabilized, (1.26), and can be precipitated by cation exchange.



(1.25)



(1.26)

1.3.1.3.2 Salt stabilization through solvation

The following observations may be explained by a consideration of the solvation ability of the solvent.

1. The reaction of silver nitrate with barium chloride in water yields silver chloride and barium nitrate, (1.27).
2. The reaction of barium nitrate with silver chloride in ammonia yields barium chloride and silver nitrate, (1.28).

$$2\,AgNO_3 + BaCl_2 \xrightarrow{H_2O} 2\,AgCl\downarrow + Ba^{2+} + 2\,NO_3^- \tag{1.27}$$

$$2\,\mathrm{AgCl} + \mathrm{Ba(NO_3)_2} \xrightarrow{\mathrm{NH_3}} \mathrm{BaCl_2}\downarrow + 2\,\mathrm{Ag^+} + 2\,\mathrm{NO_3^-} \quad (1.28)$$

Since silver nitrate and barium nitrate are soluble in both solvents, the differences must be due to differences in the solubility of the chlorides in each solvent. A consideration of the relative stability of solid silver chloride versus the solvated species (Figure 1.61) shows that the enthalpy of solvation in water is less than the lattice energy. Thus, if silver chloride were present as Ag^+ and Cl^- in water it would spontaneously precipitate. In contrast, the enthalpy of solvation in ammonia is greater than the lattice energy, thus solid AgCl will dissolve readily in liquid ammonia. The reason for the extra stabilization from the specific solvation of the silver cation by the ammonia, i.e., the formation of the covalent complex $[Ag(NH_3)_2]^+$.

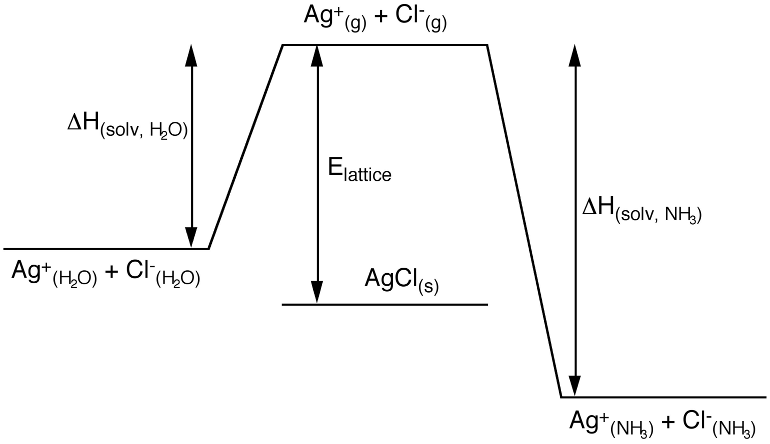


Figure 1.61: Enthalpy of solvation of silver chloride in water and ammonia in comparison to the lattice energy.

As may be seen from Figure 1.62, the opposite effect occurs for barium chloride. Here the enthalpy of solvation in ammonia is less than the lattice energy. Thus, if barium chloride were present as Ba^{2+} and Cl^- in ammonia it would spontaneously precipitate. In contrast, the enthalpy of solvation in water is greater than the lattice energy, thus solid $BaCl_2$ will dissolve readily in water. The stabilization of Ba^{2+}(aq) occurs because water will have a larger sphere of non-specific solvation as a consequence of having two lone pairs, allowing interaction with the Ba^{2+} as well as other water molecules (Figure 1.63).

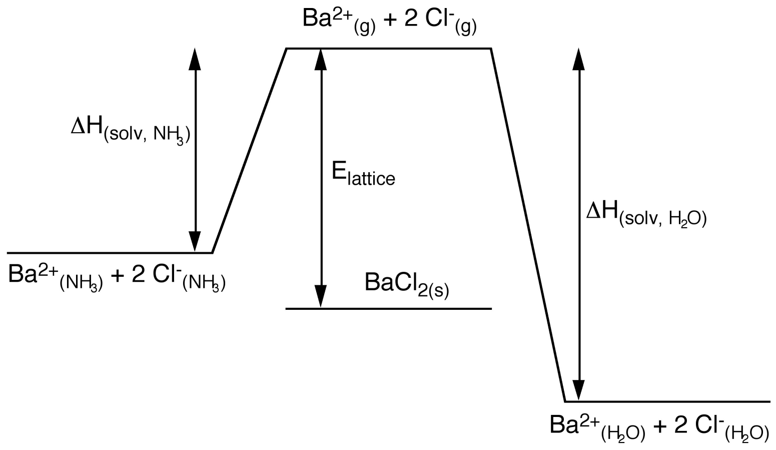


Figure 1.62: Enthalpy of solvation of barium chloride in water and ammonia in comparison to the lattice energy.

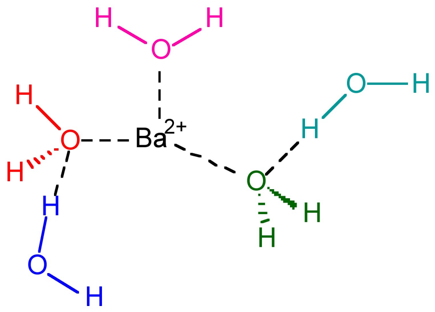


Figure 1.63: Schematic representation of the extended water solvation (aquation) sphere about Ba^{2+} cation.

1.3.1.4 Electron transfer reactions

A consideration of the oxidation, (1.29), and reduction, (1.30), reactions that occur for pure water at neutral pH (where $[H^+] = 10^{-7}$) would suggest that water will not tolerate oxidants whose E_0 is greater than 0.82 V nor tolerate reductants whose E_0 is less than -0.41 V.

$$2\,H^+ + {}^1/_2\,O_2 + 2\,e^- \rightarrow H_2O \qquad E_0 = +0.82\text{ V} \tag{1.29}$$

$$H^+ + e^- \rightarrow {}^1/_2\,H_2 \qquad E_0 = -0.41\text{ V} \tag{1.30}$$

Thus, while water has a fair range to support redox reactions it is not very good at the extremes with strong reducing agents or strong oxidizing agents. Liquid ammonia is an excellent solvent for very strong reducing agents because of the stabilization of solvated electrons, i.e., $[e^-(NH_3)_6]$. In contrast, hydrochloric acid is a good solvent for reactions involving very strong oxidizing agents.

1.4 Chemical Reactivity

1.4.1 The Basics of Combustion[9]

When discussing the combustion of a compound it is ordinarily referring to the reaction of an organic compound (hydrocarbon) with oxygen, in which the carbon is converted to carbon dioxide (CO_2) and the hydrogen forms water (H_2O) as a vapor, e.g., (1.31).

$$CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O \tag{1.31}$$

However, this only a narrow view of combustion, and a more general definition should be that combustion or burning is *the sequence of exothermic chemical reactions between a fuel and an oxidant accompanied by the production of heat and conversion of chemical species*. Based upon this definition methane can combust in the presence of fluorine (F_2) as strong oxidant, (1.32).

$$CH_4 + 4\,F_2 \rightarrow CF_4 + 4\,HF \tag{1.32}$$

In considering the combustion of any flammable compound, for example gasoline, it should be noted that the compounds that make up gasoline are quiet stable in the absence of a source of oxygen (usually from the air). Furthermore, some form of energy input (heat, flame, or spark) must be provided. Thus, the combustion of gasoline provides the archetypal example of the three component explosive system typical of a traditional chemical explosive: fuel (something that will burn), an oxidizer (usually a source of oxygen), and energy (ignition). In this regard, combustion also includes the exothermic reactions of many metals with oxygen, (1.33).

$$6\,Al + 3\,O_2 \rightarrow 2\,Al_2O_3 \tag{1.33}$$

It is not just reactive metals that can be used as the fuel component of combustion, but many of their compounds as well. The formation of water from the hydrogen in organic compounds, in combination with an oxygen source, releases significant energy. It stands to reason therefore that any compound comprising of hydrogen and an element can be a potential fuel: a compound of hydrogen and another element is known as a hydride. This is especially true for the hydrides of reactive metals such as aluminum and sodium (and metalloids such as boron, (1.34)), but is also true for the hydrides of silicon and phosphorus. These hydride compounds react with an oxidizer in a manner analogous to that of a hydrocarbon, as may be seen by a comparison of (1.35) and (1.31).

$$2\,BH_3 + 3\,O_2 \rightarrow B_2O_3 + 3\,H_2O \tag{1.34}$$

$$SiH_4 + 2\,O_2 \rightarrow SiO_2 + 2\,H_2O \tag{1.35}$$

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[9] This content is available online at <http://cnx.org/content/m33088/1.2/>.

Figure 1.64 shows a comparison of the heat of combustion of various inorganic fuels with commonly used jet fuels (JP-10 and JP-8). Hydrocarbons heat of combustion is limited by the C:H ratio, while graphite is the limiting case. Boron and boron compounds have greater volumetric andgravimetric energy density than hydrocarbons, and therefore were studied as potential high-energy fuels.

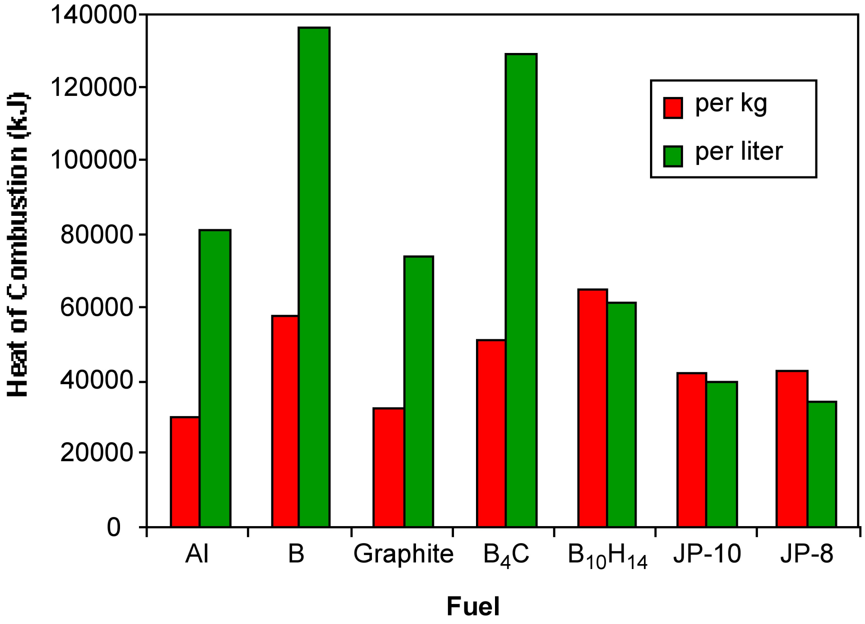

Figure 1.64: Heat of combustion of various fuels.

NOTE: Ammonia has been proposed as a practical alternative to fossil fuel for internal combustion engines. The energy value of ammonia is 22.5 MJ/kg, which is about half that of diesel. In a normal engine, in which the water vapor is not condensed, the calorific value of ammonia will be about 21% less than this value; however, it can be used in existing engines with only minor modifications to carburetors/fuel injectors.

Oxygen (O_2) from the air does not have to be the source of oxidizer. Alternatives such as hydrogen peroxide (H_2O_2), nitrous oxide (N_2O), and nitrates (e.g., ammonium nitrate, $NH_4(NO_3)$) are all sources of oxygen for combustion or explosions. However, this does not mean that every compound containing oxygen can be an oxidizer. For example, alcohols such as methanol will burn (in the presence of additional oxygen), but they will not act as an oxidizer. The oxygen within any compound must be "reactive". By this we mean that it must be able to be released, preferentially as the more reactive oxygen atom (O) rather than O_2, or be attached (chemically bonded to an element that wants to get rid of the oxygen (i.e., an element that is readily reduced). The most likely element in this case is nitrogen, with sulfur and phosphorus also potential candidates. Almost all compounds containing nitrogen bonded to oxygen can act as an oxidizer. Generally, the more oxygen atoms attached to nitrogen the more reactive the compound.

The efficiency of a chemical reaction such as combustion is dependent on how well the fuel and oxidizer are mixed at the molecular scale. Obviously the best situation is if both components are in the same molecule. Self-oxidizers are compounds containing oxygen in a reactive form as well as a suitable fuel (carbon or hydrogen). The most common self-oxidizers are organic nitrates. It should be pointed out that in spite of the presence of reactive oxygen, self-oxidizers may still require an external source of oxygen to ensure complete reaction, and some form of energy input (ignition) is still required.

1.4.1.1 Oxygen balance

While many compounds contain oxygen that does not mean they will combust efficiently in the absence of an external oxidizer, or whether they have sufficient oxygen to completely self-combust, or whether they can act as an oxidizer for other compounds. The simplest test for a compound's potential to fulfill these roles is its "oxygen balance". The oxygen balance for a chemical is the amount of oxygen needed or produced to ensure the complete oxidation of all the carbon, hydrogen, or other elements.

Compounds such as trinitrotoluene (TNT, Figure 1.65a) have a negative oxygen balance since extra oxygen is needed for complete formation of all the CO_2 and H_2O possible, (1.36). Thus, despite its reputation as an explosive, TNT is only efficient in the presence of an external oxidant, which may be air or another compound that provides a positive oxygen balance.

$$2\, C_7H_5N_3O_6 + 21\, \text{“O”} \rightarrow 14\, CO_2 + 5\, H_2O + 3\, N_2 \tag{1.36}$$

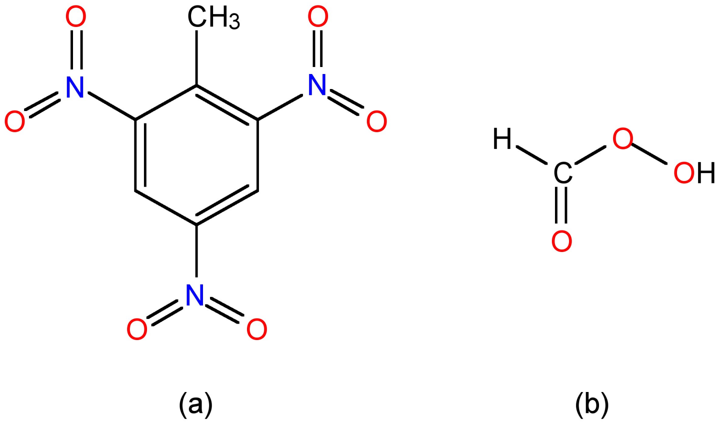

Figure 1.65: The structurse of (a) trinitrotoluene (TNT) and (b) The structure of performic acid.

In contrast to TNT, performic acid (Figure 1.65b) is an example of a compound with a zero oxygen balance: it has all the oxygen it needs for complete combustion, (1.37), and hence only requires energy to detonate making at a much more dangerous compound per se than TNT.

$$2\, CH_2O_3 \rightarrow CO_2 + H_2O \tag{1.37}$$

A positive oxygen balance means that the compound liberates oxygen surplus to its own needs, for example the decomposition of ammonium nitrate provides one atom of oxygen per molecule, (1.38). Clearly, any compound with a positive oxygen balance makes a good oxidizer and is highly incompatible with combustible chemicals.

$$NH_4(NO_3) \rightarrow 2\, H_2O + N_2 + \text{“O”} \tag{1.38}$$

1.4.1.1.1 Quantification of oxygen balance

A quantification of oxygen balance allows for the determination of approximate ratio of reagents to optimize combustion/explosion. In this regard *oxygen balance* is defined as the number of moles of oxygen (excess or deficient) for 100 g of a compound of a known molecular weight (M_w), (1.39) where x = number of atoms of carbon, y = number of atoms of hydrogen, z = number of atoms of oxygen, and m = number of atoms of metal oxide produced.

$$\mathrm{OB\%} = \frac{-1600}{M_w} \times (2x + (y/2) + m - z) \tag{1.39}$$

Example 1.2
In the case of TNT, the M_w = 227.1 g/mol, the number of carbon atoms (x) = 7, the number of hydrogen atoms (y) = 5, the number of oxygen atoms (z) = 6, and the number of atoms of metal oxide produced (m) = 0. Therefore:

$$\mathrm{OB\%} = \frac{-1600}{227.1} \times (14 + 2.5 + 0 - 6) = -74\%$$

A summary of selected oxygen balance values is given in Table 1.11.

Element or compound	**Oxygen balance (%)**
Carbon	-266.7
Sulfur	-100
Aluminum powder	-89
Trinitrotoluene	-74
nitroglycerine	+3.5
Ammonium nitrate	+20
Ammonium perchlorate	+34
Potassium chlorate	+39.2
Sodium chlorate	+45
Sodium nitrate	+47
Tetranitromethane	+49
Lithium perchlorate	+60

Table 1.11: Oxygen balance of selected compounds.

1.5 Periodic Trends for the Main Group Elements[10]

Within the main group (s- and p-block) elements of the Periodic Table (Figure 1.66) there are some general trends that we can observe for the elemental form, as well as the hydrides, oxides, and halides.

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[10] This content is available online at <http://cnx.org/content/m31489/1.3/>.

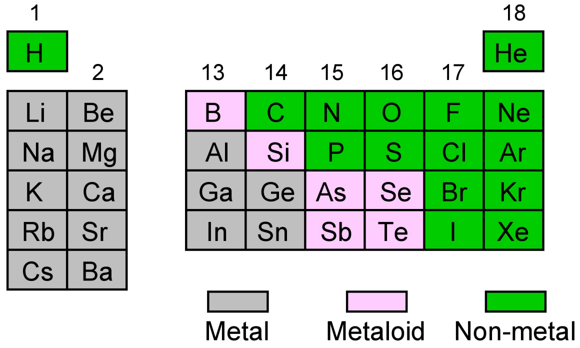

Figure 1.66: The main group elements (Adapted from www.meta-synthesis.com).

1.5.1 Periodic trends for the main group elements

Within the main group (s- and p-block) elements there are some general trends that we can observe.

- The further down a given Group the elements have increased metallic character, i.e., good conductors of both heat and electricity, and exhibit delocalized bonding.
- Moving from left to right across a Period the elements have greater non-metallic character, they are insulators with localized bonding.
- Within the p-block at the boundary between the metallic elements (Figure 1.66, grey elements) and nonmetal elements (Figure 1.66, green elements) there is positioned boron and silicon that are metalloid in character (Figure 1.66, pink elements), i.e., they have low electrical conductivity but it increases with temperature.

As an example of these changes Table 1.12 shows the trends across one Period.

Element	**Na**	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**	**Ar**
Properties	Electropositive metal	Electropositive metal	Metal but forms covalent bonds	Metalloid semiconductor metal/non-metal character	E-E bonding in elements	E-E bonding in elements	Simple molecule	Mono atomic gas

Table 1.12: Summary of trends for elements across the Periodic Table.

1.5.2 Periodic trends for the main group hydrides

The properties of main group hydrides are dependant on the difference in electronegativity between the element and hydrogen (Table 1.13). Elements on the left of the Periodic Table are highly electropositive and form ionic hydrides, while those of the center and right are covalent in character. However, of those with covalent E-H bonds, there is a change from polymeric hydrides to molecular compounds. For example, the Group 13 element hydrides (i.e., BH_3) form hydrogen-bridged oligomers (i.e., B_2H_6). In contrast, HCl is a diatomic molecule.

Hydride	**Element electronegativity**	**Hydrogen electronegativity**	**E-H polarity**	**Structure**	**Comments**
NaH	0.9	2.1	$M^+ H^-$	Ionic	Reacts with H_2O to liberate H_2
BH_3	2.0	2.1	$B^{\delta+}$-$H^{\delta-}$	Oligomeric and polymeric	Reacts slowly with H_2O
CH_4	2.5	2.1	$C^{\delta-}$-$H^{\delta+}$	Molecular	Insoluble in H_2O
HCl	3.0	2.1	$Cl^{\delta-}$-$H^{\delta+}$	Molecular	Dissolves in H_2O to form H^+ and Cl^-

Table 1.13: Summary of properties of selected main group hydrides as a function of the relative electronegativities.

1.5.3 Periodic trends for the main group oxides

As with hydrides the properties of main group oxides are dependant on the difference in electronegativity between the element and oxygen. Highly electropositive metals for ionic oxides, while other elements for covalent bonds (albeit polar in character) with oxygen. In addition, the aggregation of covalent oxides decreased across the Period from left to right (Table 1.14). As may also be seen from Table 1.14, oxides of elements on the left of the Periodic Table dissolve in water to form basic solutions, while those on the right form acidic solutions. There is a class of oxides (especially those of Group 13 and 14) that can react as either an acid or a base. These are known as amphoteric substances.

NOTE: The word is from the Greek prefix *ampho* meaning "both".

Oxide	**Bonding**	**Reactivity with H_2O**	**Description**
Na_2O	Ionic	Dissolves to give a strong base	Basic
Al_2O_3	Covalent polymeric	Dissolves in both acidic and basic solution	Amphoteric
SiO_2	Covalent polymeric	Dissolves in both acidic and basic solution	Amphoteric
CO_2	Covalent molecular	Dissolves to give a weak acid	Acidic
SO_3	Covalent molecular	Dissolves to give a strong acid	Acidic

Table 1.14: Comparison of oxides across the Periodic Table.

In summary, oxides of the main group elements show two trends.

1) From left to right across a Period, the oxides change from ionic → oligomeric/polymeric covalent → molecular covalent.
2) From left to right across a Period, the oxides change from ionic → oligomeric/polymeric covalent → molecular covalent.

1.5.4 Periodic trends for the main group chlorides

The trend between ionic and non-ionic/covalent in moving across a Period is also true for the chlorides of the main group elements. Those on the left (i.e., Group 1 and 2) are ionic and soluble in water, while those to the right tend to give acidic solutions due to reactions with the water and the formation of hydrochloric acid, e.g., (1.40).

$$SiCl_4 + 2\,H_2O \rightarrow SiO_2 + 4\,HCl_{(aq)} \tag{1.40}$$

Solutions to Exercises in Chapter 1

Solution to Exercise 1.1.1.1 (p. 3):

The two sodium atoms each have an oxidation state of +1, while the oxygen atoms have an oxidation state of −2, and the overall charge is 0.

Step 1. overall charge = sum of oxidation states
Step 2. 0 = (2 x oxidation state of Na) + (oxidation state of S) + (4 x oxidation state of O)
Step 3. 0 = (2 x +1) + (oxidation state of S) + (4 x -2)
Step 4. oxidation state of S = 0 – (2 x +1) - (4 x −2)
Step 5. oxidation state of S = +6

Solution to Exercise 1.1.1.2 (p. 3)

The two sodium atoms each have an oxidation state of +1, while the oxygen atoms have an oxidation state of −2, and the overall charge is 0.

- overall charge = sum of oxidation states
- 0 = (2 x oxidation state of Na) + (oxidation state of S) + (3 x oxidation state of O)
- 0 = (2 x +1) + (oxidation state of S) + (3 x -2)
- oxidation state of S = 0 – (2 x +1) - (3 x −2)
- oxidation state of S = +4

Solution to Exercise 1.1.1.3 (p. 4)

The two hydrogen atoms each have an oxidation state of +1 and the overall charge is 0.

- overall charge = sum of oxidation states
- 0 = (2 x oxidation state of H) + (oxidation state of S)
- 0 = (2 x +1) + (oxidation state of S)
- oxidation state of S = 0 – (2 x +1)
- oxidation state of S = -2

Solution to Exercise 1.2.1.1 (p. 13)

Step 1. Mercury has 2 valence electrons
Step 2. Add 2 electrons for the two σ-bonds: 2 + 2 = 4
Step 3. Divide the number of electrons by two to give the number of electron pairs: 4/2 = 2
Step 4. Two bonding pairs and no lone pairs = linear geometry

Solution to Exercise 1.2.1.2 (p. 13)

Step 1. Carbon has 4 valence electrons
Step 2. Add 3 electrons for the three σ-bonds: 4 + 3 = 7
Step 3. Subtract one electron for each π-bond: 7 – 1 = 6
Step 4. Divide the number of electrons by two to give the number of electron pairs: 6/2 = 3
Step 5. Two bonding pairs and no lone pairs = triangular geometry