Chemistry
A Molecular Science

3rd Edition

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Chapter 1 – The Early Experiments

Introduction

Chemistry is the science of matter, its properties, and the changes it undergoes. Chemists seek to understand our material universe at a molecular level and to use this understanding to improve our interaction with it, often creating new products that enhance our lives. Chemists often design these products by considering the properties of the desired substance and then proposing reactions of atoms or molecules that might yield the substances of choice. This design process involves particles and processes chemists can imagine but cannot see. They can observe the results of a reaction, such as a color change or the formation of a gas or a solid, but they cannot view directly the collisions of the atoms or molecules in a reaction or the changes these collisions produce. However, chemists are confident that these collisions and changes do take place, and we begin our study of chemistry by examining how we came to the point where we could envision these invisible processes.

1.1 The Scientific Method

Introduction

Chemistry is that branch of science that deals with matter and the changes it undergoes, and ***science*** is that branch of knowledge that is gained by the application of the scientific method. In this section, we explain the scientific method and show an example of its use.

Objectives

- Apply the scientific method to simple problems.

1.1-1. Scientific Method

The entire body of knowledge called science was achieved through the application of the scientific method.

Our understanding of atoms and molecules was gained by repeated application of the scientific method[1].

There are four steps in the scientific method:

1 **Observe:** Observations can be either quantitative or qualitative.
  - ***Quantitative observations*** involve numbers. "The mass of the substance is 3.0 g and its volume is 36 cm^3" are quantitative observations.
  - ***Qualitative observations*** do not involve numbers. "The substance is shiny and reacts with oxygen" are qualitative observations.

2 **Hypothesize:** Form a ***hypothesis***; i.e., suggest an explanation for the observation.
  - If the observation is that the substance is shiny and reacts with oxygen, the hypothesis might be that the substance is a metal.

3 **Predict:** Use the hypothesis to make predictions.
  - If the substance is a metal, then it should conduct electricity.

4 **Test:** Do the experiment to test the prediction. If the test supports the hypothesis, return to Step 3 and make another prediction to test the hypothesis. If the test does not support the hypothesis, return to Step 2 and modify the hypothesis to include the results of the test.
  - Apply a voltage across the substance to see if it does indeed conduct electricity. If it does, make another prediction based on the first hypothesis. If the first hypothesis fails the test, another hypothesis must be made and a new prediction must be tested.

The above process is repeated over and over again with new predictions and new tests (experiments). If a hypothesis stands up to many such tests and becomes accepted as the explanation for the observation, then the hypothesis becomes a theory. A ***theory*** is an accepted explanation of an observation. Theories can be supported by experiment, but they cannot be proven.

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[1] http://www.accessexcellence.org/AB/BC/Elegant_Experiments.html

1.1-2. Phlogiston

Phlogiston theory, one of the first theories that attempted to explain a property of matter, was proposed in the late 17th century to explain fire. The following is an application of the scientific method to phlogiston theory. In it, we examine some chemical and physical properties of magnesium.

- ***Chemical property***: a property of one substance that is related to another substance. For example, "magnesium burns in air" is a chemical property because the property of magnesium requires the presence of air.
- ***Physical property***: a property of one substance that is independent of other substances. For example, "magnesium is a shiny metal" is a physical property.

OBSERVATIONS:

Magnesium is a shiny metal.

Magnesium releases something to produce a brilliant white light when it is burned.

Burning the magnesium converts it from a shiny metal to a gray powder.

HYPOTHESIS:

Magnesium metal contains a substance that is released when the magnesium is burned. The substance was named "phlogiston." The gray powder was the magnesium without its phlogiston, so it was the "dephlogisticated" form of the metal, which was called "calx." Thus, burning magnesium would have been represented as

magnesium → calx of magnesium + phlogiston

PREDICTION:

If the metal contains both the calx and phlogiston, then **the mass of the metal should be greater than the mass of the calx**.

TEST:

The mass of the calx was greater than the mass of the metal. The phlogiston hypothesis withstood experiment for over 100 years, but this experiment, which was performed by a scientist named Antoine Lavoisier, destroyed the theory. Although some argued that mass was irrelevant to the study, others agreed with Lavoisier's conclusion that phlogiston theory was incorrect.

Thus, application of the scientific method led to the downfall of phlogiston theory, and its continued application to other hypotheses has led us to our current understanding of the universe.

1.2 Lavoisier and the Birth of Modern Chemistry

Introduction

Measurements of the ratios in which the masses of substances combined with one another led to the statements of three laws: conservation of mass, constant composition, and multiple proportions. In this section, we briefly examine these three laws because they give us our next clues about the composition of matter.

Objectives

- Define a law.
- Explain a theory and give an example.

1.2-1. Laws

Laws summarize observations.

Lavoisier made many careful measurements of the masses of the reactants and products of reactions, and he observed that the total mass (products plus reactants) never changed during a reaction. He summarized his observation in the law of conservation of mass.

- ***Law of conservation of mass***: The total mass of reactants and products remains constant during a chemical reaction. That is, mass is neither created nor destroyed in a chemical reaction.

Note that the above *law* simply *summarizes* the observations; it does not explain them. The explanation (theory) would not come for another decade.

Lavoisier summarized his observations in the law of conservation of mass, and his work convinced many scientists that phlogiston did not exist. The emerging chemists of the early 19th century began testing the concept that matter consisted of elements and compounds and that mass was indeed relevant to chemistry. After a great number of measurements of relative masses had been performed, the following two laws were also accepted:

- ***Law of definite proportions***: The elements of a compound are always present in definite proportions by mass. For example,
  - Table salt is always 39% Na and 61% Cl by mass.
  - Water is always 11% H and 89% O by mass.
- ***Law of multiple proportions***: When two different compounds are formed from the same two elements, the masses of one element that combine with a fixed mass of the other are in a ratio of small whole numbers. (If the ratio is one, then the two samples consist of the same compound.)

EXAMPLE:

For example, one oxide of iron contains $\frac{3.490\text{ g Fe}}{1\text{ g O}}$, while another contains $\frac{2.327\text{ g Fe}}{1\text{ g O}}$. Both amounts of iron are combined with the same mass of oxygen (1 g), and the ratio of the masses is determined as follows:

$$\frac{3.490\text{ g Fe}}{2.327\text{ g Fe}} = 1.50 = \frac{3}{2}$$

which is a ratio of small whole numbers.

1.2-2. Mass Law Exercise

EXERCISE 1.1:

Na and O form two compounds. 100 g of each compound contains the following masses of the elements.

Compound I: 59 g Na 41 g O

Compound II: 74 g Na 26 g O

Show that the data is consistent with the Law of Multiple Proportions.

Step 1. Determine the mass of Na that combines with a fixed mass (1 g) of O in each compound.

Compound I mass Na/mass O = ______________ g Na/g O

Compound II mass Na/mass O = ______________ g Na/g O

Step 2. Determine the ratio of the mass of Na combined with 1 g of O in Compound II to Compound I.

Compound II/Compound I = ______________

Step 3. Express the result of Step 2 as a reduced fraction of small whole numbers.

numerator ______________

denominator ______________

1.2-3. Theories

Theories explain laws and observations. They can be accepted but not proven.

Theories are valid only as long as they are not disproven by experiment. In general, theories are continually modified or even discarded as more sophisticated experiments are carried out. The work of Antoine Lavoisier discredited phlogiston, so Lavoisier proposed a new hypothesis, which, after acceptance by others, became known as the theory of combustion. After further experiments, he presented the hypothesis that the mass of a metal increased when burned because burning was the combination of two substances, not the release of one. His combustion hypothesis was that burning is the reaction of a substance with oxygen. He named the product "the oxide" of the substance to indicate that the substance had oxygen added to it. Thus, he would have represented the burning of magnesium as

$$\text{magnesium} + \text{oxygen} \rightarrow \text{magnesium oxide}$$

Lavoisier began to classify matter as elements and compounds.

- An element is a pure substance that cannot be broken down into a simpler substance by chemical means.
- A compound is a pure substance that consists of more than one element.

Thus, magnesium and oxygen are elements, and magnesium oxide is a compound that is composed of the two elements magnesium and oxygen. Lavoisier's hypothesis was to be accepted by most other scientists and became the chemical *theory* that was used to *explain* matter and chemical reactions.

1.3 John Dalton and Atomic Theory

Introduction

We now explore the emergence of atoms and molecules, and examine the meaning of chemical formulas and equations.

The atoms of an element had the same mass, and they combined in fixed ratios in compounds. These two facts allowed scientists to determine the relative numbers of atoms of the elements present in a sample; i.e., they were able to determine chemical formulas.

Objectives

- Distinguish between atoms and molecules.
- Convert between the name and symbol of fifty elements.
- Write the formula of a compound given the number and types of atoms that it contains.

1.3-1. Dalton's Atomic Theory

Atomic theory explains the mass relationships in substances and in reactions.

The chemists of the early 19th century had three laws (observations) to explain: conservation of mass, definite proportions, and multiple proportions. It was time for a hypothesis to explain the laws. In 1804, John Dalton suggested the explanation. His hypothesis, now known as Dalton's atomic theory, was based on the assumption that elements consisted of tiny spheres, called ***atoms***.

Dalton's atomic theory:

1. Elements are composed of atoms. The atoms of an element all exhibit identical chemical properties (they all react the same way with other atoms), while atoms of different elements have different chemical properties.
2. Atoms are not changed in chemical reactions; they simply change partners.
3. Compounds are combinations of atoms of different elements. The number of atoms of each element in the compound is integral and constant.

The second postulate explains the law of mass conservation and is the basis of balancing chemical equations. The third postulate explains the laws of definite and multiple proportions.

Dalton's theory explained all of the observations of his time and was accepted without change for nearly 100 years.

Dalton used the term "atom" to refer to both a single atom and a combination of atoms. However, a combination of atoms is now called a ***molecule***. We will use "molecule" to simplify our discussion. Dalton assumed that an atom was the smallest unit of an element, while a molecule was the smallest unit of a compound. This was not quite correct because, as we shall soon see, some elements exist as molecules.

1.3-2. Atom or Molecule Exercise

EXERCISE 1.2:

Indicate whether each of the following is an atom or a molecule.

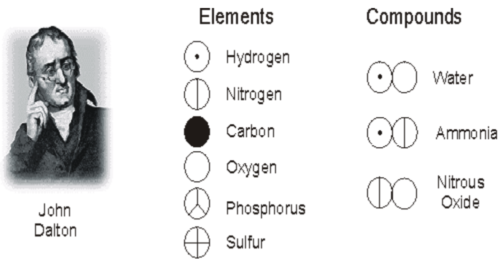
Ar
atom
molecule

O_3
atom
molecule

HCl
atom
molecule

1.3-3. Naming Atoms

Dalton suggested a series of symbols to represent atoms and molecules. The symbols suggested by Dalton for some atoms and molecules are shown below.



Dalton assumed a 1:1 ratio for the atoms in compounds whose atom ratios were unknown. The figure shows three compounds where this assumption was incorrect.

- Water contains two hydrogen atoms and one oxygen atom.
- Ammonia has three hydrogen atoms and one nitrogen atom.
- Nitrous oxide contains two nitrogen atoms and one oxygen atom.

1.3-4. Atom symbols

It is important to know the names and symbols of the fifty most common elements.

Today, the symbols of most of the elements are the first one or two letters of the element's name. **You should learn the following table of names and symbols of the fifty most-used elements in this course.**

hydrogen	H
helium	He
lithium	Li
beryllium	Be
boron	B
carbon	C
nitrogen	N
oxygen	O
fluorine	F
neon	Ne
sodium	Na
magnesium	Mg
aluminum	Al

silicon	Si
phosphorus	P
sulfur	S
chlorine	Cl
argon	Ar
potassium	K
calcium	Ca
scandium	Sc
titanium	Ti
vanadium	V
chromium	Cr
manganese	Mn
iron	Fe

cobalt	Co
nickel	Ni
copper	Cu
zinc	Zn
gallium	Ga
germanium	Ge
arsenic	As
selenium	Se
bromine	Br
krypton	Kr
rubidium	Rb
strontium	Sr
silver	Ag

cadmium	Cd
tin	Sn
iodine	I
xenon	Xe
cesium	Cs
barium	Ba
platinum	Pt
gold	Au
mercury	Hg
thallium	Tl
lead	Pb

1.3-5. Names from Symbols Exercise

EXERCISE 1.3:

Write the name of the element from its symbol.

Br ________________
Li ________________
Ca ________________
Be ________________
B ________________
C ________________
N ________________
O ________________
F ________________
Ne ________________
Zn ________________
Pt ________________
Ge ________________
He ________________
Au ________________
P ________________
Se ________________

Sr ________________
Sc ________________
Cl ________________
Ti ________________
V ________________
Cr ________________
Mn ________________
Fe ________________
Co ________________
Ni ________________
Hg ________________
K ________________
Pb ________________
Na ________________
Ga ________________
As ________________
Kr ________________

Ar ________________
H ________________
Ag ________________
Cd ________________
Sn ________________
I ________________
Xe ________________
Cs ________________
Ba ________________
Mg ________________
Al ________________
Si ________________
Rb ________________
Cu ________________
Tl ________________
S ________________

1.3-6. Symbols from Names Exercise

EXERCISE 1.4:

Write the symbols of the elements given their names.

- The first letter of each symbol must be upper case, and the second letter in any symbol must be lower case.

bromine ________________
vanadium ________________
strontium ________________
boron ________________
aluminum ________________
neon ________________
oxygen ________________
fluorine ________________
sodium ________________
scandium ________________
beryllium ________________
mercury ________________
lead ________________
sulfur ________________

argon ________________
tin ________________
lithium ________________
cobalt ________________
gallium ________________
carbon ________________
iron ________________
nickel ________________
copper ________________
silver ________________
titanium ________________
silicon ________________
phosphorus ________________
chromium ________________

krypton ________________
thallium ________________
cadmium ________________
calcium ________________
barium ________________
xenon ________________
cesium ________________
platinum ________________
gold ________________
helium ________________
zinc ________________
germanium ________________
arsenic ________________
iodine ________________

hydrogen ________________

magnesium ________________

selenium ________________

potassium ________________

nitrogen ________________

chlorine ________________

rubidium ________________

manganese ________________

1.3-7. Molecule Symbols

Molecules are represented by their constituent atoms. If there is more than one atom of an element present in a molecule, then the number is given as a subscript in the molecular formula.

water	H_2O	two hydrogen atoms + one oxygen atom
ammonia	NH_3	one nitrogen atom + three hydrogen atoms
nitrous oxide	N_2O	two nitrogen atoms + one oxygen atom
sugar	$C_{12}H_{22}O_{11}$	12 C atoms + 22 H atoms + 11 O atoms

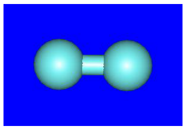
1.3-8. Writing Formulas Exercise

EXERCISE 1.5:

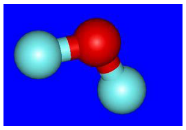
Use the ball-and-stick models and the atom color codes below to write chemical formulas for the molecules.

- light blue: H
- red: O
- gray: C
- purple: N

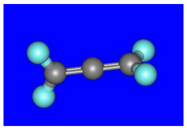
Write the symbols in the order C, H, N, O.



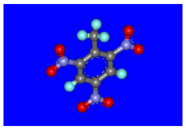
hydrogen molecule ________________



water ________________



allene ________________



TNT ________________

1.3-9. A Common Misconception

As was evident in the previous exercise, hydrogen atoms are present in many compounds, but H_2 molecules are present only in the hydrogen molecule. Thus, both H_2 and H_2O contain two H atoms, but there are two H atoms, not a single H_2 molecule in water. As we shall see in the next section, several elements exist as diatomic molecules (H_2, N_2, O_2, F_2, Cl_2, Br_2, and I_2). But they are diatomic only as free molecules and never in compounds. Thus, allene (C_3H_4) contains four H atoms, not two H_2 molecules.

1.4 Atoms and Molecules

Introduction

Atoms and molecules are too small to be seen, so scientists work with large numbers of them. The unit we use to describe this large number is called the mole.

Objectives

- Distinguish between elements and compounds.

1.4-1. Laws Concerning Gases

In 1808, Joseph Gay-Lussac published the ***law of combining volumes***:

- The volumes of reacting gases measured at the same temperature and pressure are always in the ratio of small whole numbers.

Gay-Lussac's law of combining volumes was soon explained by Amedeo Avogadro[2]. His explanation is now known as ***Avogadro's law***:

- Equal volumes of gases at the same temperature and pressure contain equal numbers of molecules.

1.4-2. Discovering the Formula of Water

We now use the law of combining volumes and Avogadro's law to show how the early scientists discovered the formulas of water, hydrogen, and oxygen.

INITIALLY:

In the absence of any information to the contrary, early scientists assumed that atoms combined in a one-to-one ratio. Thus, water would have been represented as HO. They also believed that the smallest unit of an element was an atom, so the reaction of hydrogen and oxygen to produce water was thought to be the following:

$$\mathrm{H} + \mathrm{O} \rightarrow \mathrm{HO}$$

APPLICATION OF AVOGADRO'S LAW:

Experiments showed that the reacting volume of hydrogen was twice that of oxygen. This fact, combined with Avogadro's law, meant that two hydrogen atoms must react with one oxygen atom, so water must be H_2O, and the reaction should be written as

$$2\ \mathrm{H} + \mathrm{O} \rightarrow \mathrm{H_2O}$$

CURRENT VIEW:

The volume of water that is produced was later shown to be the same as the volume of hydrogen and one-half the volume of oxygen that react. Therefore, the coefficients of hydrogen and water had to be the same, and each had to be twice that of oxygen. This presented a dilemma until Avogadro concluded that elements did not have to exist as atoms; they could exist as molecules! The equation could be balanced only if hydrogen and oxygen each existed as ***diatomic molecules***; i.e., as molecules with two atoms. The following is the way we now view the reaction of hydrogen and oxygen to produce water:

$$2\ \mathrm{H_2} + \mathrm{O_2} \rightarrow 2\ \mathrm{H_2O}$$

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[2] http://www.bulldog.u-net.com/avogadro/avoga.html

1.4-3. Elements can be Molecules

Some common elements occur as molecules rather than atoms.

Other elements also exist as diatomic molecules. The diatomic elements are:

1. H_2
2. N_2
3. O_2
4. F_2
5. Cl_2
6. Br_2
7. I_2

In addition, some elements exist as molecules with more than two atoms. For example, P_4 and S_8.

1.4-4. Elements or Compounds

Combining Dalton's atomic theory and Avogadro's suggestion that elements did not have to occur as atoms, we can define elements and compounds in terms of their constituent atoms.

- An ***element*** is a substance that contains only one **type** of atom.
- A ***compound*** is a substance that contains more than one type of atom.

Note that it is the number of types of atoms, not the number of atoms, that distinguishes an element from a compound. S_8 has more than one atom, so it is a molecule, but it contains only one type of atom (S), so it is an element.

1.4-5. Element or Compound Exercise

EXERCISE 1.6:

Indicate whether each of the following is an element or a compound.

Ar	O_3	HCl
element	element	element
compound	compound	compound

1.4-6. Balancing Chemical Equations Video

A video or simulation is available online.

1.4-7. Balancing Chemical Equations

The number of each type of atom must be the same on both sides of a balanced chemical equation.

Dalton's atomic theory indicates that atoms change partners in a chemical reaction, but they do not change their identity. Thus, the number of atoms of each type must be the same on both sides of a chemical equation. In other words, chemical equations must be balanced. However, **subscripts cannot be changed as that would change the identity of the molecules**, so chemical equations must be balanced by changing only the coefficients of the molecules.

The following steps should lead to a balanced equation:

1. Pick the molecule with the greatest number of atoms and make its coefficient one unless another choice is obviously better. For example, sometimes a 2 must be used to assure an even number of one of the atoms.

2 Determine which atoms are fixed by the coefficient used in Step 1, then balance those atoms on the other side of the equation.

3 Determine which atoms are fixed by the coefficient(s) created in Step 2, then balance those atoms on the other side of the equation.

4 Repeat Step 3 until the equation is balanced.

Note that ones are not usually included in the balanced equation.

EXAMPLE:

As an example, we will follow the steps above to balance the following chemical equation.

$$\_\_\_\ HCl + \_\_\_\ MnO_2 \rightarrow \_\_\_\ MnCl_2 + \_\_\_\ H_2O + \_\_\_\ Cl_2$$

1 Make the coefficient of either MnO_2 or $MnCl_2$ one. We choose MnO_2.

$$\_\_\_\ HCl + \mathbf{1}\ MnO_2 \rightarrow \_\_\_\ MnCl_2 + \_\_\_\ H_2O + \_\_\_\ Cl_2$$

2 The coefficient used in Step 1 fixes the number of Mn atoms at 1 and O atoms at 2, so we balance the Mn atoms with a coefficient of 1 for $MnCl_2$ and the oxygen atoms with a coefficient of 2 for water.

$$\_\_\_\ HCl + 1\ MnO_2 \rightarrow \mathbf{1}\ MnCl_2 + \mathbf{2}\ H_2O + \_\_\_\ Cl_2$$

3 The coefficient of water fixes the number of hydrogen atoms at four, so we balance the H atoms with a coefficient of 4 for HCl. Note that the coefficient of $MnCl_2$ does not fix the number of Cl atoms because it is not the only source of Cl.

$$\mathbf{4}\ HCl + 1\ MnO_2 \rightarrow \mathbf{1}\ MnCl_2 + 2\ H_2O + \_\_\_\ Cl_2$$

4 The coefficient of HCl fixes the number of chlorine atoms at four, but there are already 2 Cl atoms in 1 $MnCl_2$, so we balance the Cl atoms on the other side of the equation with a coefficient of 1 for Cl_2.

$$4\ HCl + 1\ MnO_2 \rightarrow 1\ MnCl_2 + 2\ H_2O + \mathbf{1}\ Cl_2$$

5 Each side of the equation contains 4 H atoms, 1 Mn atom, 2 O atoms, and 4 Cl atoms.

The equation is now balanced, but ones are not usually written. Thus, the balanced equation is usually written as shown in the last step.

$$4\ HCl + \ MnO_2 \rightarrow \ MnCl_2 + 2\ H_2O + \ Cl_2$$

1.4-8. Balanced Equations Exercise

EXERCISE 1.7:

Balance the equations in the activity area with smallest integer coefficients. Click "Submit" after all coefficients have been entered. Use the following steps to help:

1. Pick the molecule with the greatest number of atoms and make its coefficient one if there is not another obvious choice.
2. Determine which atoms have been fixed by the coefficient in Step 1, then balance those atoms on the other side of the equation.
3. Determine which atoms are fixed by the coefficient(s) created in Step 2, then balance those atoms on the other side of the equation.
4. Continue Step 3 until the equation is balanced.

____________ N_2 + ____________ O_2 → ____________ N_2O_5

____________ Na + ____________ H_2O → ____________ NaOH + ____________ H_2

____________ P_4 + ____________ Cl_2 → ____________ PCl_3

____________ $C_6H_{12}O_6$ + ____________ O_2 → ____________ CO_2 + ____________ H_2O

1.5 The Mole and Molar Mass

Introduction

Dalton recognized that the mass of an atom is an important characteristic, but individual atoms are much too small to weigh. However, the relative masses of the atoms in a compound can be determined, so Dalton devised a scale of *relative* masses. In this section, we examine these atomic masses or weights and extend them into molecular masses or weights.

Objectives

- Determine the molecular mass of a compound from the atomic masses of its constituent atoms.
- Define the term *mole*.
- Use molar mass to convert between mass and moles of a substance.

1.5-1. Atomic mass

Atomic masses (or weights) describe the relative masses of atoms and molecules.

An ***atomic mass*** is simply a number that indicates the relative mass of an atom. Dalton reasoned that H was the lightest element, so he assigned it a relative mass of 1, which he called its atomic weight. Note that **atomic mass and atomic weight mean the same thing because the masses are relative, so the two terms are used interchangeably**. The atomic weights of the other elements could then be assigned from the experimentally determined masses of the reacting elements and the formulas of the compounds they form. For example, consider the following reaction of H_2 and O_2 to produce H_2O.

$$\begin{array}{ccccc} 2\ H_2 & + & O_2 & \rightarrow & 2\ H_2O \\ 1.0\text{ g} & + & 8.0\text{ g} & \rightarrow & 9.0\text{ g} \end{array}$$

The above data imply that two oxygen atoms (one O_2 molecule) has eight times more mass than four hydrogen atoms (two H_2 molecules), or 1 O atom is sixteen times heavier than 1 H atom. The relative mass of an H atom was established as 1, so the atomic weight of O must be 16. Similarly, two water molecules have nine times more mass than 4 H atoms, or one water molecule is 18 times heavier than a hydrogen atom. Thus, the relative mass of water is 18. The relative mass of a molecule is called its ***molecular mass*** or weight.

1.5-2. Relative Mass Exercise

EXERCISE 1.8:

Given the atomic weights: H = 1 and O = 16, determine the atomic weight of the element X in each of the following mass relationships.

$3\text{ g X} + 1\text{ g H}_2 \rightarrow 4\text{ g XH}_4$ ____________

$3\text{ g X} + 2\text{ g O}_2 \rightarrow 5\text{ g XO}$ ____________

$9\text{ g X} + 8\text{ g O}_2 \rightarrow 17\text{ g X}_2\text{O}_3$ ____________

1.5-3. Atomic Masses vs. Molecular Masses

A molecular mass equals the sum of the atomic masses of the atoms that comprise the molecule.

The modern atomic weight scale is no longer based on hydrogen. Instead, it is based on the mass of the most common form of carbon, which is assigned a relative mass (atomic weight) of exactly 12. The masses of individual atoms and molecules are often given in ***atomic mass units*** (amu) or Daltons (D). 1 amu = 1 D = 1/12 of the mass of a carbon atom. The atomic masses of the ten lightest atoms are given in the accompanying table.

H	1.01	**C**	12.01
He	4.00	**N**	14.01
Li	6.94	**O**	16.00
Be	9.01	**F**	19.00
B	10.81	**Ne**	20.18

Molecular masses (or weights) are simply the sum of the atomic masses of the atoms that make up the molecule. For example, the molecular mass of CO_2, $M(CO_2)$, would be determined as follows:

$$M(\text{CO}_2) = n(\text{C}) \times M(\text{C}) + n(\text{O}) \times M(\text{O}) = 1(12) + 2(16) = 44$$

where n(C) is the number of C atoms in the molecule and M(C) is the atomic mass of a carbon atom.

EXERCISE 1.9:

Use the atomic masses above to determine the molecular mass of each of the following.

BF_3 ____________

N_2O_5 ____________

$H_2C_2O_4$ ____________

1.5-4. The Mole

Atoms and molecules react in the ratio specified in a balanced chemical equation, and chemists usually mix the reactants in ratios close to those predicted by the equation. However, chemists convert the ratios of atoms and molecules to ratios of mass in order to quickly deliver the correct amounts of material. The conversion between numbers of atoms or molecules and mass is made with the use of the mole. **A *mole* is the number of molecules or atoms in a sample of a compound or element that has a mass equal to its molecular or atomic mass expressed in grams.** It is abbreviated *mol*. It is a number just as a pair is 2 and a dozen is 12. The number of items in a mole is called ***Avogadro's number***, N_A.

$$N_A = 6.02 \times 10^{23}\ \text{mol}^{-1}$$

Avogadro's number is used to convert between a number of moles and a number of molecules or atoms just as 12 is used to convert between a number of dozens and a number of eggs.

EXAMPLE:

For example, determining the number of C atoms in 2 moles of carbon atoms or in 2 dozen carbon atoms is done exactly the same.

$$\begin{aligned} 2\text{ mol C} \times \frac{6\times10^{23}\text{ C atoms}}{1\text{ mol C}} &= 1.2\times10^{24}\text{ C atoms} \\ 2\text{ doz C} \times \frac{12\text{ C atoms}}{1\text{ doz C}} &= 24\text{ C atoms} \end{aligned}$$

EXAMPLE:

Similarly, the number of ammonia molecules in 8 moles of ammonia is determined as

$$8\text{ mol NH}_3 \times \frac{6\times10^{23}\text{ NH}_3\text{ molecules}}{1\text{ mol NH}_3} = 4.8\times10^{24}\text{ NH}_3\text{ molecules}$$

Avogadro's number is very large. Consider that one mole of dice that are 1/2" on a side would cover the 48 contiguous states of the USA to a height of 100 miles!

Molecules are very small. A mole of water molecules has a volume of only 18 mL.

1.5-5. Individual Atoms and Molecules

The molar mass has units of g/mol and is used to convert between mass and moles of a substance.

The mass of a mole is called the ***molar mass***, M_m. Molar mass has units of g/mol. The molar mass of H_2 is $M_m = 2$ g/mol and that of carbon is $M_m = 12$ g/mol. Thus, 2 g of H_2 contain 6.02×10^{23} H_2 molecules and 12 g of C contain 6.02×10^{23} C atoms.

The ***factor label method*** uses conversion factors to convert given quantities into desired quantities. Molar mass has units of g/mol, so it is the conversion factor that is used to convert grams into moles or moles into grams. For example, if compound A has a molar mass M_m, then the number of moles of A present in Z grams of A is

$$Z\text{ g A} \times \frac{1\text{ mol A}}{M_m\text{ g A}} = \frac{Z}{M_m}\text{ mol A}$$

Note that the units of the given quantity (g A) cancel with the denominator of the conversion factor to yield the correct units for the answer. We can determine the mass of n moles of A in a similar manner.

$$n\text{ mol A} \times \frac{M_m\text{ g A}}{1\text{ mol A}} = nM_m\text{ g A}$$

Again, the units of the given quantity are converted into the units of the desired quantity by the conversion factor (molar mass of A).

1.5-6. Mass and Moles Exercise

EXERCISE 1.10:

The atomic masses of N, O, and F are 14, 16, and 19, respectively.

The mass of 0.25 mole of N_2O_3 = ______________ g N_2O_3

The number of moles of NF_3 in 11.8 g = ______________ mol NF_3

1.6 Stoichiometry

Objectives

- Determine the number of moles or the mass of one element in a compound from the number of moles or mass of another element in the compound and the chemical formula of the compound.
- Determine the number of moles or mass of one substance that is produced by or reacts with a given amount of another substance in the reaction.

1.6-1. Stoichiometry Video

A video or simulation is available online.

1.6-2. Subscripts as Stoichiometric Factors

The stoichiometric factor used to determine the amount of one atom that is combined with a given mass of another is the ratio of the subscripts of the given to sought elements.

Chemists often need to convert the amount of one substance into the chemically equivalent amount of another substance. The study of such conversions is referred to as ***stoichiometry***. The conversion factor that converts one substance into another is called the ***stoichiometric factor***. In this and the next section, we use the chemical formula of a compound to derive stoichiometric factors for substances.

The following conversion factors can be written from the formula Na_3PO_4.

$\frac{3\text{ mol Na}}{1\text{ mol Na}_3\text{PO}_4}$	$\frac{3\text{ mol Na}}{4\text{ mol O}}$	$\frac{4\text{ mol O}}{1\text{ mol Na}_3\text{PO}_4}$

The above ratios and their reciprocals can be used to convert a given number of moles of one substance into the chemically equivalent number of moles of another substance in the formula. For example, the number of moles of oxygen in a sample of Na_3PO_4 that contains 6 mol of sodium can be determined as follows.

$$6\text{ mol Na} \times \frac{4\text{ mol O}}{3\text{ mol Na}} = 8\text{ mol O}$$

Thus, a sample of Na_3PO_4 that contains 6 mol Na also contains 8 mol O. Note how the stoichiometric factor is derived from the subscripts in the chemical formula.

Once the number of moles of the desired substance is known, its mass can be determined by multiplying the number of moles by the molar mass.

1.6-3. Coefficients as Stoichiometric Factors

The stoichiometric factor used to determine the amount of one substance that reacts with or is formed from another equals the ratio of the coefficients of the sought to given substances in the balanced equation.

The ratios of the coefficients in balanced chemical equations can be used as stoichiometric factors. Consider the following reaction and the factors derived from the coefficients in the balanced equation.

$\mathbf{2}\ N_2 + \mathbf{3}\ O_2 \rightarrow \mathbf{2}\ N_2O_3$		
$\frac{2\text{ mol } N_2 \text{ react}}{2\text{ mol } N_2O_3 \text{ forms}}$	$\frac{3\text{ mol } O_2 \text{ react}}{2\text{ mol } N_2O_3 \text{ forms}}$	$\frac{2\text{ mol } N_2 \text{ react}}{3\text{ mol } O_2 \text{ react}}$

Thus, the number of moles of nitrogen that react with 6 mol O_2 in the above reaction can be determined using the factor label method and the balanced equation as follows.

$$6\text{ mol } O_2 \times \frac{2\text{ mol } N_2}{3\text{ mol } O_2} = 4\text{ mol } N_2$$

Thus, if 6 mol O_2 are to react then at least 4 mol N_2 must be present. Note that the stoichiometric factor is derived from the coefficients in the balanced equation.

1.6-4. Mole-Mole Substance Stoichiometry Exercise

EXERCISE 1.11:

How many moles of NH_3 are in a sample that contains 27 mol of H atoms?

______________ mol NH_3

A sample of Al_2O_3 contains 9 mol of O. How many mol of Al does it contain?

______________ mol Al

1.6-5. Mass-Mass Stoichiometry Exercise

EXERCISE 1.12:

What is the mass of sulfur is in a 5.00 g sample of Ca_2S_3? The atomic mass of Ca is 40 and that of S is 32.

First, convert the amount of given mass into moles.

molar mass of Ca_2S_3 = ______________ g/mol

number of moles in a 5.00 g sample = ______________ mol Ca_2S_3

Next, convert the moles of Ca_2S_3 into the chemically equivalent number of moles of sulfur.

______________ mol S

Finally, convert the number of moles of sulfur into its mass in grams to obtain the answer.

______________ g S

1.6-6. Mole-Mole Reaction Stoichiometry Exercise

EXERCISE 1.13:

How many moles of each reactant are required to produce 68 g of NH_3 by the following reaction? The atomic weights of N and H are 14 and 1, respectively.

$$N_2 + 3\ H_2 \rightarrow 2\ NH_3$$

1. First convert the given amount into moles! The number of moles of NH_3 to be prepared is

_______________ mol NH_3

2. Once the number of moles of the ammonia are known, the number of moles of each reactant can be determined. We first determine the number of moles of H_2 that would be required.

_______________ mol H_2

3. Finally, determine the number of moles of N_2 that are needed.

_______________ mol N_2

1.6-7. Mole-Mass Reaction Stoichiometry Exercise

EXERCISE 1.14:

Once the numbers of moles of reactants and products have been determined, the masses can be obtained by multiplying by the molar masses. In this example, we determine the number of moles of O_2 that are required to react with 0.30 mol K and the mass of K_2O that is produced in the following reaction.

$$4\ K + O_2 \rightarrow 2\ K_2O$$

The number of moles of O_2 required = _______________ mol

The number of moles of K_2O produced = _______________ mol

The mass of potassium oxide that forms = _______________ g

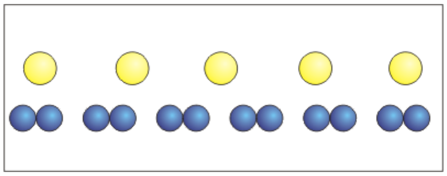
1.6-8. Limiting Reactants Video

A video or simulation is available online.

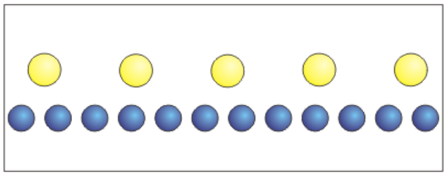
1.6-9. Limiting Reactants

When reactants are not added in the required stoichiometric ratio, the amount of reaction is dictated by the limiting reactant.

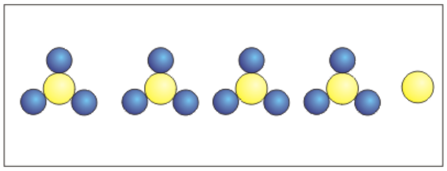
Chemists seldom add chemicals in the exact stoichiometric ratio, so the amount of product that forms depends upon the amount of the reactant, called the limiting reactant, that is consumed first. In the following, we examine the reaction of 5 mol S and 6 mol O_2 to produce SO_3.



Initially there are 5 mol S, the five yellow spheres in the figure, and 6 mol O_2, the six pairs of blue spheres.



There are 12 mol O atoms in 6 mol O_2, so there are 5 mol S and 12 mol O.



Each mole of SO_3 requires one mole of S, so there is enough S present to produce 5 mol SO_3. Each mole of SO_3 also requires 3 mol of O, so there are enough oxygen atoms to make only $12/3 = 4$ mol SO_3. Since less SO_3 can be made with the oxygen, it is the limiting reactant. Consumption of 6 mol O_2 produces 4 mol SO_3, so that is all that can be made. Initially, there were 5 mol S, but making 4 mol SO_3 requires only 4 moles. Therefore, there is 1 mol S left over.

1.6-10. Limiting Reactants 2

Typically, the limiting reactant is determined by applying the stoichiometric factors for the reaction to the given numbers of moles of reactant to determine which reactant produces the least amount of product; i.e., to determine the limiting reactant. Consider the reaction of 5 mol S with 6 mol O_2 as discussed in the previous section. The chemical equation for the reaction is $2\ S + 3\ O_2 \rightarrow 2\ SO_3$. The amount of SO_3 that can be produced from 5 mol S and 6 mol O_2 is then determined to be

$$5 \text{ mol S} \times \frac{2 \text{ mol SO}_3}{2 \text{ mol S}} = 5 \text{ mol SO}_3$$

and

$$6 \text{ mol O}_2 \times \frac{2 \text{ mol SO}_3}{3 \text{ mol O}_2} = 4 \text{ mol SO}_3$$

Oxygen produces less product, so it is the limiting reactant and the amounts of all products that form and the amounts of reactants that react are based on the number of moles of O_2 that react.

1.6-11. Limiting Reactant Exercise

EXERCISE 1.15:

What mass of Al_2O_3 can be produced from 10.0 mol Al and 9.0 mol O_2?

$$4\ \text{Al} + 3\ \text{O}_2 \rightarrow 2\ \text{Al}_2\text{O}_3$$

The number of moles of Al_2O_3 produced from 10.0 mol Al = ______________ mol

The number of moles of Al_2O_3 produced from 9.0 mol O_2 = ______________ mol

The limiting reactant is ______________ .

The maximum number of moles of Al_2O_3 that can be produced = ______________ mol

The molar mass of Al_2O_3 = ______________ g/mol

The mass of Al_2O_3 that can be produced = ______________ g

1.7 Energy

Introduction

Chemical processes are driven by energy differences, which result from changes in the interactions between charges. We now examine two types of energy and the energy of interaction between charged particles.

Objectives

- Distinguish between kinetic and potential energy.
- State the direction of energy change in most processes in nature.

1.7-1. Energy

There are two forms of energy: kinetic energy and potential energy.

In simple terms, energy is the capacity to move something. The energy of an object is the sum of two terms.

- ***Kinetic energy*** is energy due to motion.
- ***Potential energy*** is energy due to position.

An object that is moving can make another object move by colliding with it. The kinetic energy of a particle of mass m moving with a velocity v is $KE = \frac{1}{2}mv^2$. Molecules and atoms are in constant motion, and their speed (kinetic energy) is dictated by their temperature.

An object that has the capacity to move due to its position has potential energy. Two examples of potential energy:

1 A truck parked at the top of a hill has potential energy because it will move and gain kinetic energy if its brake is released.

2 A compressed spring has potential energy because the ends of the spring move and gain kinetic energy when the force that compresses the spring is removed and the spring returns to its uncompressed state.

Molecules and atoms have potential energy because they interact with one another. The change in potential energy caused by these interactions is responsible for the formation of chemical bonds and the condensation and freezing of molecules.

1.7-2. Energy Change

Systems in nature seek to minimize their energy, so energy changes for most processes are negative.

The energy of an object is a relative quantity and cannot be measured absolutely. For example, a ball at rest on the floor has neither kinetic nor potential energy relative to the floor, but it does have kinetic energy relative to the sun and potential energy relative to the center of the Earth. Consequently, it is energy **change**, not absolute energy, that is typically measured. The symbol Δ (Delta) is used to represent change and the symbol E is used for energy, so the energy change is expressed as ΔE. By convention, energy change is the final energy minus the initial energy.

$$\Delta E = E_{\text{final}} - E_{\text{initial}}$$

Thus, $\Delta E < 0$ means that the object loses energy because its final energy is less than its initial energy. A very important concept in chemistry is that **systems naturally seek the position of lowest energy; i.e., nature favors processes for which $\Delta E < 0$**. Although energy change in chemical processes is not discussed in detail until Chapter 9, we will use the concept that molecules undergo chemical processes in order to reduce their potential energy in every chapter of this text.

EXAMPLE:

As an example of the amount of energy that can be released in a common reaction, consider the combustion of octane, a component of gasoline. The chemical equation for the combustion is

$$C_8H_{18} + 12.5\ O_2 \rightarrow 8\ CO_2 + 9\ H_2O$$

$\Delta E < 0$ for this reaction, and the energy that is released is used to power many automobiles. The amount of energy released in the reaction can be better appreciated by considering the following:

- In order to deliver the same amount of energy as all of the kinetic energy of a 2200 pound (1000 kg) car moving at 40 mph (18 m/s), you would have to burn only 3 g of octane (∼0.0008 gal).

1.8 Electromagnetism and Coulomb's Law

Introduction

The attraction of opposite charge and the repulsion of like charge are the result of the electromagnetic force. The electromagnetic force, which is responsible for all of the interactions between atoms and molecules discussed in this course, is the topic of this section.

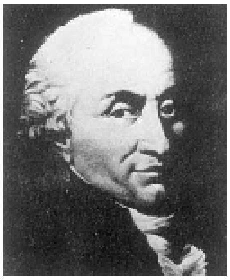
Objectives

- Use Coulomb's law to predict the sign and relative magnitude of the energy change resulting when two charged particles approach one another.
- Explain the role of the medium in the magnitude of the interaction between two charged particles.

1.8-1. Electromagnetism and Coulomb's Law

Coulomb's law describes the force exerted between two charged particles. The Coulombic force is responsible for the forces in molecules.

In the 1800's, scientists recognized that charged particles interacted, but Charles Coulomb was the first to measure the electromagnetic force.



Charles Coulomb
1736 - 1806

He observed that the force of interaction between two charged particles was

1. proportional to the charges on the particles,
2. inversely proportional to the square of the distance between them,
3. attractive when the charges were of opposite sign and repulsive when they had the same sign.

His observations are summarized by ***Coulomb's law***: Two particles with charges q_1 and q_2 and separated by a distance r experience the following force F.

$$F = \frac{kq_1q_2}{\epsilon r^2} \qquad \text{The Coulombic Force} \qquad (1.1)$$

- $k = 8.9875 \times 10^9\ \mathrm{N \cdot m^2 \cdot C^{-2}}$ and is called Coulomb's constant.
- ϵ is the ***dielectric constant*** of the medium separating the charges. The dielectric constant indicates how well the medium shields the charges from one another.
- When the charges are of the same sign, $F > 0$ and the force is repulsive. When the charges are of opposite sign, $F < 0$ and the force is attractive.

1.8-2. Energy of Interaction

Opposite charges attract and like charges repel because doing so lowers their potential energy (energy of interaction).

Energy is a force exerted through a distance ($E = Fr$). Consequently, the potential energy of two charged particles separated by a distance r is determined by multiplying Equation 1.1 by r:

$$\Delta E = \frac{kq_1q_2}{\epsilon r} \qquad \text{Energy of Interaction of 2 Charged Particles} \qquad (1.2)$$

ΔE, which is referred to as the ***energy of interaction***, is the potential energy of the two particles separated by a distance r relative to their potential energy when they are separated by an infinite distance (i.e., not interacting).

$$\Delta E = E_r - E_\infty = E_r - 0 = E_r = E$$

Consequently, the energy of interaction is often written without the Δ. Note that the energy change is negative (the energy decreases) as r decreases when q_1 and q_2 have opposite signs, therefore particles of opposite charge lower their energy as they get closer. Systems strive to lower their energy, so particles of opposite sign are attracted. However, the energy change is positive (the energy increases) when q_1 and q_2 have the same sign, which means that the energy of two particles of the same sign increases as they get closer. Consequently, particles of the same charge move apart to lower their energy; i.e., particles of like charge are repelled. The energy of interaction of two charged particles as a function of the distance between them is shown in Figure 1.1.

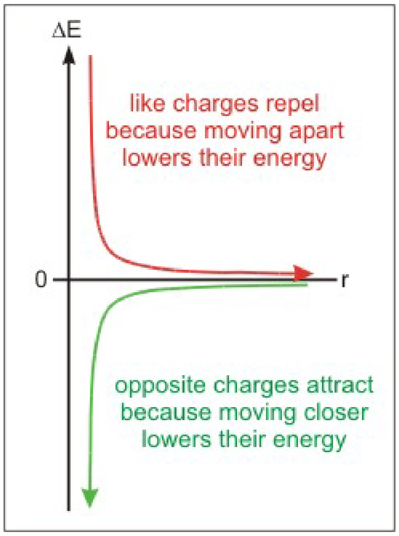
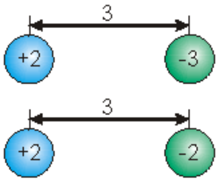


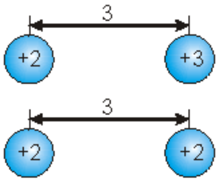
Figure 1.1 Energy of Interaction: The energy of like-charged particles increases as they get closer, while the energy of oppositely-charged particles decreases as they get closer. Thus, particles of like charge avoid (are repelled by) one another, while particles of opposite charge are attracted to one another.

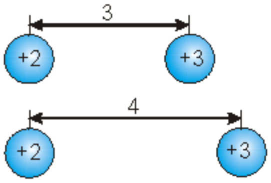
1.8-3. Coulomb's Law Exercise

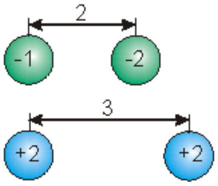
EXERCISE 1.16:

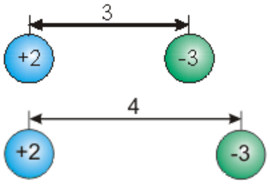
Pick the system in each pair that has the lower potential energy.

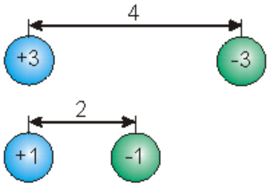












1.9 Atomic Structure

Introduction

New technology led to new experiments at the end of the 19th century, experiments that Dalton's atomic theory could not explain. We now examine three of the most important of those experiments and take the atom to the next step.

Objectives

- Describe Thomson's cathode ray experiment and his conclusions.
- Describe Millikan's oil drop experiment and his conclusions.
- Describe Rutherford's gold foil experiment and his conclusions.
- Describe the Rutherford model of the atom.

1.9-1. Thomson Experiment

J. J. Thomson
1856 - 1940

In 1897, the British physicist J. J. Thomson discovered the electron while he was exploring the nature of the "cathode rays." In his experiment, which is demonstrated schematically below, he examined the effect of electric fields on cathode rays.

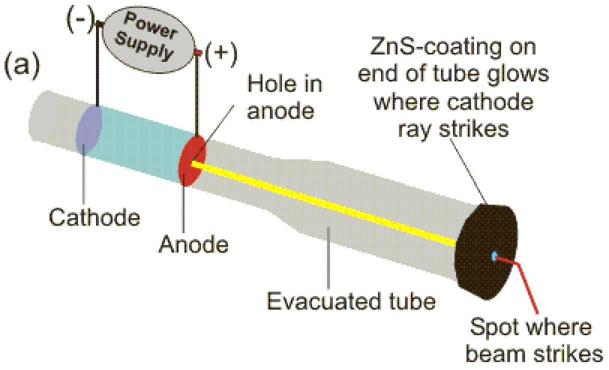


Figure 1.2a: Cathode Ray Tube

Two metal plates, which are connected to a power supply, are sealed into an evacuated glass tube. One of the plates has a small hole in its center. When a high voltage is applied across the metal plates, a "ray" originating at the cathode $(-)$ (hence their name "cathode rays") passes through the hole in the other plate, which is the anode $(+)$ and hits the end of the tube, which is coated with ZnS. ZnS glows when struck with cathode rays to produce the dot in the end of the tube. The yellow line represents the trajectory of the ray, but cathode rays are not visible, which is why ZnS was necessary.

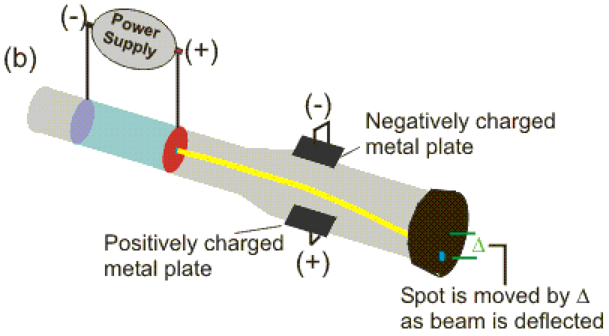


Figure 1.2b: Deflected Cathode Ray

The "ray" was deflected when an electric field was applied. The extent of deflection is given by the value of Δ, the amount by which the spot moves from its position in the absence of the electric field. Thomson noted the direction of the deflection and carefully measured the value of Δ at several field strengths.

1.9-2. Thomson Observations

Cathode rays are beams of negatively-charged particles.

Thomson made the following observations and conclusions:

Observation:

- The "rays" were deflected by electric and magnetic fields.

Conclusion:

- Cathode rays are not light rays because light rays are not deflected by these fields. Therefore, **the "rays" were actually charged particles**, which are now called ***electrons***.

Observation:

- The deflection was away from the negative plate and toward the positive plate.

Conclusion:

- **The particles were negatively charged.**

Observation:

- The deflection was large.

Conclusion:

- The amount of deflection depended upon the strength of the field and on the charge and mass of the particles. The greater the charge on the particle (q), the greater the deflection, but the greater its mass (m), the smaller the deflection. Thus, $\Delta \propto q/m$. Thus, the large deflection meant that either the particle had a very high charge or a very small mass. He was familiar with charges observed by others in different experiments and reasoned that the charge could not be the reason for the large deflection. He concluded that **the mass of the particle must be less than one-thousandth that of the hydrogen atom**. He was shocked! This meant that the hydrogen atom was not the smallest unit of matter as Dalton had suggested nearly a century earlier.

Observation:

- The value of Δ

Conclusion:

- Thomson used the experimental value of Δ as shown in Figure 1.2b and the strength of the electric field that caused the deflection to determine the charge-to-mass ratio for the electron.

$$\frac{q_e}{m_e} = -1.76 \times 10^{11}\ \text{kg} \cdot \text{C}^{-1}$$

1.9-3. Millikan Experiment

Robert Millikan, an American physicist at the University of Chicago, was the first to accurately determine the charge on the electron.

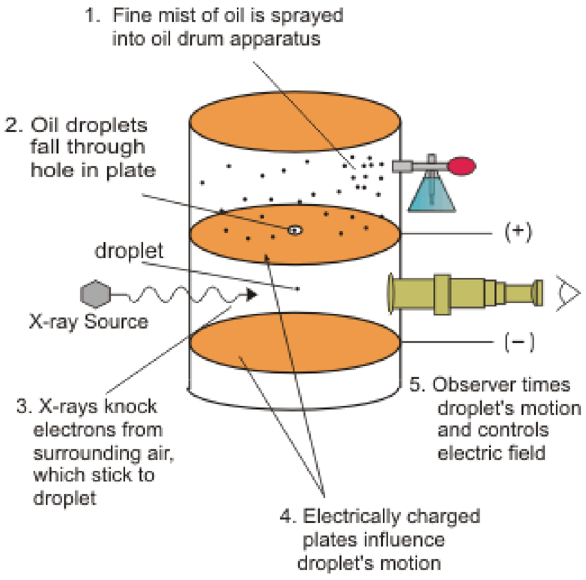


Figure 1.3: Oil Drop Experiment

- Two plates were welded into an oil drum as shown in the figure. The upper plate had a small hole drilled into it.
- Above the hole, he created a fine mist of oil droplets. Individual oil droplets passed randomly through the hole one-by-one to descend toward the lower plate.
- He used a microscope to observe the fall of an individual droplet. Initially, the drop accelerated due to gravity, but eventually the resistance due to the air stopped its acceleration and the drop began to fall at a constant speed called its terminal speed. He determined the droplet's terminal speed and used it to determine the mass of the droplet.
- He then fired X-rays into the drum, which removed electrons from some of the molecules in the air. Some of the released electrons attached to the oil droplet, creating a negative charge (q) on its surface.
- Next, he applied an electric field (E) across the two plates, creating a positive charge on the top plate and a negative charge on the bottom plate. As the electric field increased, the rate of descent of the droplet slowed as it was increasingly attracted to the positive upper plate and repelled by the lower plate.
- Millikan adjusted the voltage across the two plates until the droplet became suspended, moving neither up nor down.

1.9-4. Millikan Observations

The mass of an electron is only 1/1800 the mass of a hydrogen atom.

Robert Millikan
1868 - 1953

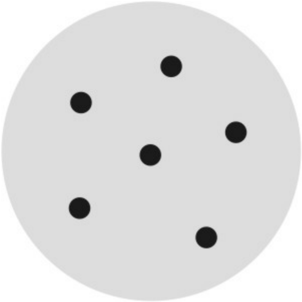
At the point where the particle moved neither up nor down, the electrostatic force (qE) that pulled the droplet up equaled the gravitational force (mg) that pulled it down, so $q = \frac{mg}{E}$. E, m, and g were all known, so he was able to determine the charge on the droplet. Various experiments yielded different values of q for different droplets, but all of the measured charges were multiples of the same charge, -1.6×10^{-19} C . Millikan reasoned that the charges on the droplets were different because each droplet had a different number of electrons; i.e., $q = nq_e$, where n is the number of electrons and q_e is the charge on each electron. In this way he was able to determine that the charge on an electron must be $q_e = 1.6 \times 10^{-19}$ C. With this charge and Thomson's charge-to-mass ratio, Millikan was able to determine the mass of the electron to be 9.1×10^{-31} kg, which is approximately 1/1800 the mass of the hydrogen atom.

charge on the electron	**mass of electron**
$q_e = 1.6 \times 10^{-19}$ C	$m_e = 9.1 \times 10^{-31}$ kg

1.9-5. Kelvin-Thomson Model

Clearly, it was time to refine Dalton's atomic model. One proposed model was the "**raisin pudding**" model of Lord Kelvin and J. J. Thomson. They reasoned that because atoms are uncharged themselves, they must contain enough positive charge to balance the negative charge of the electrons. In the Kelvin-Thomson model, the atom resembled raisin pudding with the negatively-charged electrons (the raisins) embedded in a mass of diffuse positive charge (the pudding).

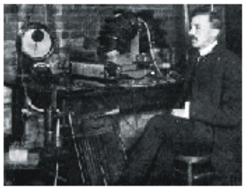
In the accompanying figure of the raisin pudding model, six electrons or raisins are embedded in a mass of positive charge. The raisins carry very little mass but all of the negative charge, while the pudding carries almost all of the mass and all of the positive charge in a (grey area). Since the positive charge was thought to be spread over a relatively large volume, it was thought to be diffuse. Atoms are neutral, so the positive charge in the bulk of the mass must equal the negative charge of the electrons.



Raisin-Pudding model of an atom with six electrons.

1.9-6. Rutherford Experiment

Almost all of the mass and all of the positive charge in an atom is concentrated in its nucleus.



Ernest Rutherford
1871 - 1937
Figure also shows his equipment

In another classic experiment, Ernest Rutherford tested the raisin pudding model in 1911 and discovered the nucleus of the atom.

Rutherford bombarded a very thin gold foil with α particles (particles with atomic mass = 4 and charge = +2) moving at 10,000 mi/s. If the raisin pudding model was correct, most of the particles would pass through the foil undeflected because the positive charge of the atom was assumed to encompass the entire atom, which would make it diffuse. Some particles were expected to experience minor deflection. Consistent with the predictions, most of the particles did indeed pass through undeflected or with only minor deflection. However, a few (1 in 20,000) were deflected back at acute angles, and these few showed that the raisin pudding model could not be correct!

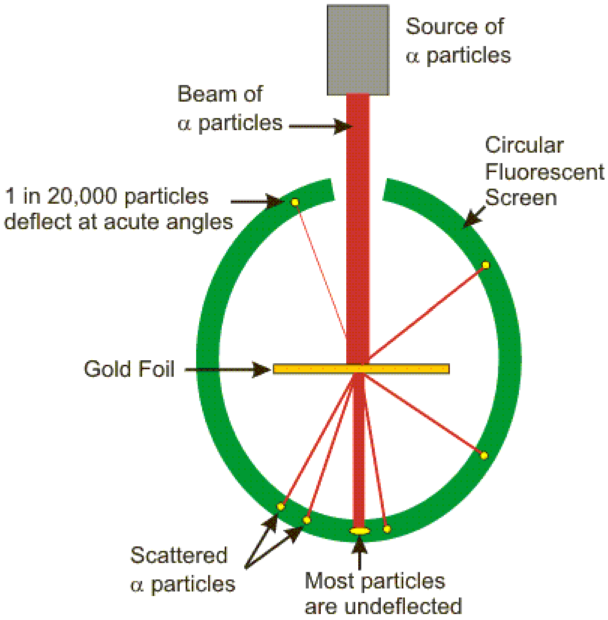


Figure 1.4: The Rutherford Experiment

1.9-7. Rutherford Observations

His experiment showed that the raisin pudding model was incorrect, so Rutherford had to view his observations in light of a new model. The following observations had to be explained.

Observation:
- Most particles passed through undeflected.

Explanation:
- Most of the volume of the atom contained very little mass to deflect the massive, positively-charged α particles.

Observation:
- Some minor deflections were observed.

Explanation:
- Small deflections of the α particles were caused by near misses with a massive particle within the atom.

Observation:
- One particle in 20,000 was deflected at an acute angle.

Explanation:
- Only a very massive and highly, positively-charged particle could cause the high-energy, positively-charged α particles to reverse direction. The fact that only one particle in 20,000 was deflected meant that the cross-sectional area of this positive charge was only 1/20,000 of the cross section of the atom. Thus, most of the mass and all of the positive charge of the atom was concentrated in a very small particle, which is called the ***nucleus***.

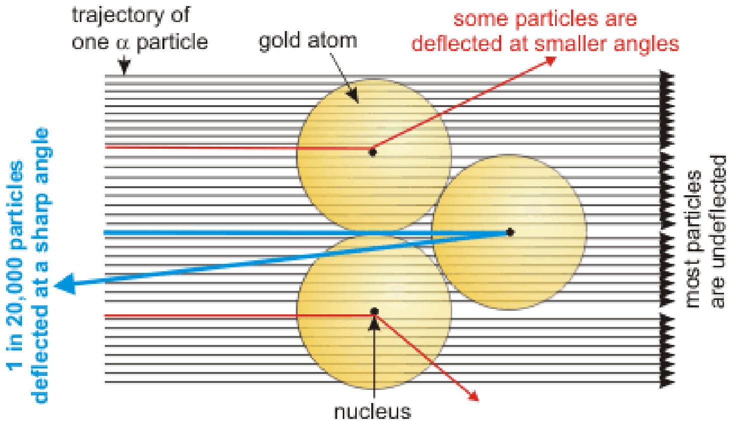


Figure 1.5 Rutherford's Nuclear Model of the Atom: The positive charge and most of the mass resides in the nucleus as represented by the black dots. Only near-collisions with the very small, massive, and highly-positively-charged nuclei resulted in acute deflections.

1.9-8. Nuclear Model of the Atom

As a result of the work of Thomson, Millikan, and Rutherford, we had a very different view of the atom. It was no longer the "billiard ball" put forth by Dalton 100 years earlier. Based on his experiments and those of his contemporaries, Rutherford presented his nuclear model of the atom: ***All of the positive charge and most of the mass of the atom was contained in the very small nucleus at its center. The negative charge, but almost none of the mass, was carried by electrons, which orbited the nucleus much like the planets***

orbit the sun. His model was a giant step forward, but Rutherford was not satisfied with it because he could not understand why the electromagnetic force between the negatively-charged electrons and the positively-charged nucleus would not cause them to combine. The answer, which would dramatically alter the way we understand matter and the universe, would not be forthcoming for another decade.

1.10 Subatomic Particles, Isotopes, and Ions

Introduction

A third subatomic particle, the neutron, was discovered about 20 years after Rutherford introduced the nuclear model of the atom. The atom now consisted of three particles: neutrons and protons in the nucleus and electrons surrounding it. We now examine the effect that each of these particles has on the characteristics of the atom.

Objectives
- Name the major subatomic particles and give their masses and their charges.
- Define an isotope.
- Convert between the symbol and charge of a species and the number of protons and electrons that it contains.
- Distinguish between atoms, anions, and cations.

1.10-1. Subatomic Particles

The major *subatomic* particles are:

particle	mass (amu)	charge
electron	5×10^{-4}	-1
proton	1.0073	+1
neutron	1.0087	0

The ***proton*** is the source of the positive charge that balances the negative charge of the electrons to produce neutral atoms; i.e., the number of electrons equals the number of protons in an atom. The ***neutron*** is slightly more massive than the proton, but it carries no charge. Neutrons somehow keep the positively charged protons together in the nucleus.

1.10-2. Atomic Number, *Z*

It is the number of protons in the nucleus (the atomic number) that characterizes an atom.

The ***atomic number***, Z, is the number of protons in the nucleus. It is the number that characterizes the element. Sulfur is the element that has sixteen protons in its nucleus; i.e., $Z = 16$ for sulfur. The number of neutrons determines the mass, and the number of electrons determines its charge. The atomic numbers of the first ten elements are:

H	He	Li	Be	B	C	N	O	F	Ne
1	2	3	4	5	6	7	8	9	10

1.10-3. Mass Number, *A*

The mass number, A, is the number of protons plus neutrons in the nucleus.

The ***mass number***, A, is the number of protons plus the number of neutrons in the nucleus. It is sometimes given as a superscript preceding the symbol. For example, an atom of ^{19}F (read "fluorine-19") has 9 protons because it is fluorine and 10 neutrons because its mass is 19
$(10 + 9 = 19)$. The mass of a neutron and a proton are each ~1 amu, so the atomic mass is close to 19 amu, the mass number. Note that the symbol ^{19}F does not include the atomic number because the number of protons is known if the element (F) is known. However, it is sometimes included to aid in balancing nuclear reactions. In these cases, the atomic number is found as a subscript preceding the symbol.

$${}^{A}_{Z}\text{X} = {}^{\text{number of protons \& neutrons}}_{\text{number of protons}}\text{Symbol}$$

1.10-4. Isotopes

Isotopes have the same Z but different A.

Isotopes are atoms with the same atomic number but different mass numbers. For example, naturally occurring chlorine is a mixture of two isotopes: ^{35}Cl and ^{37}Cl (chlorine-35 and chlorine-37). They are both chlorine atoms, so they both contain 17 protons, but they differ in the number of neutrons.

- ^{35}Cl contains 18 neutrons $(35 - 17)$.
- ^{37}Cl contains 20 neutrons $(37 - 17)$.

Elements that have atomic masses that are not nearly integers exist in more than one isotope.

EXAMPLE:

For example, the atomic mass of chlorine is 35.5 because naturally occurring chlorine is 75.8% ^{35}Cl and 24.2% ^{37}Cl. That is, one mole of chlorine contains 0.758 mol ^{35}Cl and 0.242 mol ^{37}Cl. The mass of one mole of chlorine atoms is therefore

$$\frac{0.758\ \cancel{\text{mol}\ ^{35}\text{Cl}}}{\text{mol Cl}} \times \frac{35.0\ \text{g Cl}}{\cancel{\text{mol}\ ^{35}\text{Cl}}} + \frac{0.242\ \cancel{\text{mol}\ ^{37}\text{Cl}}}{\text{mol Cl}} \times \frac{37.0\ \text{g Cl}}{\cancel{\text{mol}\ ^{37}\text{Cl}}} = \frac{35.5\ \text{g Cl}}{\text{mol Cl}}$$

1.10-5. Ions

An ion is a charged particle. The charge is shown as a superscript after the symbol.

Atoms are neutral because they have an equal number of protons and electrons. However, electrons can be added to or removed from atoms to produce ***ions***.

- ***Cations*** are positively-charged ions because the number of protons exceeds the number of electrons.
- ***Anions*** are negatively-charged ions because the number of electrons exceeds the number of protons.

$$\text{Ion charge} = \text{number of protons} - \text{number of electrons}$$

The charge of the ion is given as a superscript with the number and then the sign as in the F^{1-} anion and the Ca^{2+} cation. (The “1” in 1− and 1+ ions is normally not written; however, it is included in this course because a superscript of “−” is too easily missed.) Remember that it is the number of protons that characterizes the element, and the number of protons does not change when an ion is formed from its elements. Thus, F and F^{1-} each have 9 protons, but F has 9 electrons while F^{1-} has 10. Similarly, Ca and Ca^{2+} each have 20 protons, but Ca has 20 electrons while Ca^{2+} has only 18 electrons.

1.10-6. Exercise on Particles in Ions

EXERCISE 1.17:

Indicate whether each species is an atom, a cation, or an anion, and give the number of electrons, protons, and neutrons present.

The atomic numbers of the elements can be found in the Elements resource.

$^{27}Al^{3+}$

Type:
- atom
- cation
- anion

Protons = __________ Neutrons = __________ Electrons = __________

$^{32}S^{2-}$

Type:
- atom
- cation
- anion

Protons = __________ Neutrons = __________ Electrons = __________

$^{56}Fe^{2+}$

Type:
- atom
- cation
- anion

Protons = __________ Neutrons = __________ Electrons = __________

^{80}Br

Type
- atom
- cation
- anion

Protons = __________ Neutrons = __________ Electrons = __________

1.10-7. Exercise on Writing Symbols

EXERCISE 1.18:

Determine the symbol for the listed species.
The atomic numbers of the elements can be found in the Elements resource.

6 protons, 8 electrons, 6 neutrons __________

28 protons, 26 electrons, 32 neutrons __________

32 protons, 32 electrons, 40 neutrons __________

15 protons, 18 electrons, 16 neutrons __________

1.10-8. Exercise on Protons, Neutrons and Electrons

EXERCISE 1.19:

Determine the number of protons, neutrons and electrons for the species below.

(a) $^{16}O^{2-}$

Protons = ______ Neutrons = ______ Electrons = ______

(b) $^{27}Al^{3+}$

Protons = ______ Neutrons = ______ Electrons = ______

(c) ^{25}Mg

Protons = ______ Neutrons = ______ Electrons = ______

(d) ^{19}F

Protons = ______ Neutrons = ______ Electrons = ______

(e) $^{48}Ti^{4+}$

Protons = ______ Neutrons = ______ Electrons = ______

1.11 Dimitri Mendeleev and The Periodic Law

Introduction

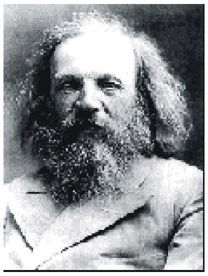
As the number of known elements and the properties grew, it became clear that there had to be some way of organizing all of the information if chemistry was to grow as a science. The organization came in what is now called the ***periodic law***. We now turn our study to this very powerful tool.

Objectives

- Define chemical groups and periods.
- Distinguish between metals and nonmetals based on their properties.
- Determine whether an element is a metal, a metalloid, or a nonmetal from its position in the periodic table.
- Describe the meaning of the numbers and symbols found in the periodic table.
- Distinguish a main group element from a transition element.
- Identify the alkali metals, the alkaline earth metals, the halogens, and the noble gases.

Periodic Trends

Arranged in the order of their atomic numbers, the elements exhibit periodicity in their chemical and physical properties.



Dimitri Mendeleev
1834-1907

Sixty years after Dalton published his atomic theory but 28 years before Thomson's discovery of the electron, Dimitri Mendeleev, a Russian chemist, was writing a textbook. As he tried to determine how best to break the book into chapters, he placed all of the elements in order of increasing atomic mass. He noticed that both the physical and chemical properties of the elements varied in a periodic manner. In order to maintain the periodicity, he had to reverse order of two elements (Te and I) and insert some spaces for yet undiscovered elements. His observations were summarized as the periodic law in 1869: The elements, if arranged in an order that closely approximates that of their atomic weights, exhibit an obvious periodicity in their properties.

The reason some elements had to be reversed is that it is the atomic number, not atomic weight, that characterizes an element, but atomic numbers were unknown when he discovered this relationship. Today, the periodic law is stated slightly differently.

- **Periodic law:** Arranged in the order of their atomic numbers, the elements exhibit periodicity in their chemical and physical properties.

Mendeleev arranged the elements in rows of a length such that elements of similar properties fell directly beneath one another. Elements that fell in the same column had similar properties and formed chemical families or ***groups***. Elements that fell in the same row formed a ***period***. The properties of the elements in a period changed gradually in going from left to right in the period. This behavior is demonstrated for a physical property (melting points) and a chemical property (formula of oxides) in the following section.

1.11-2. Examples

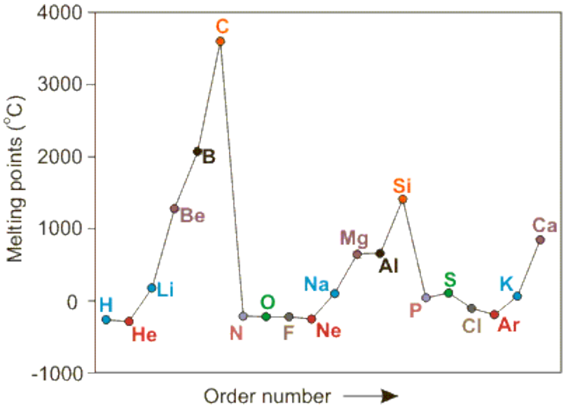


Figure 1.6: Periodicity of Physical Properties

Figure 1.6 shows a plot of the melting points of the elements. Elements in the same family or group share the same color. Note that K and Ar have been reversed from the order of mass.

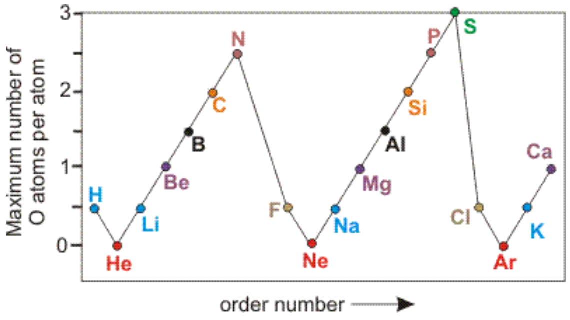


Figure 1.7: Periodicity of Chemical Properties

Figure 1.7 represents the **maximum** number of oxygen atoms that combine with one atom of each element. For example, nitrogen is at 2.5 because it forms an oxide with the formula N_2O_5, so there are 2.5 oxygen atoms for each nitrogen atom. Oxygen itself has been omitted. Also, K and Ar have been reversed from the order of mass.

1.11-3 Periodicity Exercise

EXERCISE 1.20:

Identify each formula.

What is the formula of potassium sulfide if that of sodium sulfide is Na_2S?

____

What is the formula of calcium chloride if that of sodium chloride is NaCl and that of aluminum chloride is $AlCl_3$?

____

What is the formula of fluoride of nitrogen if those of carbon and oxygen are CF_4 and OF_2?

____

What is the formula of aluminum oxide given the formulas Na_2O, MgO and SiO_2?

____

What is the formula of phosphorus oxide given the information in the previous question?

____

1.11-4. Metals and Nonmetals

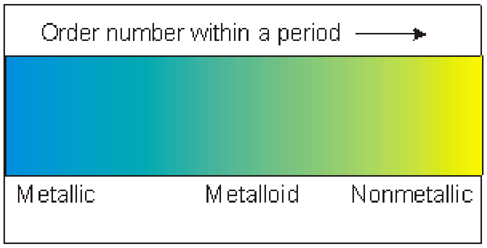
Elements on the left side of the periodic table are metallic, and elements on the right side are nonmetallic.

Elements fall into three classes:

- ***Metals*** tend to be lustrous (shiny) solids (only mercury is a liquid at room conditions) that are ductile (can be drawn into wires) and malleable (can be beaten into a form). Metals are good conductors of both heat and electricity. They comprise about 75% of the elements.
- ***Nonmetals*** tend to be gases or dull, brittle solids that are poor conductors of electricity or heat. Seventeen elements are nonmetals.

- ***Metalloids*** have properties intermediate between the metals and nonmetals. They are shiny but brittle. They are not good conductors of heat or electricity. Indeed, they are semiconductors. Eight elements are metalloids.

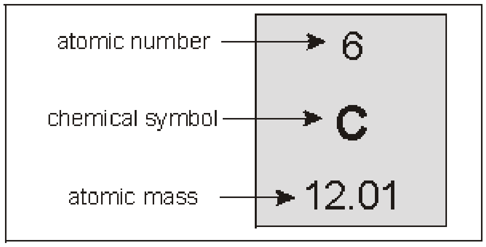
The elements on the left side of a period are metallic, those on the right are nonmetallic, and those lying between the two broader classes are metalloid. Thus, the elements start out metallic and become less metallic and more nonmetallic as you move from lower order number to higher order number (left to right) within a period.



In the above image, the gradual change of colors from blue to yellow represents the manner in which the elements change gradually in a period from metallic on the left to nonmetallic on the right. There are one or two elements between the two larger classes in each period that have properties of both. These elements are called metalloids.

1.11-5. Information Available in the Periodic Table

The periodic table not only gives the order of the elements, it also gives important information about each element. Indeed, some periodic tables can show a large amount of data for each element. However, the periodic table found in the resource titled Periodic Table gives the information as shown in the figure.



1.11-6. Other Periodic Tables

Mendeleev's arrangement of the elements has become known as the periodic chart or the ***periodic table*** and is the source of a great deal of information about the physical and chemical properties of the elements. The columns define groups, which consist of elements with similar properties. The rows define periods, which contain elements whose properties change gradually. There are two methods of numbering the groups in the periodic table, the American method, 1A–8A and 1B–8B, and the newer method, which numbers the groups as 1–18. Both numbering schemes are shown on the Periodic Table. However, we use the older method in discussions in this text.

The elements discussed in this course can also be classified in the following way:

- ***Main Group Elements*** are the elements in Groups 1A–8A or Groups 1–2 and 13–18.
- ***Transition Metals*** or ***Transition Elements*** are the elements in Groups 1B–8B or Groups 3–12.

A current periodic table that includes chemical symbols, atomic masses, and atomic numbers can be found by going to the "Resources Menu" above and selecting "Periodic Table." For more information about the elements, click "WebElements" below and to see the use of the elements in comic books, click "Comic Books."

1.11-7. Some Commonly Named Groups

Several chemical groups have common names that we will use throughout the course. Note that the last element in each group is radioactive and not included in the figure.

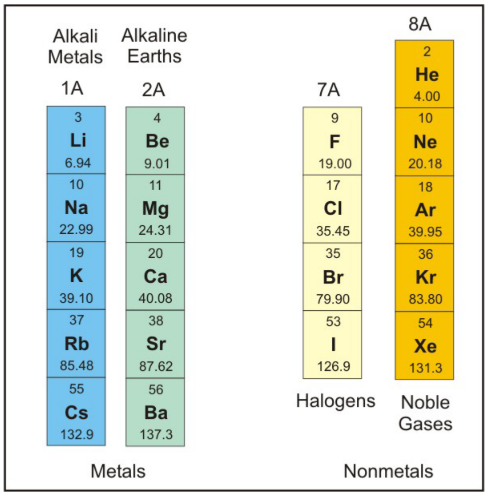


Figure 1.8: Common Named Chemical Groups

- ***Alkali metal***: a Group 1A element. They are the first members of a period. They are all very reactive metals and readily lose an electron to form +1 ions.
- ***Alkaline earth metal***: a Group 2A element. They are the second member of a period. They are all also reactive, but not as reactive as the alkali metals. The alkaline earth metals lose two electrons to form +2 ions.
- ***Halogen***: a Group 7A element. They are the next-to-last elements of each period. They all exist as diatomic nonmetals (the elements are all of the form X_2). They are reactive and tend to gain one electron to become −1 ions.
- ***Noble gas***: a Group 8A element. As their name implies, they are unreactive and are all gases. They are the last elements in each period.

1.11-8. Periodic Table Exercise

EXERCISE 1.21:

Use the Periodic Table to identify each element by symbol.

The halogen in the third period

____

The alkaline earth in the fourth period

____

The Group 4 metalloid in the fourth period

____

The noble gas in the fifth period

____

The third transition metal in the first row transition metals

____

1.12 Exercises and Solutions

Links to view either the end-of-chapter exercises or the solutions to the odd exercises are available in the HTML version of the chapter.

Chapter 2 – Quantum Theory

Introduction

Quantum theory explains our world at the atomic and molecular levels. A few brilliant scientists, who were trying to explain the results of experiments that defied the physics of the day, launched a theory that would change our view of not only the atom and the molecule, but of the universe as well. In this chapter, some of the key experiments leading to quantum theory are described, and then the theory is applied to the electrons in an atom.

2.1 The Nature of Light

Introduction

Although we do not see atoms and molecules, much of our understanding of them is based on the way they interact with light. This lesson deals with the nature of light.

Objectives

- Describe the relationship between the speed, wavelength, and frequency of a light wave.
- Determine the relative wavelengths and frequencies of two light waves given the region of the electromagnetic spectrum in which they lie.

2.1-1. Wavelength

Light is electromagnetic radiation; that is, it is an oscillating electric and magnetic field that travels through space at a constant speed, $c = 2.998 \times 10^8$ m/s, the speed of light. The electric and magnetic fields are perpendicular to one another, but only the electric field is shown in the figures in this section.

A light wave is characterized by its amplitude, which is the distance between the valley and the peak of the wave, and its ***wavelength***, λ, which is the distance between two adjacent maxima or minima in the electric (or magnetic) field. The amplitude indicates the brightness of the light, and the wavelength tells us what kind of light it is.

Visible light, the light visible to the human eye, is only a small fraction of all electromagnetic radiation, and the different colors that we see differ because they have different wavelengths. Red light has the longest wavelength in the visible region and violet light has the shortest.

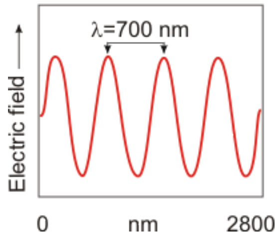


Figure 2.1a: A 2800-nm Segment of Red Light Red light has the longest wavelength of visible light. The red wave shown here has a wavelength of 700 nm. The 2800-nm segment contains four wavelengths of red light.

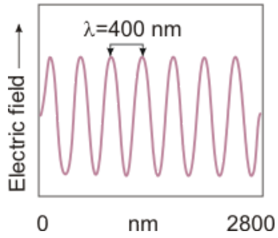


Figure 2.1b: A 2800-nm Segment of Violet Light Violet light has the shortest wavelength of visible light. The violet wave shown here has a wavelength of 400 nm. The 2800-nm segment contains seven wavelengths of violet light.

Note that both figures show a segment of wave that is 2800 nm in length. However, the two segments contain a different number of wavelengths. Thus, the waves are more *frequent* in the violet wave. Indeed, this property, called the frequency of the light, is another very important characteristic of the light wave that is taken up next.

2.1-2. Frequency

The product of the wavelength and frequency of a light wave equals the speed of light.

Electromagnetic radiation can also be characterized by its ***frequency***, ν. The frequency of a light wave is the number of oscillations of the electromagnetic field per second (i.e., the number of waves that pass a point per second). How many waves that pass the point depends upon how fast the wave is moving and how close the waves are to one another. All light waves travel at the same speed (c) and the distance between the waves is the wavelength (λ). Thus, a shorter wavelength means closely packed waves, which means that more waves will pass per second (i.e., the greater the frequency of the light). The speed (c), frequency (ν), and the wavelength (λ) of light are related by the following expression.

$$c = \nu\lambda \tag{2.1}$$

As shown in the above expression, the frequency of a light wave increases as its wavelength decreases. This is demonstrated below where the frequencies of red and violet light are compared.

EXAMPLE:

As an example, consider the frequencies of violet ($\lambda = 400$ nm $= 4 \times 10^{-7}$ m) and red light ($\lambda = 700$ nm $= 7.00 \times 10^{-7}$ m), which would be calculated as follows.

$$\nu_{\text{violet}} = \frac{c}{\lambda} = \frac{3.00 \times 10^{8}\ \text{m} \cdot\ \text{s}^{-1}}{4.00 \times 10^{-7}\ \text{m}} = 7.50 \times 10^{14}\ \text{s}^{-1}$$

$$\nu_{\text{red}} = \frac{c}{\lambda} = \frac{3.00 \times 10^{8}\ \text{m} \cdot\ \text{s}^{-1}}{7.00 \times 10^{-7}\ \text{m}} = 4.29 \times 10^{14}\ \text{s}^{-1}$$

2.1-3. Electromagnetic Spectrum

An electromagnetic ***spectrum*** is a display of the component colors of a light beam, separated by their wavelengths. Raindrops can sometimes separate the component colors of white light by their wavelengths to produce a rainbow, which is a display of the spectrum of white light. Because the colors all merge into one another continuously, the resulting spectrum is called a ***continuous spectrum***. A continuous spectrum can also be obtained by dispersing white light through a prism or from a grating. It should be noted that the visible region of the electromagnetic spectrum (that portion the eye can perceive) is but a small part of the entire spectrum. Further information about the EM spectrum can be found at http://imagine.gsfc.nasa.gov/docs/science/know_l1/emspectrum.html[3].

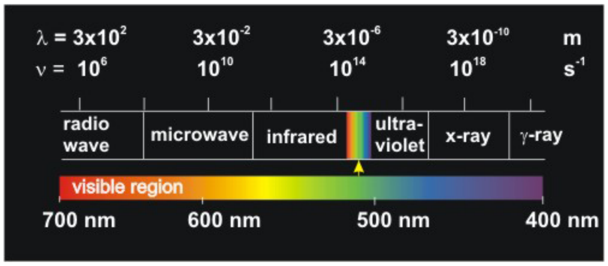


Figure 2.2: The Electromagnetic (EM) Spectrum The visible region (400 − 700 nm), which is a very small portion of the spectrum, is expanded.

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[3] http://imagine.gsfc.nasa.gov/docs/science/know_l1/emspectrum.html

2.2 Quantization

Introduction

In this lesson, we introduce the concept of quantization, i.e., that energy comes in small packets called quanta.

Objectives

- Define the terms *quantized* and *photon*.
- Calculate the energy of a photon from its frequency.
- Explain what is meant by 'wave-particle duality.'
- Define continuous spectrum and describe the spectrum of white light.
- Use the Rydberg equation to determine the frequency of a spectral line from the quantum numbers of the levels involved.

Blackbody Radiation

2.2-1. Blackbody Radiation Experiment

All objects emit electromagnetic waves, and as their temperature increases, so too do the total intensity and the average frequency of the radiation. At sufficiently high temperatures, a significant portion of the radiation is in the visible region of the spectrum. For example, a burner in an electric oven emits invisible but warm infrared radiation on a low setting, but it becomes 'red hot' on a high setting as it emits both infrared and visible radiation. Similarly, the tungsten filament of a light bulb becomes 'white hot' because all of the colors in the visible region are being emitted. This emission of electromagnetic waves from a warm body is called blackbody radiation.

A video or simulation is available online.

2.2-2. Blackbody Radiation Explanation

A photon is a bundle of light energy, which is proportional to the frequency of the light.

The model used by physicists in the late 1800s assumed that the energy of a wave depended only upon its amplitude (intensity), so each light wave that was emitted by a blackbody radiator was thought to contain the same amount of energy. Since an infinite number of waves were allowed and each wave had the same energy, the model predicted that there should be an infinite amount of energy given off!

Max Planck discovered that the infinite energy dilemma was removed if the energy of a wave is quantized. That is, the total energy of a wave could not be varied continuously because it is composed of many tiny bundles of energy called quanta. Quanta of light are called photons. Thus, a light wave is comprised of photons much like a wave of water is comprised of water molecules except that photons do not have mass. The energy of one ***quantum*** of light (photon) depends only upon its frequency. That is,

$$E = h\nu \tag{2.2}$$

where $h = 6.626 \times 10^{-34}$ J-s is called ***Planck's constant***. The amount of energy in a wave that contains n quanta (photons) is then the following.

$$E = nh\nu$$

Planck's model for the quantization of wave energy correctly accounted for blackbody radiation, but the only reason he could offer for proposing this remarkable behavior was that it worked.

2.2-3. Photon Energy Exercise

EXERCISE 2.1:

What are the energies of the following in Joules? Express small numbers with the e format, e.g., 1.23e-12.

a photon red with a frequency of 4.60e14 s^{-1} ______________ J

a mole of photons with frequency of 4.60e14 s^{-1} ______________ J

The Photoelectric Effect

2.2-4. The Photoelectric Effect Experiment

Another observation of the late 1800s that could not be understood with the classical picture of light was that certain metals, when irradiated with light, ejected electrons. The kinetic energy of the electrons depended only upon the metal and the frequency of light. Increasing the intensity of the light increases the number of electrons that are ejected, but not their kinetic energy. For these metals, there is a minimum frequency below which no electrons are ejected, no matter how intense the light. This minimum frequency is called the threshold frequency of the metal, ν_o. As shown in Figure 2.3, a plot of the ejected electron's kinetic energy versus the frequency of the light striking the metal is a straight line.

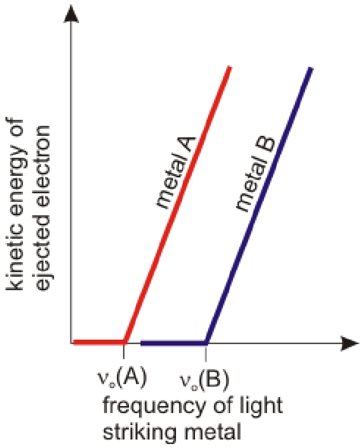

Figure 2.3: Photoelectric Effect No electrons are ejected when a metal is irradiated with light at frequencies below the threshold frequency (ν_o). At frequencies above the threshold frequency of the metal, electrons are ejected with a kinetic energy that increases linearly with the frequency of the light.

2.2-5. The Photoelectric Effect Explanation

In order to explain the photoelectric effect, Albert Einstein used Planck's hypothesis that light was composed of energy quanta. He proposed that light consisted of particles of energy, which we now call ***photons***, each with an energy $h\nu$. He reasoned that, if the electrons are bound to a metal by an energy, W, then the threshold frequency for electron ejection from a metal (ν_o) is that frequency for which $h\nu_o = W$. When the frequency (energy) of the photon is less than the threshold frequency of the metal, electrons cannot be removed because the energy that binds them to the metal is greater than the energy of the photon. However, when the energy of each photon exceeds the energy that binds the electron to the metal ($h\nu > W$), the energy of the photon is transferred to the electron. A portion of the photon's energy, W, is used to overcome the potential energy binding the electron to the metal and the excess energy is converted into the kinetic energy of the ejected electron (KE).

$$KE = h\nu - W = h\nu - h\nu_o$$

According to Einstein, the intensity of a light wave reflects the number of photons that it contains. A beam that contains n photons has a total energy of $nh\nu$, but when light interacts with matter, it does so one photon at a time. Thus, it is the energy of each photon that dictates the energy of a molecular process that is initiated by the light, while the number of events that occur per unit time, i.e., the rate of the process is dictated by the intensity of the light.

Planck and Einstein had shown that light consisted of particles of energy called photons, but classical experiments showed that light is also a wave. This property of behaving as both a particle and a wave is called ***wave-particle duality***.

Atomic Spectra

2.2-6. Continuous Spectrum

All wavelengths of visible light are present in white light, so when white light is dispersed as shown in Figure 2.4, the colors merge into one another continuously to produce a continuous spectrum.

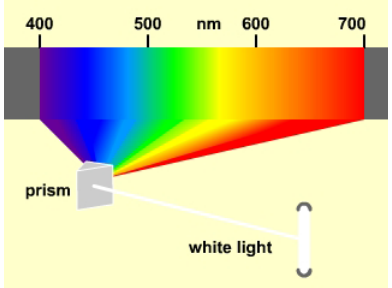

Figure 2.4

2.2-7. Gas Discharge Tubes

A gas discharge tube is an evacuated tube that has been filled with a gas at low pressure. When high-energy electrons are passed through a discharge tube (a high voltage is placed across it), the tube glows with a color that is characteristic of the gas. As shown in Figure 2.5, a neon light has a characteristic red color, while a gas discharge tube filled with hydrogen glows with purple-blue color.

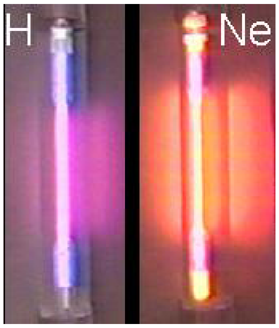

Figure 2.5

The color of the glow from a hydrogen discharge tube is not white, so not all wavelengths of visible light are present. This means that when this light is dispersed, many of the wavelengths present in the continuous spectrum of white light are missing. We examine the hydrogen spectrum in the following section.

2.2-8. Line Spectra

Atomic spectra are line spectra.

The colors observed in the spectrum of a gas discharge tube do not merge into one another. Instead the spectra consist of series of lines. Since the colors are observed as lines, the spectra are called ***line spectra***. The purple-blue color of the hydrogen discharge is due to the presence of light of only four different wavelengths of visible light as shown in Figure 2.6.

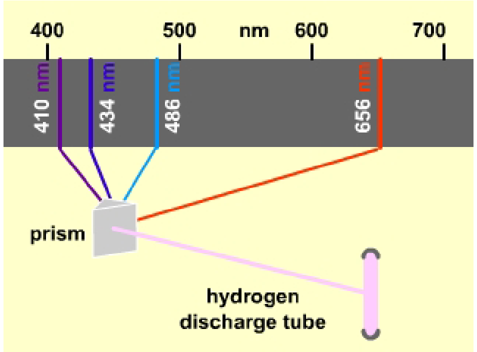

Figure 2.6: Line Spectrum of Hydrogen When the glow from a hydrogen discharge tube is focused down to the image of a slit and passed through a prism, it is broken down into four component wavelengths: 410 nm (violet), 434 nm (blue), 486 nm (green), and 656 nm (red). The four colors are observed as lines in the visible spectrum of hydrogen. However, there are over forty such lines observed throughout the ultraviolet, the visible, and the infrared.

Each element has a characteristic spectrum that can be used to identify the element. Visit a site at the University of Oregon[4] to view line spectra of the elements. The default is the absorption spectrum, so be sure to select 'emission'. Then click on an element. You can even determine the wavelengths of the lines by clicking in the spectrum. The number that appears is in ***Angstroms***, so divide it by 10 to get nanometers.

1. Look at Ne and compare the spectrum to the color of a neon light.
2. Verify that Lithium has a strong line at 610 nm.
3. Examine the spectra of the alkali metals. What general statement can be made about how the spectra of the atoms change as you proceed down a group?

2.2-9. Calculating the Line Spectrum of Hydrogen

Scientists did not understand the origin of line spectra, but Johannes Rydberg found a relatively simple mathematical expression, called the ***Rydberg equation*** and shown as Equation 2.3a below, that allowed him to calculate the frequency of every line in the hydrogen spectrum (over 40 lines). Multiplication of frequency in the Rydberg equation by Planck's constant yields the energy of the emitted photon in joules ($E = h\nu$) as shown in Equation 2.3b.

$$\nu = R_\mathrm{H}\left(\frac{1}{n_\mathrm{lo}^2} - \frac{1}{n_\mathrm{hi}^2}\right) = 3.290 \times 10^{15}\left(\frac{1}{n_\mathrm{lo}^2} - \frac{1}{n_\mathrm{hi}^2}\right)\ \mathrm{s}^{-1} \tag{2.3a}$$

$$E_\mathrm{photon} = h\nu = hR_\mathrm{H} = \left(\frac{1}{n_\mathrm{lo}^2} - \frac{1}{n_\mathrm{hi}^2}\right) = 2.180 \times 10^{-18}\left(\frac{1}{n_\mathrm{lo}^2} - \frac{1}{n_\mathrm{hi}^2}\right)\ \mathrm{J} \tag{2.3b}$$

- ν is the frequency of the emitted photon in s^{-1}.
- E_photon is the energy of the emitted photon with frequency ν.
- $n_\mathrm{lo} < n_\mathrm{hi}$ are positive integers.
- $R_\mathrm{H} = 3.290 \times 10^{15}\ \mathrm{s}^{-1}$ is the Rydberg constant for hydrogen.

2.2-10. Rydberg Exercise

EXERCISE 2.2:

Use Equation 2.3a to determine the frequencies and wavelengths of the following spectral lines. Indicate whether each line falls in the infrared, visible, or ultraviolet region of the electromagnetic spectrum.

$n_\mathrm{lo} = 2$, $n_\mathrm{hi} = 4$ $\nu =$ ________________ s^{-1}

$n_\mathrm{lo} = 2$, $n_\mathrm{hi} = 4$ $\lambda =$ ________________ nm

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[4] http://jersey.uoregon.edu/vlab/elements/Elements.html

$n_{\mathrm{lo}} = 2$, $n_{\mathrm{hi}} = 4$ region:
infrared
visible
ultraviolet

$n_{\mathrm{lo}} = 1$, $n_{\mathrm{hi}} = 2$ $\nu =$ ______________ s^{-1}

$n_{\mathrm{lo}} = 1$, $n_{\mathrm{hi}} = 2$ $\lambda =$ ______________ nm

$n_{\mathrm{lo}} = 1$, $n_{\mathrm{hi}} = 2$ region:
infrared
visible
ultraviolet

$n_{\mathrm{lo}} = 4$, $n_{\mathrm{hi}} = 7$ $\nu =$ ______________ s^{-1}

$n_{\mathrm{lo}} = 4$, $n_{\mathrm{hi}} = 7$ $\lambda =$ ______________ nm

$n_{\mathrm{lo}} = 4$, $n_{\mathrm{hi}} = 7$ region:
infrared
visible
ultraviolet

2.3 Bohr Model

Introduction

In the Rutherford model, electrons moved in circular orbits, but particles tend to move in straight lines not circles, so circular orbits require a force, called the centripetal force, to pull the orbiting particle toward the center. Earth is kept in its orbit by the gravitational attraction of the sun, and the electron is kept in its orbit by the Coulombic attraction of the nucleus. However, there was one major flaw with these orbiting electrons: the orbit would be unstable because a charged particle moving in this way would radiate energy, which would cause it to spiral into the nucleus, but clearly that was not the case in the hydrogen atom!

Prerequisites

- 1.8 Electromagnetism and Coulomb's Law (Relate the energy of interaction between two charged particles to the distance separating them.)

Objectives

- Relate energy of an electron to its n quantum number and the nuclear charge.
- Draw an energy level diagram for the hydrogen atom that shows the relative separations between the energy levels.

2.3-1. Bohr Radius

Note that the discussions of this section all ignore interactions between electrons, so they pertain only to systems that involve a **single** electron interacting with a nucleus with Z protons. Thus, the discussions are relevant to a H atom ($Z = 1$),but they do not apply to other atoms because all other atoms contain more than one electron. However, they do apply to the one-electron ions of other atoms such as He^{1+}, Li^{2+}, Be^{3+}, etc.

Niels Bohr[5], a Danish physicist, postulated the reason for the stability of the atom: the electron remains in its orbit because its angular momentum is quantized. He proposed that the angular momentum was proportional to an integer, called the principal quantum number, n ($n = 1, 2, 3, 4, \cdots$).By forbidding $n = 0$, he assured that the electron always had some angular momentum, which stabilized the orbit and kept the electron moving in its circular path! He used Coulomb's Law to evaluate the electron-nuclear attraction ($\mathrm{F_e}$ in Figure 2.7) and the quantized angular momentum to determine the centripetal force ($\mathrm{F_c}$ in Figure 2.7). He then equated the two forces to determine the stable radii of rotation to be the following.

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[5] http://www-groups.dcs.st-and.ac.uk/~history/Mathematicians/Bohr_Niels.html

$$r_n = (5.292 \times 10^{-11}) \left(\frac{n^2}{z}\right) \text{ m} = (52.92) \left(\frac{n^2}{z}\right) \text{ pm} \tag{2.4}$$

The n^2 dependence expressed of the radius that appears in the equation is shown in Figure 2.7. The constant (52.92 pm) was calculated from known physical constants, such as Planck's constant, and the mass and charge of the electron and the proton. Z is the atomic number (number of positive charges in the nucleus). For a hydrogen atom, $n = 1$ and $Z = 1$, so the distance between the electron and the proton was determined to be $r_1 = 52.92$ pm, which is called the Bohr radius.

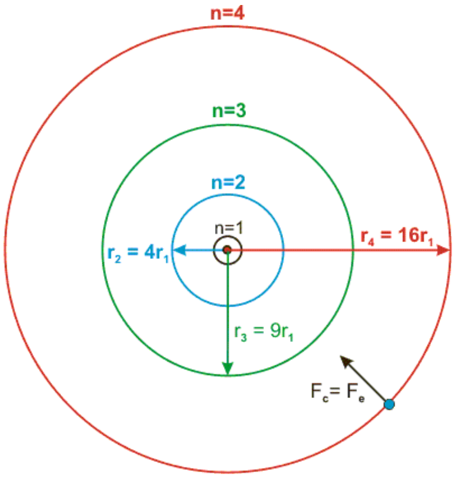

Figure 2.7: Relative Radii of First Four Bohr Orbits $r_1 = 52.92$ pm, and $r_n = n^2 r_1$

2.3-2. Electron Energy

The energy of an electron in an atom is quantized, so electrons are said to occupy energy levels.

The total energy of the electron (E) is the sum of its kinetic energy (KE) and its potential energy (U); i.e., $E = KE + U$. The potential energy of the electron in a one-electron system arises from its Coulombic energy of interaction with the nucleus, and its kinetic energy from its circular motion about the nucleus. However, the fact that the centripetal force resulted from the Coulombic force required that the kinetic energy be one-half of the Coulombic energy but opposite in sign (i.e., $KE = -1/2U$). The total energy is then $E = KE + U = -1/2U + U = 1/2U$. The Coulombic energy of interaction between the nucleus and the electron is given by Coulomb's Law (Equation 1.2), so the total energy of an electron in the n^{th} orbit is the following.

$$E_n = \frac{1}{2}U_n = \frac{1}{2}\left(\frac{kq_e q_N}{\epsilon r_n}\right)$$

The basic unit of charge is $q = 1.602 \times 10^{-18}$ C, so the charge on an electron is $q_e = -q$ and the charge on a nucleus with Z protons is $q_N = +Zq$. The value of ϵ in a vacuum is one, and r is the radius of the n^{th} orbit as given in Equation 2.4. Substitution of these known quantities into the preceding energy expression yields the total energy of an electron in the n^{th} orbit in terms of the n quantum number.

$$E_n = (-2.180 \times 10^{-18}) \left(\frac{Z^2}{n^2}\right) \text{ J} = (-hR_{\text{H}}) \left(\frac{Z^2}{n^2}\right) \tag{2.5}$$

The constant determined by Bohr, 2.180×10^{-18} J, was the same as the experimental value determined by Rydberg for hR_{H} in Equation 2.3b (i.e., $2.180 \times 10^{-18} = hR_{\text{H}}$). This agreement with experiment was strong support for the Bohr model.

The energy associated with each value of n in Equation 2.5 is called an ***energy level***. In the case of a hydrogen atom, $Z = 1$, so the energy of the $n = 1$level is -2.180×10^{-18} J, and that of the $n = 2$ level is $-2.180 \times 10^{-18}(1^2/2^2) = -5.450 \times 10^{-19}$ J. The energies are negative because the energy of an electron in an atom is less than that of a free electron.

2.3-3. Bohr Model Exercise

EXERCISE 2.3:

Use the Bohr model to determine the orbtial radius and energy of an electron in the $n = 1$ level of a Li^{2+} ion. We use the +2 ion because the Bohr model only applies to species with one electron.

$Z =$ ______________ $n =$ ______________

$r_n =$ ______________ pm $E_n =$ ______________ J

2.3-4. Energy Level Diagram

Atomic spectra can be understood in terms of the electron moving from one energy level into another, which is referred to as an ***electronic transition***. If n_{hi} is the higher quantum number and n_{lo} is the lower quantum number, then the energy difference between the two energy levels is $\Delta E = E_{n_{\text{hi}}} - E_{n_{\text{lo}}}$, which can be determined with Equation 2.5 to be the following.

$$\Delta E_{\text{atom}} = E_{n_{\text{hi}}} - E_{n_{\text{lo}}} = -hR_{\text{H}}Z^2\left(\frac{1}{n_{\text{hi}}^2} - \frac{1}{n_{\text{lo}}^2}\right) = hR_{\text{H}}Z^2\left(\frac{1}{n_{\text{lo}}^2} - \frac{1}{n_{\text{hi}}^2}\right) \tag{2.6}$$

ΔE_{atom} in Equation 2.6 is identical to E_{photon} in the empirical Equation 2.3b. Thus, an electron's energy can change by ΔE_{atom} by either absorbing of emitting a photon with an energy of E_{photon}.

- ***Absorption***: a photon is absorbed if n_{lo} is the initial level. The absorption of energy increases the energy of the electron to the level of n_{hi}.
- ***Emission***: a photon is emitted if n_{hi} is the initial level. The emission of energy decreases the energy of the electron to the level of n_{lo}.

The electronic transitions resulting in some of the 40 lines in the emission spectrum of a hydrogen atom are represented with the vertical arrows in Figure 2.8. The lowest energy line in the visible series occurs for $n_{\text{lo}} = 2$ and $n_{\text{hi}} = 3$, which is designated as the $n = 3ton = 2$ transition (3 → 2). The violet line in the H atom spectrum is the highest energy line in the visible region; it results from the 6 → 2 transition. Note that the lines would correspond to absorptions if the arrows were pointed in the opposite direction. For example, the 2 → 3 transition is an absorption because the initial level is n_{lo}. Note the following for hydrogen atom spectrum:

- $n_{\text{lo}} = 1$ for all lines in the ultraviolet region.
- $n_{\text{lo}} = 2$ for all lines in the visible region.

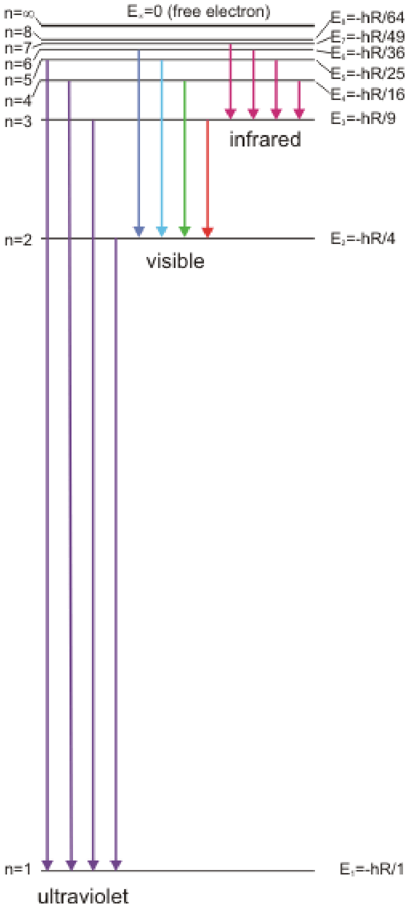

Figure 2.8: Energy Level Diagram for Hydrogen

2.3-5. Color

In a gas discharge tube, a high energy electron collides with an atom and transfers some of its energy to an electron in the atom, exciting the electron into a higher energy level (energy is absorbed). However, electrons always seek the lowest energy level, so the excited electron soon returns to a lower energy level. When it does so, it must give up all or some of the energy that it absorbed initially. Many of the electrons that are excited in this manner give up their energy by emitting photons. Only a fraction of the emitted photons fall in the visible region of the spectrum, but they are the ones that produce the glow in the tube.

Light is a form of energy that results from changes that occur during atomic and molecular processes, and its frequency depends upon the type of process. For example, molecules absorb microwave radiation when they rotate, and they absorb infrared radiation when their atoms vibrate back and forth against their bonds. Visible light originates in electronic transitions; all color is the result of these transitions. A red shirt appears red because it reflects the red portion of white light and absorbs the green portion. The fabric of the shirt contains dye molecules that have electrons that absorb green light when they undergo electronic transitions between energy levels. The levels, however, are not separated by an energy equal to the energy of red photons, so the red photons are reflected and not absorbed. Our eyes perceive the reflected red photons but not the green ones that are absorbed by the shirt.

2.4 Quantum Theory

Introduction

The theory that explains blackbody radiation, the photoelectric effect, and line spectra is called quantum theory. Quantum theory completely changed the way we think about matter. This lesson completes our study of the evolution of chemical theory from Lavoisier's introduction of elements and compounds to where it is today.

Objectives

- Explain what is meant by *electron density* and why it is used instead of electron position.

2.4-1. Vibrating Strings

The reason behind quantization was the cause of much discussion, and the answer was finally presented by a graduate student in his Ph.D. thesis. Louis deBroglie[6] recognized a similarity between the behavior of electrons and that of a vibrating string!

Plucking a string of length L that is tied at both ends produces standing waves as shown in Figure 2.9. Since the string is tied down at each end, there must be an integral number of half-wavelengths in the distance L, i.e., the wavelength of each wave (λ) must obey the relationship $L = n \times (\lambda/2)$ or $\lambda = 2L/n$. The various values of the integer n define the harmonics. Note that $L = 0$ (no string) when $n = 0$, so n cannot be zero. This is analogous to the Bohr model where the n quantum number is a positive, nonzero integer.

The points where the waves have zero amplitude are called **nodes** (indicated by arrows for $n = 2$ and $n = 3$). Each wave has $(n - 1)$ nodes, not counting the two ends.

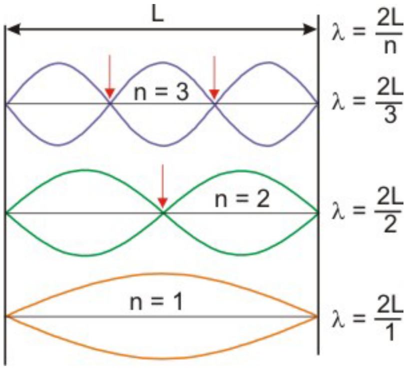

Figure 2.9: Standing Waves in a Vibrating String If the length of the string is L, then the wavelength of each wave is $\lambda = 2L/n$, where n is a nonzero integer. The number of nodes, points of zero amplitude, present in each wave as dictated by the red arrows is $n - 1$.

2.4-2. Quantum Theory

Electrons can behave as either particles or waves.

deBroglie concluded that the quantization proposed by Bohr resulted because the electron has wave properties. His hypothesis was later confirmed by experiment. Like light, the electron had to be treated as both a particle and a wave! The hypothesis seemed crazy, even Einstein said so. “But, it is really sound!” Einstein admitted. The electron’s behavior is dictated by the experiment. Thus, Thomson and Millikan measured the charge and mass of a particle because their experiments were setup to detect particles, but other experiments demonstrated that electrons are diffracted just like waves.

The fact that the electron has wave properties imparts some uncertainty about its position and trajectory. Thus, we cannot predict exactly where an electron will be at any given time. Instead, we must talk about the probability that the electron will be found in some region of space, and the larger the region of space, the greater the probability that the electron will be found in it. As a result, we usually refer to regions of ***electron density*** rather than the position of the electrons. The electron density is high in regions where the probability of finding an electron is high.

Visit the IBM site[7] to see the effect of electrons interfering with each other in some great STM (scanning tunneling microscopy) images.

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[6] http://www-groups.dcs.st-and.ac.uk/~history/Mathematicians/Broglie.html

[7] http://www.almaden.ibm.com/vis/stm/stm.html

2.5 The Quantum Numbers

Introduction

Electrons must be treated like waves in modern quantum theory, and their full description requires four numbers called quantum numbers. In this section, we identify the four quantum numbers for an electron in an atom and explain the relationships between them.

Objectives

- State the restrictions on each of the quantum numbers.
- Indicate the information available from each quantum number.
- Differentiate between an acceptable and unacceptable sets of quantum numbers and correct unacceptable sets.
- Give the letter used to describe each value of the l quantum number.
- Indicate the relative energies of several sublevels given their n and l quantum numbers.

2.5-1. Quantum Numbers and Orbital Energy Video

A video or simulation is available online.

2.5-2. Introduction

Four quantum numbers are required for the complete description of an electron in an atom.

In 1926, Erwin Schrödinger applied the wave equation of a vibrating string to the electron. Solving the wave equation produces mathematical functions called ***wave functions***. A wave function contains all of the pertinent information about the electron in the atom. Thus, an electron is treated mathematically like a vibrating string in modern quantum theory, and its full description requires four ***quantum numbers***. With these four quantum numbers and their relationships to one another, a convincing picture of the electronic structure of the atom can be drawn, one that explains both atomic spectra and chemical periodicity.

The four quantum numbers required to fully characterize an electron are: n, l, m_l, and m_s. The relationships between the quantum number, which are discussed below, are responsible for the periodicity of the chemical properties of the elements.

2.5-3. n Quantum Number

The n quantum number dictates the energy level of the electron.

n is the **principal quantum number**.

- The ***principal quantum number*** dictates the energy ***level*** of the electron, so it is the *primary*, but not sole indicator of the electron's energy.
- n also indicates the *average* distance from the nucleus. On the average, electrons with high n quantum numbers are farther from the nucleus than those with lower n quantum numbers.
- Restrictions on n: n must be a nonzero, positive integer, i.e., $n = 1, 2, 3, \cdots, \infty$.

2.5-4. l Quantum Number

The n and l quantum numbers determine an electron's sublevel, which determines the electron's energy.

l is the **angular momentum quantum number**.

- n and l define the ***sublevel***. The energy of the electron depends upon the sublevel it occupies.
- Restrictions on l: l is an integer such that $0 \leq l < n$ in any sublevel.
- There are n sublevels in each level. For example, if $n = 3$ level, then l can be 0, 1, or 2 for a total of three sublevels.

The following letters are normally used in lieu of the l quantum number to indicate a sublevel.

l quantum number	letter designation
0	s
1	p
2	d
3	f

Note: the letters are derived from the appearance of the lines in an atomic line spectrum: s = sharp, p = principle, d = diffuse, f = fundamental. Sublevels with $l > 3$ are labeled in order as g, h, i, ...

2.5-5. m_l Quantum Number

n, l, and m_l specify the electron's orbital.

m_l is the **magnetic orbital quantum number**.

- n, l, and m_l specify the ***orbital***.
- l and m_l dictate the shape of the orbital, while n defines its size.
- Restrictions: the allowed values of m_l depend upon the sublevel. $-l \leq m_l \leq +l$, so there are $2l + 1$ orbitals in a sublevel.

Electrons reside in orbitals that are characterized by a unique set of three quantum numbers (n, l and m_l). The restrictions on the quantum numbers dictate the number of orbitals in a sublevel and the number of sublevels in a level. Consider the case of the $n = 3$ level shown in Figure 2.10, where each line represents one orbital. Because $n = 3$, there are three sublevels: $l = 0, 1,$ and 2,which correspond to the 3s, 3p and 3d sublevels, respectively. In an $l = 0$ sublevel, there can be only one value of m_l and, therefore, only one orbital ($m_l = 0$). This is the 3s orbital. In an $l = 1$ sublevel, there are three allowed values of m_l (-1, 0, $+1$) and, consequently, three orbitals. These three orbitals are the 3p orbitals. In the $l = 2$ sublevel, $m_l = -2, -1, 0, +1,$ and $+2$ for the five orbitals in the 3d sublevel. Thus, in the $n = 3$ level, there are three sublevels and nine orbitals.

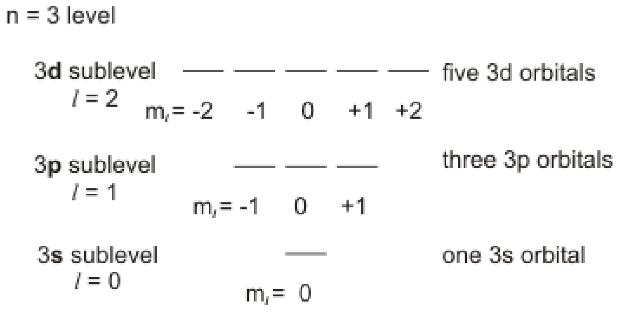


Figure 2.10: Sublevels and Orbitals of the $n = 3$ Level

2.5-6. m_s Quantum Number

m_s determines the electron's spin. All magnetic fields are due to spin.

m_s is the **spin quantum number** that has values of $+1/2$ and $-1/2$ only. Electron spin is responsible for magnetic fields. Although the "spin" property of an electron is a relativistic one, it is common to represent it with a classical analog because a charge moving in a circle does generate a magnetic field. Indeed, the circular motion of electrons is the basis for electromagnets.

A video or simulation is available online.

The wave equation developed by Schrödinger required only the n, l and m_l quantum numbers, but many details of the emission spectra of the atoms could not be explained using only this set of quantum numbers. In addition, silver atoms that are passed through a magnetic field are divided into two beams. All of these problems could be explained only if the electron had magnetic properties, which required a new quantum number, the electron spin. Electron spin is a quantum mechanical effect that is as much a property of the electron as is its charge. However, a simple macroscopic analogy is often used to describe this quantum mechanical effect. In the analogy (Figure 2.11), electron spin results from the rotation of the electron about its axis (analogous to the 24 hour rotation of the Earth about its axis). The rate of rotation is the same for all electrons, but there are two different directions of rotation, which are distinguished by the spin quantum number, m_s, which has only two possible values: $m_s = +1/2$ and $m_s = -1/2$. All magnetic properties are attributed to electron spin, so it is often represented as the spin of the electron about its own axis in a clockwise ($m_s = +1/2$) or counterclockwise ($m_s = -1/2$) direction because a magnetic field is produced by a charge moving in a circular path. Thus, the 'spinning charge' can be thought to generate a magnetic field as indicated by the arrows in Figure 2.11. The arrow representing the magnetic field is often used to represent the m_s quantum number of the electron. An up arrow ('up spin') is used to indicate an electron with $m_s = +1/2$ and a down arrow ('down spin') indicates an electron with $m_s = -1/2$.

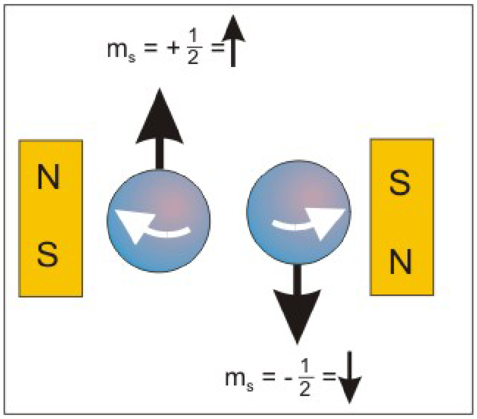


Figure 2.11 The two values of m_s are represented with up or down arrows.

2.5-7. Energy Levels and Quantum Numbers

Sublevels are named by giving the n quantum number followed by the letter that designates the l quantum number.

Sublevels are named by giving the n quantum number followed by the letter that designates the l quantum number. Thus, the sublevel with $n = 3$ and $l = 2$ is referred to as the 3d sublevel.

The relative energies of the sublevels can be determined from the following:

- They increase with the value of $(n + l)$ for the sublevel.
- The energies of sublevels with the same value of $(n + l)$ increase with increasing n.

2.5-8. Quantum Number Exercise

EXERCISE 2.4:

What are the n and l quantum numbers for a 6f electron?

$n =$ ______________

$l =$ ______________

What is the designation of each of the following sublevels?

$n = 3$, $l = 2$ ________________

$n = 5$, $l = 1$ ________________

$n = 6$, $l = 3$ ________________

$n = 4$, $l = 0$ ________________

How many sublevels are in an $n = 4$ level?

____

Which sublevel is at lower energy?
4s
3d

Which sublevel is at lower energy?
4p
3d

2.5-9. Quantum Number Restrictions Exercise

EXERCISE 2.5:

The following sets of quantum numbers are not valid but can be made so by correcting one value. Identify the invalid quantum number as n, l, m_l, or m_s in each and supply an acceptable value. If there is more than one acceptable value enter the lowest, positive value or zero.

$n = 3$, $l = 3$, $m_l = -3$, $m_s = +1/2$
invalid number:
n
l
m_l
m_s
acceptable value ________________

$n = 75$, $l = 74$, $m_l = 0$, $m_s = 0$
invalid quantum number:
n
l
m_l
m_s
acceptable value ________________

$n = 6$, $l = -5$, $m_l = -5$, $m_s = -1/2$
invalid quantum number:
n
l
m_l
m_s
acceptable value ________________

$n = 2$, $l = 0$, $m_l = 2$, $m_s = +1/2$
invalid quantum number:
n
l
m_l
m_s
acceptable value ________________

2.6 Orbital Shapes and Sizes

Introduction

Orbitals are at the heart of chemistry because it is the interaction between orbitals that produces chemical bonds. Mathematically, an orbital is a wave function with specified values for n, l, and m_l. Like other functions, they can be positive or negative, and the sign of the orbital will be important when we combine them to produce molecular orbitals in Chapter 6. In this section, we consider the shapes of only the s and p orbitals because they are the only orbital types that will be used in the next several chapters.

Objectives

- Draw s orbitals.
- Draw p orbitals and define nodal planes.

2.6-1. s Orbitals

s orbitals are spherical and positive everywhere.

n, l, and m_l designate an orbital. Orbital pictures are used to represent regions where the electrons are most likely to be found (i.e., occupied orbitals are regions of high electron density). Chemical bonding results from the interaction of orbitals and the electrons in them. l and m_l dictate the shape and orientation of the orbital, respectively, and n dictates its size.

l is zero for an s orbital, so m_l must also be zero. Therefore, there can be only one orbital (an s orbital) in an s sublevel. s orbitals are all spherical (the charge is distributed equally in all directions). The sign of an s wave function is always positive. s orbitals in different levels differ only in size and energy.

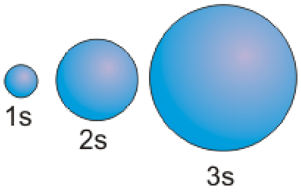


Figure 2.12: s Orbitals The relative sizes of the 1s, 2s, and 3s orbitals of an atom

2.6-2. p Orbitals

p orbitals each contain a nodal plane.

$l = 1$ for p orbitals. There are three values of m_l (-1, 0, $+1$), so there are three orbitals in a p sublevel. The three p orbitals are perpendicular to one another and are referred to as the p_x, p_y, and p_z orbitals. The electron density in each p orbital lies along one of the cartesian axes, but each orbital contains a ***nodal plane***, a plane of zero electron density that passes through the nucleus of the atom. The nodal plane is shown as a gray rectangle in Figure 2.13a. In general, the number of nodal planes in an orbital is equal to its l quantum number. $l = 1$ for p orbitals, so they each have one nodal plane.

The function that describes a p orbital is positive in one lobe, zero at the nodal plane, and negative in the other lobe. The fact that the sign of the orbital functions is different in the two lobes will be important in our discussion of bonding, and this point is often emphasized by the shading of the two lobes. We use blue and red to distinguish between the two. Blue will be used to identify lobes where the function is positive and red will be used for lobes in which the function is negative.

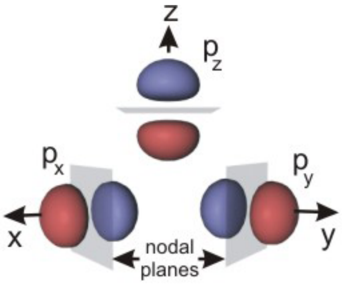


Figure 2.13a: p Orbitals: True Representation

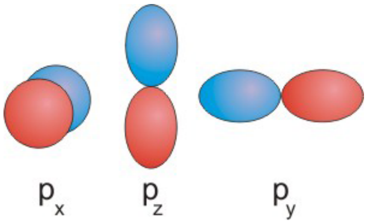


Figure 2.13b: p Orbitals: Common "Figure 8" Representation

2.6-3. d Orbitals

d orbitals each contain two nodal planes.

There are five possible values of m_l in an $l = 2$ sublevel (-2, -1, 0, $+1$, $+2$), so there are five d orbitals. Figure 2.14 shows a representation of these orbitals. The d_{z^2} (or simply z^2) orbital is directed along the z-axis, but there is a donut shaped region of electron density in the xy-plane. The $x^2 - y^2$ orbital is directed along both the x- and the y-axes in both the positive and negative directions. Much of the d_{xz} (xz) electron cloud lies in the xz-plane 45° from either axis. The shapes of the d_{yz} (yz) and d_{xy} (xy) are identical to that of the d_{xz}, only the labels of the axes change.

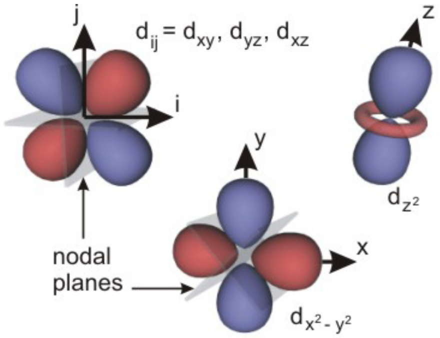


Figure 2.14: d Orbitals

2.7 Electron Configurations

Introduction

The number of electrons in each sublevel is given by the electron configuration of an atom. Electron configurations, the topic of this section, will help us predict the bonding properties of an atom.

Objectives

- Write an electron configuration from a sublevel population.
- Use the Pauli Exclusion Principle to distinguish between acceptable and unacceptable ways for electrons to occupy an orbital.
- Use Hund's Rule to determine a lowest energy electron configuration of an atom with a partially filled sublevel.
- Determine the lower energy configuration based on the sublevel populations of two different configurations
- Determine whether an arrangement of electrons represents a ground state, an excited state, or is not acceptable.
- Use an energy level diagram and the number of electrons in an atom to write the ground state electron configuration of the atom.
- Determine the number of unpaired electrons in an atom's ground state electron configuration.
- Write electron configurations using the noble gas core abbreviation.
- Write the electron configurations for the two elements in the fourth period that are exceptions to the trend in configurations.

2.7-1. Electron Configurations Video

A video or simulation is available online.

2.7-2. Electron Configurations

An electron configuration specifies the occupied sublevels and the number of electrons in each.

The sublevel in which an electron resides can be determined because the energy of the electron can be determined. However, the orbital that contains the electron cannot be determined because the orbitals in a sublevel all have the same energy and differ only in their orientation. Consequently, the electronic structure of an atom is normally given as a list of the occupied sublevels and the number of electrons in each sublevel. This list is called the atom's ***electron configuration***. The notation used for each sublevel is $n\ l^{\ p}$

- $\boldsymbol{n}$ is the n quantum number.
- $\boldsymbol{l}$ is the l quantum number of the sublevel expressed as a letter (s, p, d, ...).
- $\boldsymbol{p}$ is the sublevel population (i.e., the number of electrons in the sublevel).

For example, an electron configuration of $1s^2\ 2s^2\ 2p^3$ indicates that there are two electrons in the 1s sublevel, two electrons in the 2s sublevel, and three electrons in the 2p sublevel. The superscripts give the number of electrons in each sublevel, so the **sum of all of the superscripts in an electron configuration must equal the number of electrons in the atom or ion**. Therefore, the above configuration is for the atom that has seven electrons (2 + 2 + 3), which is the nitrogen atom.

2.7-3. Pauli Exclusion Principle

No orbital can have more than one electron of a given spin, so no orbital can have more than two electrons.

Pauli Exclusion Principle states that no two electrons in an atom can have the same set of quantum numbers.

Electrons in the same orbital have the same values of n, l, and m_l. Thus, all of the electrons in an orbital must have different m_s quantum numbers. The spin quantum number can be only $+1/2$ or $-1/2$, so the Pauli Exclusion Principle dictates that **an orbital can accommodate a maximum of two electrons, one with spin up ($\mathbf{m_s = +1/2}$) and one with spin down ($\mathbf{m_s = -1/2}$)**.

Since, the two electrons in an orbital have opposite spins, they are said to be **paired**. An electron that occupies an orbital alone is said to be **unpaired**. Similarly, an orbital with two electrons is full, while an orbital with one electron is said to be **half-filled**.

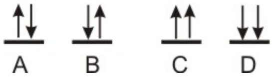


Figure 2.15: Pauli Exclusion Prinicple A and B are acceptable, but C and D are not because they violate the Pauli Exclusion Principle.

2.7-4. Hund's Rule

The lowest energy arrangement of electrons in an unfilled sublevel is the one that maximizes the number of electrons with identical spin.

Hund's Rule states that the lowest energy arrangement of electrons in an unfilled sublevel is the one that maximizes the number of electrons with identical spin. Hund's Rule is only an aid for determining the lowest energy arrangement of electrons in partially filled sublevels with more than one orbital (p, d, and f). *Arrangements that violate Hund's Rule can be acceptable, but they cannot be the lowest energy arrangement.* Hund's Rule guarantees that the number of unpaired electrons in a sublevel is maximized in atoms.

Note that the direction of the spin does not matter, but maximizing the number with identical spins does. Thus, the lowest energy arrangement of three electrons in a p sublevel consists of one electron in each orbital and all electron spins the same (all up or all down).

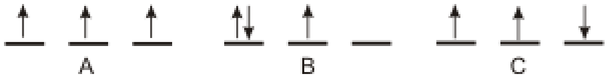


Figure 2.16: Hund's Rule A is the lowest energy configuration because it obeys Hund's Rule. The energies of B and C are greater than that of A because the three spins are not the same. B and C are excited states.

2.7-5. Lowest Energy Configurations

Electrons occupy the unfilled orbitals of lowest energy (i.e., the sublevels with the lowest value of $n + l$). Remember that the energies of sublevels with the same value of $(n + l)$ increase in order of increasing n. Also recall that l cannot be greater than $(n - 1)$. The order of sublevels in increasing energy through $(n+l) = 7$ is given below.

order	$n + 1$	n	l	sublevel
1	1	1	0	1s
2	2	2	0	2s
3	3	2	1	2p
4	3	3	0	3s
5	4	3	1	3p
6	4	4	0	4s
7	5	3	2	3d
8	5	4	1	4p

order	$n + 1$	n	l	sublevel
9	5	5	0	5s
10	6	4	2	4d
11	6	5	1	5p
12	6	6	0	6s
13	7	4	3	4f
14	7	5	2	5d
15	7	6	1	6p
16	7	7	0	7s

2.7-6. Sublevel Energy Diagram

Orbital energies increase with $n + l$. Orbitals with the same value of $n + l$ increase in order of n.

We constructed an energy level diagram for the first 19 orbitals in the Quantum Numbers and Orbital Energy Video. It shows the relative energies (increasing $n + l$) of the sublevels for an atom and the diagram and it is reproduced below. Recall that each line corresponds to an orbital (n, l, and m_l quantum numbers), so two electrons (one spin up and one spin down) can be added to each line.

The Pauli Exclusion Principle states that each orbital can house a maximum of two electrons, so a maximum of 38 electrons could occupy the 19 orbitals represented in Figure 2.17.

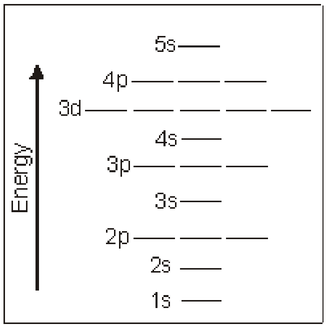


Figure 2.17: Atomic Orbitals in Order of Increasing Energy

2.7-7. Ground States

In the ground state configuration, there can be no unfilled orbitals lower in energy than the highest energy electron.

The electrons in an atom strive toward the lowest energy arrangement that is consistent with the Pauli Exclusion Principle. Such an arrangement is called the ***ground state*** configuration of the atom. The ground state configuration is the one in which

1 the Pauli Exclusion Principle is obeyed.

2 the occupied sublevels are those at lowest energy.

3 Hund's Rule is obeyed.

Configurations that do not obey the Pauli Exclusion Principle are not acceptable configurations. Those that obey the Pauli Exclusion Principle but not points '2' and/or '3' are acceptable, but they are not ground state configurations. They represent configurations with energies greater than that of the ground state. These high-energy configurations are called ***excited state*** configurations. Thus, there are many acceptable electron configurations for an atom, but only one represents its ground state; all others are excited state configurations. An atom will be found in its ground state under normal conditions, so when the electron configuration of an atom is written it is understood to be the ground state configuration. However, atoms can be excited from the ground state into one of the excited states with an input of energy.

2.7-8. Unpaired Electrons

The number of unpaired electrons in a sublevel is maximized by Hund's Rule.

The electrons in the ground state of an atom occupy the lowest energy sublevels consistent with the Pauli Exclusion Principle and Hund's Rule. This allows us to determine two important properties of an atom.

1 **Ground state electron configuration**: the listing of the occupied sublevels and their populations

2 **Unpaired electrons**: Unpaired electrons exist in unfilled sublevels and their number is maximized by Hund's Rule. (As we will see in Chapter 3, the number of unpaired electrons is an important characteristic of the atom because it dictates the atom's magnetic properties.)

2.7-9. Using Noble Gas Cores in Electron Configurations

The electron configurations of the atoms become unwieldy as the number of electrons in the atom increases. For example, iodine's electron configuration is

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

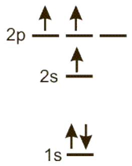
and bismuth has 30 more electrons than iodine. These lengthy configurations can be shortened considerably by using the fact that the electron configuration of every element after a noble gas consists of that noble gas configuration plus some other entries. In the configuration of iodine above, the portion in bold is the electron configuration of Kr, which is abbreviated as [Kr]. Thus, the electron configuration of iodine can be shortened substantially to the following.

$$\text{[Kr] } 5s^2 4d^{10} 5p^5$$

2.7-10. Electron Configuration Exercises

EXERCISE 2.6:

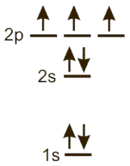
Write the electron configuration of each of the following diagrams. Also indicate whether the configuration is ground state or an excited state configuration.



configuration:

____

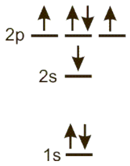
ground state
excited state



configuration:

____

ground state
excited state



configuration:

____

ground state
excited state

2.7-11. Two Exceptions

Chromium and copper are the only two exceptions we deal with.

The energy difference between the s and d sublevels within a level is relatively small, and they get smaller as n increases. The introduction of f sublevels decreases the energy difference between sublevels even more. Such small differences lead to exceptions to our predicted configurations for elements filling d and f blocks as even minor changes can cause electrons to enter a higher energy sublevel. For this reason, we consider only the first row of the transition elements and none of the inner transition elements. There are two exceptions even in the 4th period that result from the fact that the spherical charge distribution accompanying filled and half-filled sublevels lowers the energies of these configurations. Indeed, the amount by which the energy is lowered is greater than the separation between the 4s and 3d sublevels, so a single electron is promoted from the 4s to the 3d to attain these configurations. The two exceptions in which this occurs are:

1. **Chromium** promotes a 4s electron to attain an [Ar] $4s^1$ $3d^5$, which has a half-filled 3d sublevel.
2. **Copper** promotes a 4s electron to attain an [Ar] $4s^1$ $3d^{10}$, which has a filled 3d sublevel.

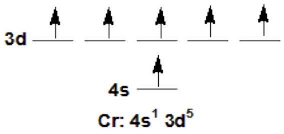


Figure 2.18 Cr promotes a 4s electron to attain a half-filled 3d sublevel.

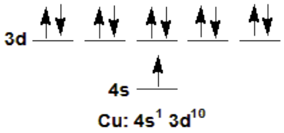


Figure 2.19 Cu promotes a 4s electron to attain a filled 3d sublevel.

2.7-12. Energy Level Exercise

EXERCISE 2.7:

Extend the energy level diagram for the sublevels to include $n + l = 6$ and $n + l = 7$. Place the lowest energy sublevel at the bottom (4d) and the highest energy sublevel at the top (7s). Include the number of orbitals in each.

sublevel 7s orbitals ____________

sublevel ____________ orbitals ____________

sublevel ____________ orbitals ____________

sublevel ____________ orbitals ____________

sublevel ____________ orbitals ____________

sublevel ____________ orbitals ____________

sublevel 4d orbitals ____________

2.7-13. Shorthand Notation Exercise

EXERCISE 2.8:

Use the energy level diagram for the sublevels through $n+l=5$ in Figure 2.17 and the levels for $n+l=6$ and 7 that were determined in the previous exercise to determine sublevel populations for the ground states of the following. Then use the noble gas core shorthand to write their electron configurations. Place a space after the noble gas and between each sublevel. The sublevel energies continue from those.

Rb ________________

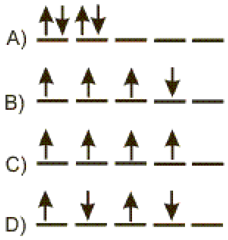
Sn ________________

Bi ________________

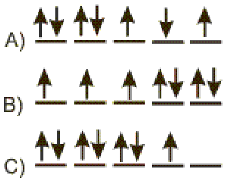
2.7-14. Hund's Rule Exercise

EXERCISE 2.9:

Which arrangement of d electrons has the lowest energy in each case?



A
B
C
D

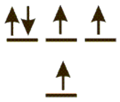


A
B
C

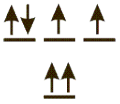
2.7-15. Indentifying States Exercise

EXERCISE 2.10:

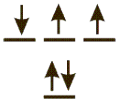
Indicate whether each of the following represents a ground state, an excited state, or are unacceptable configuration. Assume that all sublevels at lower energy are filled.



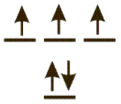
ground state
excited state
not acceptable



ground state
excited state
not acceptable



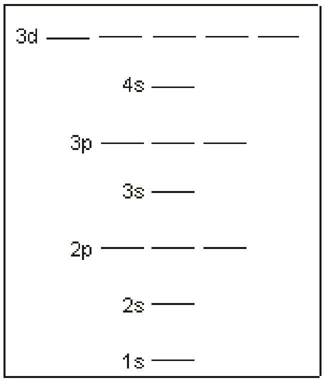
ground state
excited state
not acceptable



ground state
excited state
not acceptable

2.7-16. Unpaired Electrons Exercise

EXERCISE 2.11:



C (6 electrons):

configuration ________________ unpaired electrons ________________

Mg (12 electrons):

configuration ________________ unpaired electrons ________________

Fe (26 electrons):

configuration ________________ unpaired electrons ________________

2.8 Quantum Theory and The Periodic Table

Introduction

Like other atomic properties, the electron configurations of the atoms are periodic. This periodicity allows us to determine the electron configuration of an atom from the atom's position in the periodic table.

Objectives

- Write the electron configuration of an atom from its placement in the periodic table.

2.8-1. Periodicity of Electron Configurations Video

A video or simulation is available online.

2.8-2. Electron Configurations and Periodicity

The sublevels fill in the following order (left to right then down).

1s			
2s			2p
3s			3p
4s		3d	4p
5s		4d	5p
6s	4f	5d	6p

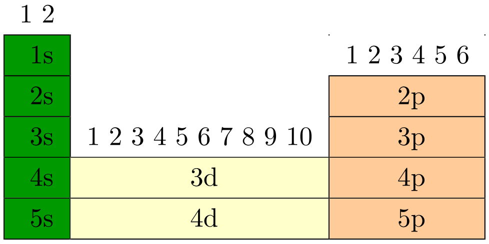
Each column represents the same type of sublevel (s, p, or d). The number of electrons required to fill each of these sublevels is

1 s sublevel: 2 electrons.

2 p sublevel: 6 electrons.

3 d sublevel: 10 electrons.

Changing the width of each column to reflect the number of electrons that are required to fill each sublevel, we obtain the following view.



The above table has exactly the same form as the periodic table. If you understand this periodicity, you can determine the electron configuration of an atom from its position in the periodic table.

2.8-3. Periodic Table and Sublevels

s Block

The $n = 1$ level contains only one s sublevel. Thus, H and He are $1s^1$ and $1s^2$, respectively. However, their positions in the periodic table are normally not with the other elements of the s block. Hydrogen is often shown in the middle of the periodic table for reasons that will be explained in Chapter 4, and He is at the top of the Group 8A elements because it is a noble gas. The rest of the s block elements are those in Groups 1A and 2A. The n quantum number of the level to which the outermost sublevel belongs is given by the row number. Thus, **the electron configurations of the outermost sublevel** for the Group 1A and 2A elements are the following.

1A	2A
$n\mathrm{s}^1$	$n\mathrm{s}^2$

p Block

The elements of Groups 3A through 8A are filling a p sublevel. The n quantum number of the level to which the outermost sublevel belongs is given by the row number. Thus, the **electron configurations of the outermost sublevel** for the Group 3A through 8A elements have the following form.

3A	4A	5A	6A	7A	8A
$n\mathrm{p}^1$	$n\mathrm{p}^2$	$n\mathrm{p}^3$	$n\mathrm{p}^4$	$n\mathrm{p}^5$	$n\mathrm{p}^6$

d Block

The elements of Groups 3B through 2B are filling a d sublevel. The n quantum number of the level to which the d sublevel belongs equals the row number − 1. Thus, elements scandium ($Z = 21$) through zinc ($Z = 30$) are filling the 3d sublevel, while yttrium ($Z = 39$) through cadmium ($Z = 48$) are filling the 4d sublevel.

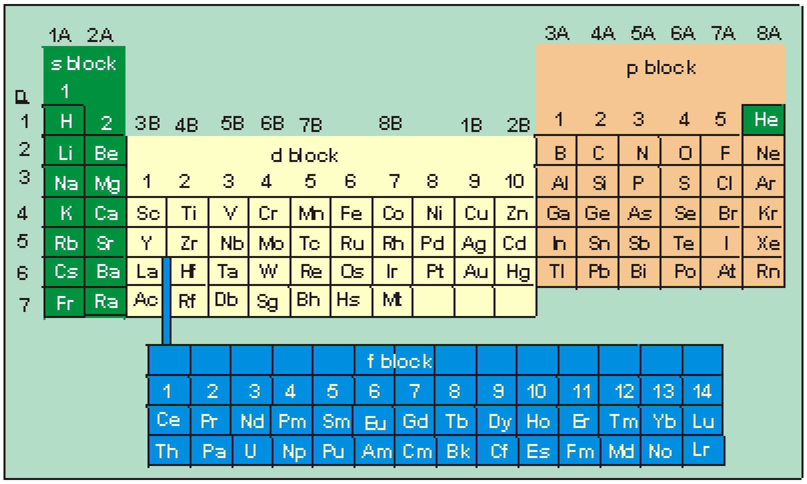


Figure 2.20: s, p, d, and f Blocks in the Periodic Table

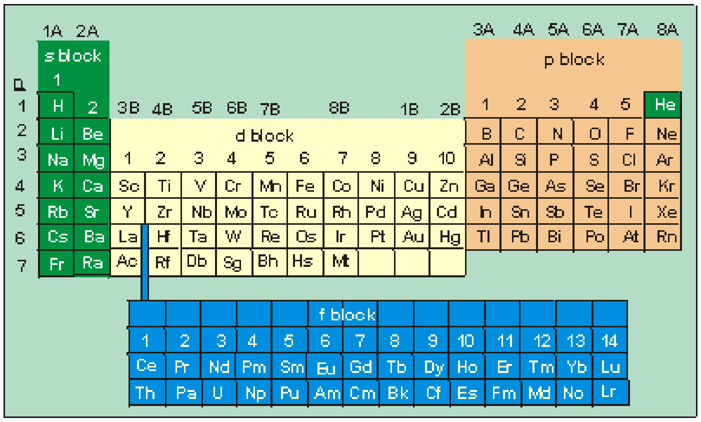
2.8-4. Table of Electron Configurations

Practice using the periodic table to predict the electron configuration of an atom. Check your answer by clicking on the element in the periodic table available online.

2.8-5. Electron Configuration Exercise

EXERCISE 2.12:

Use the periodic table to help you write electron configurations for the following atoms. Use the Noble gas core abbreviation.



Sc ________________ N ________________ Cu ________________

Bi ________________ K ________________ Co ________________

2.9 Exercises and Solutions

Links to view either the end-of-chapter exercises or the solutions to the odd exercises are available in the HTML version of the chapter.

Chapter 3 – Atomic Structure and Properties

Introduction

The nuclear atom and quantum theory are the accepted theories for the atom. In this chapter, we demonstrate their utility by using them to explain trends in atomic properties.

3.1 Valence Electrons

Introduction

Most of the properties of an atom are related to the nature of its electron cloud and how strongly the electrons interact with the nucleus. In this section, we identify the electrons that are most important in determining atomic properties.

Prerequisites

- 2.7 Electron Configurations (Write electron configurations for atoms.)

Objectives

- Distinguish between core and valence electrons.
- Determine the number of valence electrons in an atom.
- Write valence electron configurations of main group atoms.

3.1-1. Valence Electrons Video

A video or simulation is available online.

3.1-2. Valence Electron Definition

Valence electrons consist of those electrons in the outermost s sublevel and those in any unfilled sublevel.

The electrons in an atom can be divided into two groups:

- ***Core electrons*** are the tightly bound electrons that are unaffected by chemical reactions. **Core electrons reside in filled sublevels** and form a spherical shell of negative charge around the nucleus that affects the amount of nuclear charge that the outermost electrons experience.
- ***Valence electrons*** are those outermost electrons that dictate the properties of the atom and are involved in chemical bonding. **The valence electrons are those in the outermost s sublevel and any unfilled sublevels.**

The number of valence electrons in an atom equals the group number of the atom.

3.1-3. Valence Electron Configurations of Main Group Elements

All of the elements in a group have the same number of valence electrons (Group number), and their valence electron configurations are the same except for the value of the n quantum number (the period). Thus, the periodicity of chemical properties is due to the periodicity of the valence electron configurations. The table shows the generic valence electron configurations of the elements in each group of the main group elements and the specific configurations of the second period.

Group	1A	2A	3A	4A	5A	6A	7A
Configuration	ns^1	ns^2	ns^2np^1	ns^2np^2	ns^2np^3	ns^2np^4	ns^2np^5
2nd Period Element	Li	Be	B	C	N	O	F
Configuration	$2s^1$	$2s^2$	$2s^22p^1$	$2s^22p^2$	$2s^22p^3$	$2s^22p^4$	$2s^22p^5$

Table 3.1: Valence Electron Configurations

3.1-4. Valence Electron Configurations of Transition Elements

The valence electron configuration of the first row transition elements has the form $4s^23d^b$, where b is the position of the element in the d block. Cr and Cu are the two exceptions because they each promote one of their 4s electrons into the 3d sublevel to obtain half-filled and completely filled 3d sublevels. Zinc is often considered a transition element because of its location, but its d sublevel is full, and its chemistry is more like that of a Group 2A metal than a transition metal. Thus, its valence electron configuration is $4s^2$, in keeping with its Group number of 2B. Similarly, Cu is $4s^13d^{10}$, and the fact that it is a 1B element would lead you to think that its valence electron configuration should be $4s^1$. However, unlike zinc, copper does use its d orbitals in bonding. Indeed, the most common ion formed by copper is the Cu^{2+} ion. Thus, copper's chemistry is dictated by its d electrons, and its valence electron configuration is $4s^13d^{10}$.

3.1-5. Practice with Valence Electrons

Valence electrons and valence electron configurations are very important in chemistry. Practice determining the valence electron configurations for atoms and then check your answer by clicking on the element in the periodic table available online.

3.1-6. Core vs. Valence Electrons Exercise

EXERCISE 3.1:

Use the facts that all of the electrons in an atom are either core or valence electrons, and the number of valence equals the group number of the element to determine the number of valence and core electrons in each of the following atoms.

O

Valence = ______ Core = ______

Ca

Valence = ______ Core = ______

Sn

Valence = ______ Core = ______

3.1-7. Main Group Valence Configurations Exercise

EXERCISE 3.2:

Write the valence electron configuration of each of the following main group elements.

Si ($Z = 14$) ______ K ($Z = 19$) ______

Tl ($Z = 81$) ______ Br ($Z = 35$) ______

3.1-8. Transition Metal Valence Configurations Exercise

EXERCISE 3.3:

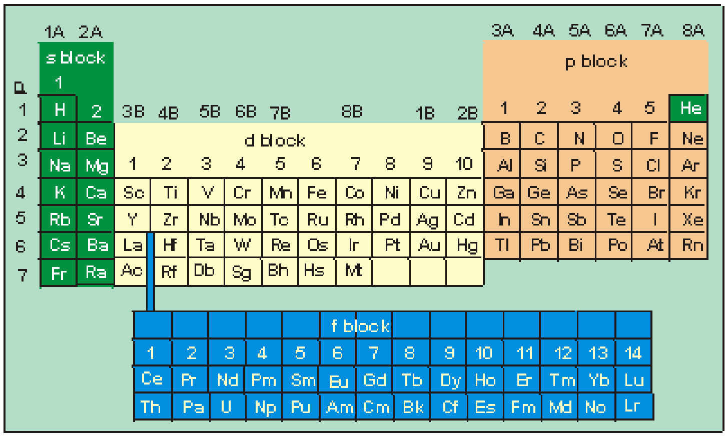
Write the valence electron configuration for each of the following transition elements.

Ti ______ Fe ______ Cu ______

3.1-9. More Valence Electron Configuration Exercises

EXERCISE 3.4:

Use the periodic table to help you write valence electron configurations for the following atoms.



Sc ________ N ________ Co ________

Bi ________ Sr ________ Mn ________

3.2 Shielding and Effective Nuclear Charge

Introduction

In this section, you will learn how to predict the relative strengths with which the valence electrons interact with the nucleus.

3.2-1. Effective Nuclear Charge Video

A video or simulation is available online.

3.2-2. Shielding and Effective Nuclear Charge

Core electrons shield valence electrons better than do other valence electrons.

The nuclear charge experienced by an electron affects the size and energy of its orbitals, so it is an important factor in determining the properties of the valence electrons and orbitals. However, a valence electron is not attracted by the full positive charge of the nucleus because it is shielded by the other electrons, mainly the core electrons. The nuclear charge that is actually experienced by a valence electron is called the ***effective nuclear charge***, Z_{eff}. The effective nuclear charge experienced by an electron is equal to the charge of the nucleus (Z) minus that portion of the nuclear charge that is shielded by the other electrons (σ).

$$Z_{\text{eff}} = Z - \sigma \qquad \text{Effective Nuclear Charge} \tag{3.1}$$

σ is the ***shielding*** of the other electrons.

A valence electron is screened both by the core electrons and other valence electrons. However, core electrons are closer to the nucleus, so **core electrons shield valence electrons better than do other valence electrons**. This important fact will be used to explain the trends of atomic properties within a period.

Figure 3.1a In the absence of any electrons, the full nuclear charge (as shown by the red color) is observed. The nuclear charge is $+Z$, where Z is the atomic number (the number of protons in the nucleus). If this were a calcium nucleus, the resulting charge would be +20.

Figure 3.1b The nuclear charge is shielded by the negative charge of the core electrons (yellow sphere). Thus, only a portion of the nuclear charge can be felt through the core electrons as shown by the fact that the red color is greatly reduced by the yellow sphere. If this were a Group 2A element, the charge that would result would be +2 as the two valence electrons are not included. Thus, the charge has been reduced from +40 to +2 by the core electrons.

Figure 3.1c Addition of the valence electrons (green sphere) results in the atom. Essentially none of the nuclear charge is felt outside the neutral atom.

3.2-3. Trends in Z_{eff}

Effective nuclear charge increases going from left to right in a period.

Trends within a period: The charge of the nucleus increases by a full unit of positive charge in going from one element to the next in a period, but the additional electrons are valence electrons, which do not shield with a full negative charge. Consequently, **effective nuclear charge increases going from left to right in a period**. This effect is very important because it explains many trends within a period.

Consider the following comparison of Li and F:

1 $Z = 3$ for Li, which is $1s^2 2s^1$. $Z_{\text{eff}} \sim 1$ according to Figure 3.2. Thus, the two 1s electrons exert a shielding of $\sigma \sim 3 - 1 = 2$.

2 $Z = 9$ for F, which is $1s^2 2s^2 2p^5$, but $Z_{\text{eff}} \sim 5$. Thus, the shielding is $\sigma \sim 9 - 5 = 4$.

Although F has five more electrons than Li, they increase the shielding by only 2 (from 2 in Li to 4 in F). This is because they are valence electrons, which do not shield very well.

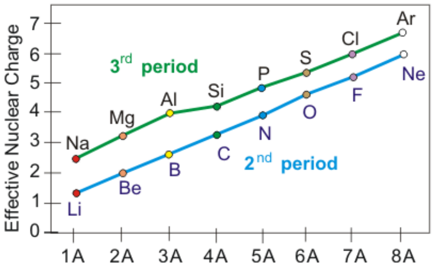


Figure 3.2 Effective Nuclear Charges of the Elements in the 2nd and 3rd Periods

Trends within a group: The shielding ability of the core electrons decreases as their n quantum number increases. As a result, the effective nuclear charge experienced by the valence electrons within a group increases with the n quantum number of the valence level. Consequently, effective nuclear charge increases going down a group. For example, the 2s electron on Li experiences an effective nuclear charge of ~1, while the 3s electron on Na experiences a charge of ~2, which shows that the $n = 2$ electrons do not shield as well as the $n = 1$ electrons.

This effect opposes that of changing the n quantum number because increasing n increases the energy of the valence levels, but increasing the effective nuclear charge lowers the energy of the valence levels. The effect of increasing n is the more important because the energies of the valence levels do increase going down a group.

3.2-4. Effective Nuclear Charge Exercise

EXERCISE 3.5:

Select the electron in each pair that experiences the greater effective nuclear charge.

2p in Cl	3p in Cl	4p in Br	5s in Rb
2p in F	3p in P	4s in Br	4s in K

3.3 Relative Atomic Size

Introduction

Atoms are not hard spheres with well defined boundaries, so the term “atomic radius” is somewhat vague and there are several definitions of what the atomic radius is. Consequently, atomic radii are not measured directly. Rather, they are inferred from the distances between atoms in molecules, which can be readily determined with several techniques. However, a discussion of how atomic radii are defined requires an understanding of chemical bonding and the solid state, so a detailed discussion of the different types of radii and their values is postponed until Chapter 8. In this section, we restrict our discussion to trends in the relative sizes of atoms.

Prerequisites

- 1.8 Electromagnetism and Coulomb’s Law
- 1.11 Dimitri Mendeleev and The Periodic Law
- 2.3 Bohr Model (Use the Bohr model to relate the size of an orbital to its n quantum number and atomic number.)

Objectives

- Explain the periodicity in the size of valence orbitals.
- Determine the relative sizes of atoms based on their positions in the periodic table.

3.3-1. The Bohr Model and Atomic Size

The size of the atom is given by the size of its valence electron clouds. Although the orbits of fixed radii suggested in the Bohr model are not correct, the conclusions of the model can still be used to gain a qualitative understanding of *trends* in atomic radii by substituting the effective nuclear charge for the atomic number in Equation 2.4 to obtain the following:

$$r_n \propto \frac{n^2}{Z_{\text{eff}}}$$

- The average size of an orbital increases as its n quantum number increases.
- The size of the electron cloud decreases as the effective nuclear charge it experiences increases.

3.3-2. Atomic Size

Atomic radii increase going down a group and decrease going across a period.

The size of an atom is defined by the size of the valence orbitals. Using the Bohr model as discussed above, we conclude that

- atomic radii increase going down a group because the n quantum number of the outermost orbitals increases, and
- atomic radii decrease going from left to right in a period because Z_{eff} increases.

Note that the atomic radii of H and Rb are 0.37 Å and 2.11 Å, respectively.

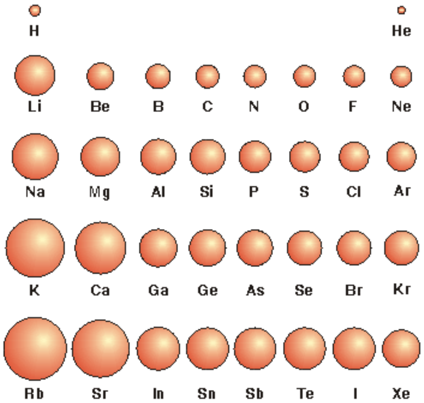


Figure 3.3 Relative Atomic Radii

3.3-3. Atomic Size Exercise

EXERCISE 3.6:

Use only a periodic table to determine the **largest** atom in each group.

Cl
F
I

Na
S
Al

Br
K
Ge

3.4 Relative Orbital Energies

Introduction

The relative energy of the valence orbitals in an atom is an important characteristic of the atom as it dictates both properties of the atom and the manner and strength of its interaction with other atoms. Indeed, we will invoke relative orbital energies in making predictions about chemical processes throughout the remainder of this course. In this section, we use the Bohr model to predict the relative energies of the valence orbitals in some small atoms.

Prerequisites

- 1.8 Electromagnetism and Coulomb's Law
- 1.11 Dimitri Mendeleev and The Periodic Law
- 2.3 Bohr Model (Use the Bohr model to relate the energy of an orbital to its n quantum number and atomic number.)

Objectives

- Determine the relative energies of electrons based on their n quantum number and the effective nuclear charge they experience.

3.4-1. Orbital Energies Video

A video or simulation is available online.

3.4-2. The Bohr Model and Orbital/Electron Energy

The ease with which an electron is lost from an atom is given by how strongly the electron is bound to the atom, which, in turn, is given by the energy of the electron in the atom. We again use the conclusions of the Bohr model in a qualitative way to understand *trends* in valence electron energies by substituting the effective nuclear charge for the atomic number in Equation 2.5 to obtain Equation 3.2.

$$E_\text{x} \propto -\frac{Z_\text{eff}^2}{n^2} \qquad \text{Electron/Orbital Energy Approximation} \qquad (3.2)$$

E_x is the energy of a valence orbital on atom X, and n is the principle quantum number of its valence shell. While Equation 3.2 is only a very rough approximation, it is useful in demonstrating how the **relative** orbital energies of the valence electrons in the atoms of the first three periods are related. We conclude that

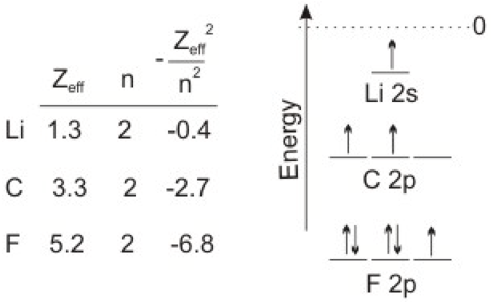
1 The energy of an electron increases (becomes less negative and is bound less tightly) as its n quantum number increases.

2 The energy of an electron decreases (becomes more negative and is bound more tightly) as the effective nuclear charge increases.

3.4-3. Relative Energies, an Example

The valence orbitals of nonmetals are relatively low in energy, while those of metals are relatively high.
A video or simulation is available online.

We now determine the relative valence orbital energies of Li, C, and F as shown in Figure 3.4. We use the fact that they are each in the second period to get n and Figure 3.2 to obtain values of Z_eff and construct the table shown in Figure 3.4. We use Equation 3.2 and the values in the table to conclude the following.



	Z_eff	n	$-\frac{Z_\text{eff}^2}{n^2}$
Li	1.3	2	-0.4
C	3.3	2	-2.7
F	5.2	2	-6.8

Figure 3.4

- The five 2p valence electrons of fluorine experience a highly positive effective nuclear charge of 5.2 and a very low n quantum number, so the value for $\frac{Z_\text{eff}^2}{n^2}$ is quite large. Thus, the energy of the valence orbitals of fluorine is very low. Indeed, they are the lowest-energy valence orbitals of any atom. Nonmetals are all characterized by low-energy valence orbitals.
- The two 2p electrons of carbon experience an effective nuclear charge of +3.3 and the same n quantum number as fluorine, so the value of $\frac{Z_\text{eff}^2}{n^2}$ is less than that of fluorine. Thus, the valence electrons of carbon are not bound as tightly as those on fluorine and the carbon valence orbitals are higher in energy than those of fluorine. However, carbon is a nonmetal, and the energy of its valence orbitals is still relatively low.
- Lithium is a metal, and its 2s valence electron experiences an effective nuclear charge of only +1.3, which produces a very low value for Z_eff squared over n squared. Consequently, the valence electron on a lithium atom is bound only weakly, and its valence orbital energy is quite high. Indeed, metals are all characterized by high-energy valence orbitals.

3.4-4. Predicting Relative Energy Exercise

EXERCISE 3.7:

Use the effective nuclear charges (Figure 3.2) and the n quantum number of the valence electrons of chlorine, oxygen, sulfur, and silicon in Equation 3.2 to predict the relative energies of their valence orbitals. Compare to the values of $\frac{Z_{\text{eff}}^2}{n^2}$ to those for Li (0.4), C (2.7), and F (6.8).

Chlorine ($Z_{\text{eff}} = 6.1$)
above Li
Li - - - - - - -
between Li and C
C - - - - - - -
between C and F
F - - - - - - -
below F

Oxygen ($Z_{\text{eff}} = 4.6$)
above Li
Li - - - - - - -
between Li and C
C - - - - - - -
between C and F
F - - - - - - -
below F

Sulfur ($Z_{\text{eff}} = 5.5$)
above Li
Li - - - - - - -
between Li and C
C - - - - - - -
between C and F
F - - - - - - -
below F

Silicon ($Z_{\text{eff}} = 4.3$)
above Li
Li - - - - - - -
between Li and C
C - - - - - - -
between C and F
F - - - - - - -
below F

3.4-5. Relative Valence Orbital Energies for Several Atoms

Before leaving our discussion of relative orbital energies, we add H ($Z_{\text{eff}} = 1$) and O ($Z_{\text{eff}} = 4.5$) to our energy diagram to obtain the following diagram that contains eight elements of the first three periods.

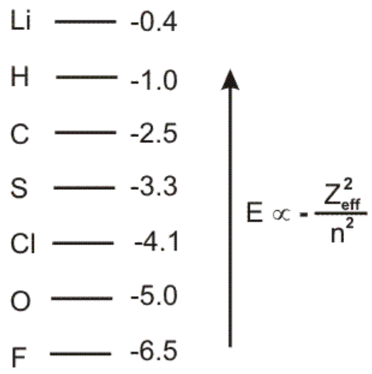


Figure 3.5 The relative energies of the valence orbitals of some atoms studied in the first three periods. Values of $-\frac{Z_{\text{eff}}^2}{n^2}$ are given to the right.

We draw the following two conclusions based on the diagram:

1 Orbital energies decrease (become more negative) going across a period because Z_{eff} increases. Thus, Li > C > O > F.

2 Orbital energies increase (become less negative) going down a group because n increases. Thus, Si > C; S > O; and Cl > F.

3.4-6. Orbital Energy Exercise

EXERCISE 3.8:

Consider the following valence orbital energy diagram that we have constructed to this point.

a
Li (−0.4)
b
H (−1.0)
c
Si (−2.0)
d
C (−2.5)
e
S (−3.3)
f
Cl (−4.2)
g
O (−5.0)
h
F (−6.5)

Where would the valence orbitals of the following atoms be placed? Give the letter of the location.

(a) N ($Z_{\text{eff}} = 3.83$)

a
b
c
d
e
f
g
h

(b) P ($Z_{\text{eff}} = 4.89$)

a
b
c
d
e
f
g
h

3.4-7. Core vs. Valence Orbital Energies Exercise

The energies of the valence orbitals of all atoms lie in a relatively narrow range due to the periodicity in Z_{eff} and an increasing n quantum number. Core electrons, on the other hand, continue to drop in energy as the number of protons increases because they are not shielded very efficiently by the valence electrons. Thus, the valence 2p orbitals of oxygen are at lower energy than the valence 3p valence orbitals on sulfur because valence orbital energies increase going down a group, but the 2p electrons in oxygen are much higher in energy than the 2p electrons on sulfur because sulfur has 16 protons while oxygen has only eight.

EXERCISE 3.9:

Select the orbital that is at lower energy in each pair.

2p on N
2s on N

2p on Br
2p on F

2p on N
2p on O

3.5 Ionization Energy

Introduction

One of the properties of an atom that is important in dictating the chemical properties of the atom is the ease with which the atom loses one or more of its valence electrons. This property of an atom is given by the atom's ionization energy or ionization potential, the topic of this section.

Prerequisites

- 1.8 Electromagnetism and Coulomb's Law
- 1.11 Dimitri Mendeleev and The Periodic Law
- 2.3 Bohr Model (Use the Bohr model to relate the energy of an orbital to its n quantum number and atomic number.)

Objectives

- Predict the relative ionization energies of atoms based on their positions in the periodic table or the relative energies of their occupied valence orbitals.

3.5-1. Ionization Energy Video

A video or simulation is available online.

3.5-2. Ionization Energy and Orbital Energy

Ionization energies measure the energy of the highest energy electron.

The ***ionization energy*** (*IE*) of an atom is the energy required to remove the highest energy electron. The ionization energy of lithium is 520 kJ/mol, which means that the electrons in a mole of lithium atoms can be removed by the input of 520 kJ. The ionization process is

$$\text{Li} \rightarrow \text{Li}^{1+} + e^{1-} \quad \Delta E = +520 \text{ kJ}$$

where $\Delta E = IE$, the ionization energy. The energy change results because the energy of the electron in the initial state is different than in the final state. In the initial state, the electron is in an orbital of energy E_n, but in the final state, it is a free electron with no potential energy. The relationship between the ionization energy and the orbital energy is obtained as follows:

$$\begin{aligned} IE &= E_{\text{final}} - E_{\text{initial}} \\ IE &= \text{free electron energy} - \text{orbital energy} \\ IE &= 0 - E_n \end{aligned}$$

Thus, $IE = -E_n$. The orbital energy of the highest energy electron can be approximated as the negative of the ionization energy of the atom.

In the above discussion, we have considered the removal of only the highest energy electron, but as shown in the following, other electrons can also be removed by successive ionizations. Thus, the energy required to remove the first electron is the first ionization energy and that required to remove the second electron is the second ionization energy, and so forth. Consider the case of the metal M.

$$\begin{array}{rcll} \text{M} & \rightarrow & \text{M}^{1+} + e^{1-} & \text{First ionization} \\ \text{M}^{1+} & \rightarrow & \text{M}^{2+} + e^{1-} & \text{Second ionization} \\ \text{M}^{2+} & \rightarrow & \text{M}^{3+} + e^{1-} & \text{Third ionization} \\ \text{M}^{3+} & \rightarrow & \text{M}^{4+} + e^{1-} & \text{Fourth ionization} \end{array}$$

The loss of an electron reduces the screening of the remaining electrons, so the remaining electrons experience greater nuclear charge and are more difficult to remove. Thus, each successive ionization energy is greater than the preceding. We use the term ionization energy to refer to the first ionization energy in the remainder of the chapter.

3.5-3. Putting Numbers to Orbital Energies

The energy required to remove one 2p electron from each atom in a mole of F atoms to produce a mole of F^{1+} ions is 1681 kJ, so the ionization energy of fluorine is 1681 kJ/mol. In addition, 1681 kJ/mole are released in the reverse process, so we conclude that the 2p orbital energy is −1681 kJ/mol. Nonmetals are characterized by high ionization energies and low valence orbital energies because they have high effective nuclear charges.

The ionization energy of carbon is 1086 kJ/mol, so the orbital energy of a 2p orbital in carbon is −1086 kJ/mol.

The ionization energy of lithium is only 520 kJ/mol, so the orbital energy of its 2s orbital is −520 kJ/mol. The valence orbitals of metals are characterized by low ionization energies and high valence orbital energies because they have low effective nuclear charges.

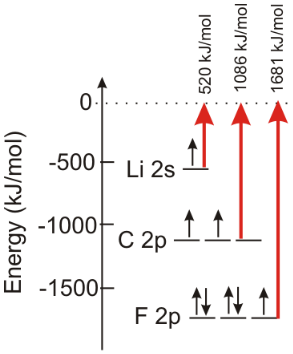


Figure 3.6 Ionization Energy and Orbital Energy

3.5-4. Ionization Energy Trends

Ionization energies increase going up a group and going from left to right in a period.

Ionization energy is the energy required to remove the highest energy electron from an atom, which can be estimated with the assumption that $IE = -E_n$; i.e., that the ionization energy equals the negative of the orbital energy of the electron. E_n can be estimated with Equation 3.2, so we conclude that ionization energies

- increase moving up a group due to the decrease in the n quantum number, and
- increase from left to right in a period due to the increase in Z_{eff}.

This trend is shown in Figure 3.7, which shows the ionization energies of the atoms in order of atomic number. However, there are some apparent exceptions that arise because **electron configurations in which sublevels are filled (Groups 2A and 8A) or half-filled (Group 5A) are unusually stable, so removing an electron from an element in one of these groups is more difficult and results in deviations from the expected periodicity**. For example, the effective nuclear charge of B is greater than that of Be, but the ionization energy of Be is greater than that of B because the electron must be removed from a filled 2s sublevel in Be. Similarly, the ionization energy of N is greater than that of O because the 2p sublevel of N is half-filled.

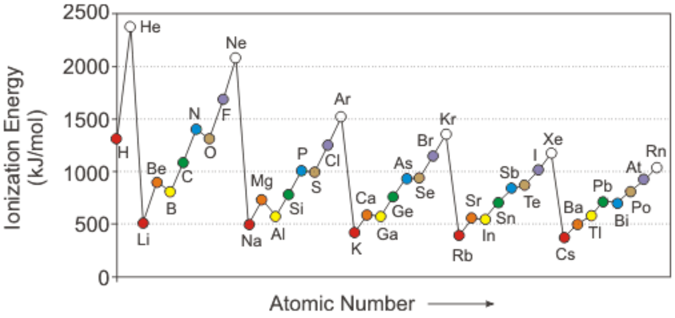


Figure 3.7 First Ionization Energies of the Main Group Elements: Circles of the same color represent elements of the same group. For example, all Group 1A elements are shown as red circles.

Summary

- **Metals** are characterized by low effective nuclear charge, so they all have low ionization energies. Consequently, **metals tend to lose electrons**, and the farther to the left of the Periodic Table, the more easily the electrons are lost. Thus, the 1A elements lose their valence electron very easily. The ionization energy also decreases going down a family, so Cs (high n and low Z_{eff}) loses its valence electron so easily that it must be stored in oil because it gives up its 6s electron to water or oxygen when exposed to the air.

- **Nonmetals** have high effective nuclear charges, so they have relatively high ionization energies. Thus, nonmetals do not lose their electrons very easily. Excluding the noble gases, F (low n and high Z_{eff}) has the highest ionization energy of any atom, which means that the valence electrons of fluorine are very tightly bound.

3.5-5. Ionization Energy Exercise

EXERCISE 3.10:

Use only a Periodic Table to determine the atom in each group with the **greatest** ionization energy.

Cl	Na	Br	Si
F	S	K	P
I	Al	Ge	S

3.6 Electronegativity

Introduction

The electrons in a bond can lower their potential energy by residing closer to the atom in the bond that has the valence orbital at lower energy. The ability of an atom to attract the bonding electrons to itself is called its ***electronegativity*** (χ). Atoms are most electronegative when their valence orbitals are low in energy. Electronegativity is the topic of this section.

Prerequisites
- 1.8 Electromagnetism and Coulomb's Law
- 1.11 Dimitri Mendeleev and The Periodic Law
- 2.3 Bohr Model (Use the Bohr model to relate the energy of an orbital to its n quantum number and atomic number.)

Objectives
- Predict the relative electronegativities of atoms based on their positions in the periodic table or the relative energies of their unfilled valence orbitals.
- Explain the differences between metals and nonmetals that arise from the differences in their ionization energies and electronegativities.

3.6-1. Electronegativity Video

A video or simulation is available online.

3.6-2. Electronegativity and Orbital Energy

Atoms with low-energy valence orbitals are highly electronegative.

Electronegativity (χ) is a measure of an atom's ability to attract bonding electrons, so electron density in a bond accumulates near those atoms with higher electronegativities. Bonding electrons reside in orbitals involving the valence orbitals of the atoms, especially those that are unfilled, and electrons seek to minimize their energy, so an atom that is highly electronegative is simply one whose valence orbitals, especially those that are unfilled, are low in energy.

EXAMPLE:

$E_n = -\frac{(Z_{\text{eff}})^2}{n^2}$, so the valence orbitals of atoms with high electronegativities have

1 large Z_{eff} (nonmetals) and

2 low n quantum numbers (high in the periodic table).

Consider the orbital energies of Li, C, and F shown in Figure 3.8. Li is a metal with a low Z_{eff}, so its orbital energy is high. The electron in it is readily lost (low ionization energy), but bonding electrons are not drawn to the high-energy orbital, so Li has a very low electronegativity. F is a nonmetal with a high Z_{eff}, so its orbital energy is low. Thus, it is very difficult to remove a 2p electron from F (high ionization energy), but bonding electrons are drawn to the low energy unfilled orbital, so F is highly electronegative. The 2p orbital energy of C is about halfway between the valence orbital energies of Li and F, and its electronegativity is also about half way between these two extremes in the period.

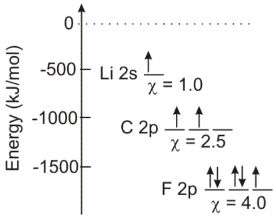


Figure 3.8 Electronegativity and Orbital Energy

3.6-3. The Meaning of Electronegativity

The electronegativity difference between two atoms dictates the type of bond that forms between them. Refer to Figure 3.9 for the following discussion.

1 The electronegativities of two fluorine atoms are identical, so the bonding electrons are shared equally by the two atoms. Bonds in which the bonding electrons are shared equally are called covalent bonds.

2 Fluorine is more electronegative than carbon, so the bonding electrons in a C-F bond reside closer to the fluorine atom. The excess of electron density close to the fluorine atom gives it a partial negative charge. A Greek delta (δ) is used to indicate that it is only a partial charge as the carbon still experiences some of the negative charge of the bonding electrons.

3 The electronegativity difference between Li and F is so great that the bonding electrons reside almost exclusively on the fluorine to give it a full negative charge. Bonds in which the bonding electrons are not shared but reside on one atom are called ionic bonds.

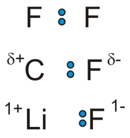


Figure 3.9

Ionic bonds are the topic of Chapter 4, and covalent bonds are discussed in Chapters 5 and 6.

3.6-4. Electronegativity Trends

Electronegativities decrease going down a group and increase going across a period.

We use the Bohr model to approximate the energy of the lowest energy empty orbital $-E_n$ and conclude that

- electronegativities decrease going down a group because n increases, which causes the orbital energies to increase, and

- electronegativities increase going from left to right in a period because Z_{eff} increases, which causes the orbital energies to decrease (become more negative).

Consequently,

- **Nonmetals** are characterized by high Z_{eff}, so their valence orbitals are low in energy. Consequently, **nonmetals are highly electronegative** (2.0 to 4.0).
- **Main group metals** have low effective nuclear charges and are characterized by high energy valence orbitals. Thus, **main group metals have very low electronegativities** (0.7 to 1.5).

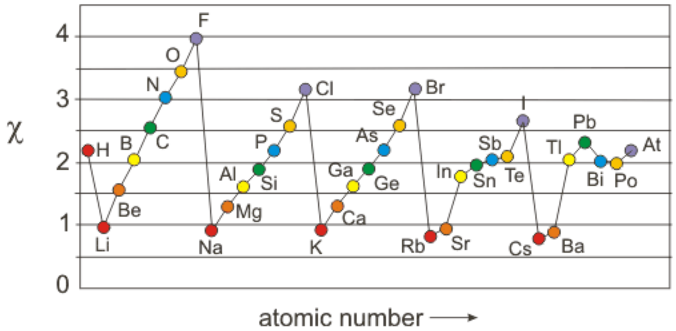


Figure 3.10 Electronegativities of the Main Group Elements: Circles of the same color represent elements of the same group. For example, all Group 1A elements are shown as red circles.

3.6-5. Late Metals

An exception to the above generality about the electronegativities of metals arises from the fact that d and f electrons do not shield very well because they contain two and three nodal planes, respectively. Therefore, the effective nuclear charge experienced by the valence orbitals in late metals (metals that lie on the right side of the Periodic Table) can be quite large. For example, Pb has 27 more protons and electrons than does Cs, but 24 of those electrons are d and f electrons, which do not shield the 27 additional protons very well. Thus, the 6p electrons in Tl and Pb experience relatively high Z_{eff} (12.25 and 12.39, respectively), which makes both of these metals fairly electronegative. Indeed, the electronegativity of Pb is much greater than that of Si even though they are in the same Group, and the valence orbitals in Pb have a much higher n quantum number. We conclude that due to their high effective nuclear charges, late metals have unusually high electronegativities (see Table 3.2), which impacts significantly on their chemical properties.

Metal	χ
Ag	1.9
Sn	2.0
Hg	2.0
Tl	2.0
Pb	2.3

Table 3.2: Electronegativities of Late Metals

3.6-6. Metals vs. Nonmetals

Metals have low ionization energies and nonmetals have high electronegativities.

Metals are characterized by lower effective nuclear charges, so they have

- relatively large atomic radii
- lower ionization energies
- lower electronegativities

Nonmetals are characterized by high effective nuclear charges, so they have

- relatively small atomic radii
- higher ionization energies

- higher electronegativities

Thus, **metals tend to lose electrons (low ionization energy), while nonmetals tend to gain electrons (high electronegativities)**.

3.6-7.Electronegativity Exercise

EXERCISE 3.11:

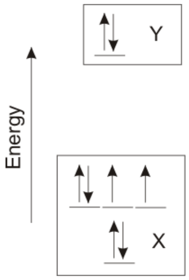
Use only a Periodic Table to determine the atom in each group with the **greatest** electronegativity.

Cl	Na	Br	Al
F	S	K	Tl
I	Al	Ge	Ga

3.6-8. Orbital Energy and Atomic Properties Exercise

EXERCISE 3.12:

Use what you have learned about the relationships between orbital energies and ionization energies and electronegativities and the valence orbital occupancies of atoms X and Y given below to answer the following questions about atoms X and Y.



The atom with the lower ionization energy:
X
Y

The atom with the higher electronegativity:
X
Y

The group of the periodic table to which each atom belongs:

X ______________ Y ______________

3.7 Magnetic Properties

Introduction

All magnetic properties are due to the magnetic fields caused by electron spin. However, no magnetic field is generated by paired electrons because the two different electron spins are opposed and their magnetic fields cancel. Consequently, the magnetic properties of an atom are due solely to its *unpaired* electrons. In this section, we give a brief introduction into the magnetic properties of atoms and materials.

Prerequisites

- 2.5 The Quantum Numbers (Explain the meaning of the m_s quantum number.)

Objectives

- Explain the origin of magnetism.
- Distinguish between paramagnetic and diamagnetic atoms.
- Explain why magnetic atoms are not always magnetic materials.

3.7-1. Paramagnetism and Diamagnetism

The paramagnetism of an atom increases with the number of unpaired electrons.

Atoms with unpaired electrons are ***paramagnetic***. Paramagnetic atoms align in magnetic fields due to the presence of the unpaired electrons. The more unpaired electrons an atom has, the more paramagnetic it is. Both Li and N have unfilled valence subshells, so both have unpaired electrons and are paramagnetic. N has three unpaired electrons while Li has only one, so N is more paramagnetic than Li.

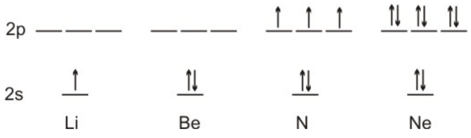


Figure 3.11

Atoms with no unpaired electrons are ***diamagnetic***. Diamagnetic atoms do not align in magnetic fields because they have no unpaired electrons. Neither Be nor Ne has any unfilled valence shells, so both are diamagnetic.

3.7-2. Ferromagnetism

Ferromagnetism is a measure of the bulk magnetism of a material, while paramagnetism is a measure of the magnetism of individual atoms.

Paramagnetism and diamagnetism are atomic properties, not bulk properties. Thus, N and Li are paramagnetic atoms, but nitrogen gas and lithium metal are not magnetic because the unpaired electrons on the atoms pair with one another to form materials that are not magnetic. The magnetism you are familiar with is called ***ferromagnetism***. It is a ***bulk property*** because it requires unpaired electrons in a material, not just in an isolated atom. Iron is the best known example. Fe atoms have four unpaired electrons, so Fe atoms are paramagnetic. When Fe atoms bond to form iron metal, there is electron pairing in the solid, but not all four electrons pair. Consequently, iron metal is magnetic and iron is a ferromagnet.

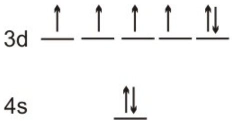


Figure 3.12 Valence orbital occupancy of Fe. It is both paramagnetic and ferromagnetic.

3.7-3. Paramagnetism Exercise

EXERCISE 3.13:

Use a Periodic Table to determine the more paramagnetic atom in each pair.

O	Na	Cr
N	Mg	Fe

3.8 Exercises and Solutions

Links to view either the end-of-chapter exercises or the solutions to the odd exercises are available in the HTML version of the chapter.

Chapter 4 – Ionic Bond

Introduction

Atoms can gain or lose valence electrons to become ions. Ions can be monatomic, such as Ca^{2+} and Cl^{1-}, or polyatomic, such as $NH_4{}^{1+}$ and $CO_3{}^{2-}$. An ***ionic bond*** is the electrostatic (Coulombic) force of attraction between two oppositely charged ions. Ions and how they bond are the topic of this chapter.

4.1 Ionic Bonding

Introduction

Ionic bonds are the electrostatic attraction of oppositely charged ions. The cation is usually a metal, and the anion is usually a nonmetal.

4.1-1. Introduction to Bonding Video

A video or simulation is available online.

4.1-2. Ionic Bonding

An ionic bond is the Coulombic attraction of two oppositely charged ions.

Compounds between metals and nonmetals are ionic.

The unfilled valence orbitals of nonmetals experience large effective nuclear charges, so they are low in energy, which makes nonmetals, such as chlorine, highly electronegative. The valence electrons of metals that lie on the left side of the periodic table experience very low effective nuclear charges, so they are characterized by low ionization energies. Therefore, metals, such as sodium, lose their valence electron easily.

When sodium bonds to chlorine, the high-energy valence electron on sodium is transferred to the low-energy unfilled orbital on chlorine. The loss of an electron by sodium produces a sodium one-plus ion, while the gain of an electron by chlorine produces a chlorine one-minus ion. The resulting ions of opposite charge lower their energy by moving close to one another. The interaction between the two interacting ions is called an ionic bond, and NaCl is an ionic compound. We will assume that all compounds between metals and nonmetals are ionic. However, recall that late metals (those that lie to the right of the periodic table) are fairly electronegative, so they do not give up their valence electrons easily, and their compounds are not very ionic.

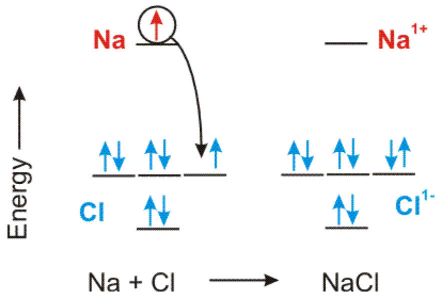


Figure 4.1: Ionic Bond Formation

4.1-3. Ionic Structure

Ionic compounds are arrays of individual ions with no identifiable molecules.

Each ion in a crystal of table salt is surrounded by six identical ions of opposite charge, and all Na–Cl distances are identical. Consequently, there are no pairs of ions that are identifiable as NaCl molecules.

A video or simulation is available online.

4.1-4. Ionic Compounds vs. Covalent Compounds

Compounds between nonmetals are covalent.

Covalent compounds are arrays of individual molecules, i.e., they are molecular.

Although covalent bonding is the topic of the following two chapters, a brief introduction is given here to allow us to compare the two different compound types in this chapter. Covalent compounds contain only nonmetals, so the atoms have similar electronegativities. Neither atom in a covalent bond has a very high energy electron that is readily transferred, so the atoms share rather than transfer the bonding electrons. Covalent bonds involve an overlap of atomic orbitals, so they are very directional, while ionic bonds are simply electrostatic interactions between spherical ions with no directionality.

While the distances between adjacent Na^{1+} and Cl^{1-} ions in a crystal of NaCl are all identical, there are two distinct distances observed between O and H atoms in an ice crystal. The existance of two distinct distances in ice allow us to identify individual water molecules as an oxygen atom and the two hydrogen atoms that are closest to it. The longer distance is then between the oxygen atom on one molecule and a hydrogen atom on an adjacent water molecule in the crystal. Thus, ice consists of individual water molecules that interact to produce the solid, while table salt consists of Na^{1+} and Cl^{1-} ions with no NaCl molecules.

4.1-5. Ionic or Covalent Exercise

EXERCISE 4.1:

Indicate whether each of the following is ionic or covalent.

$CaCl_2$
- ionic
- covalent

SF_2
- ionic
- covalent

KCl
- ionic
- covalent

CCl_4
- ionic
- covalent

Na_2O
- ionic
- covalent

F_2O
- ionic
- covalent

N_2O_3
- ionic
- covalent

Fe_2O_3
- ionic
- covalent

4.2 Naming Ions and Predicting their Charge

Introduction

Most ionic compounds form between a metal cation and a nonmetal anion. In this section, we examine the electrons that are lost by the metal and the orbitals that are filled by the nonmetal. Once we know which electrons are lost and which orbitals are filled, we can predict the probable charges on the ions and write their electron configurations.

Prerequisites
- 3.1 Valence Electrons (Write valence electron configurations for atoms.)
- 3.5 Ionization Energy (Predict relative ionization energies of atoms.)
- 3.6 Electronegativity (Predict relative electronegativities of atoms.)

Objectives
- Predict the cation that a metal is likely to adopt and write its electron configuration.
- Predict the charge on the anion that a nonmetal is likely to adopt and write its electron configuration.
- Determine the orbital occupancy of an ion given the charge on the ion and the occupancy of its atom.

4.2-1. Metal Cations

Cations are produced by the loss of valence electrons with those with the highest *n* quantum number being lost first. Consequently, first row transition metals lose their 4s electrons before they lose any 3d electrons.

Metals are characterized by low ionization energies, so they lose electrons to become cations, and the charge on the cation is determined by the number of electrons that are lost. While all of the electrons in an atom can be removed, the ionization energy of each successive ionization increases (3.5 Ionization Energy). As a result, no more than three electrons can be removed in chemical processes. In addition, core electrons are very tightly bound and are never removed in chemical processes. Thus, only the valence electrons are lost. While some metals lose all of their valence electrons, others lose only some of them. The following rules help determine which electrons are lost in chemical processes:

- Monatomic cations with charges greater than +3 do not form.
- Electrons from the outermost shell (highest n quantum number) are lost first. This is important in determining the cations formed by transition metals.
- Within a shell, electrons from the subshell with the highest l quantum number are lost first. This is important for the heavier metals in Groups 3, 4, and 5.

Group 1A & 2A Metals	**Group 3A Metals**
Lose their valence electrons to form +1 and +2 ions, respectively.	Lose all of their valence electrons to form +3 ions. Tl forms both +3 and +1 ions, but not a +2 ion. The reason is that the heavier main group elements can lose only a portion of their valence shell. Tl is $6s^2 6p^1$. Both valence sublevels are in the same level, so the one with the highest l quantum number is emptied first. Thus, Tl can lose the 6p and not the 6s to form the +1 ion, but it cannot lose the 6s and not the 6p to form a +2 ion.
Group 4A Metals	**Transition Metals**
+4 monatomic ions do not exist, so the **Group 4A metals** cannot lose all of their valence electrons. However, the heavier metals in the group (Sn and Pb) can lose the electrons in the sublevel with the highest l quantum number, the outermost p sublevel, to form +2 ions.	Lose electrons in the level with the highest n quantum number. Thus, most transition elements lose their outermost s electrons to form +2 ions. Scandium is an exception because it loses all three valence electrons to form Sc^{3+} (no +2 ion). Silver forms only a +1 ion, and copper forms both +2 and +1 ions. In addition, several transition metals form a +3 ion in addition to a +2 ion.

Table 4.1: Cations Formed by Metals

4.2-2. Nonmetal Anions

Nonmetals form anions by gaining the number of electrons required to fill their valence shell (outermost s and p sublevels).

Nonmetals are electronegative, so they tend to gain electrons to become anions. The number of electrons gained equals the number required to fill their valence shell. A filled valence shell for all nonmetals except hydrogen contains eight electrons (two s and six p electrons). Thus,

$$\text{charge on an anion} = \text{group number} - \text{eight}$$

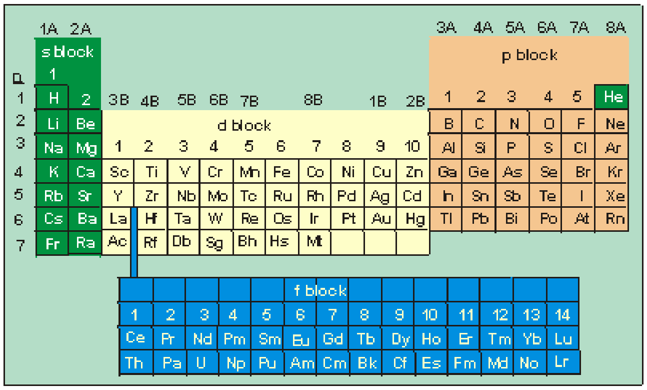
The resulting electron configuration is the same as that of the next noble gas, i.e., anions are ***isoelectronic*** with the next noble gas. Each successive electron is more difficult to add due to the Coulombic repulsion between the charge of the electron and that of the anion. Indeed, adding a fourth electron to a −3 anion is so difficult that −4 ions do not form in chemical processes.

7A	**6A**	**5A**	**4A**
−1 ions	−2 ions	−3 ions	Monatomic anions with charges of −4 do not exist, so the Group 4A nonmetals do not form anions.

Table 4.2: Anions Formed by Nonmetals

4.2-3. Predicting Charge and Electron Configuration Exercise

EXERCISE 4.2:



Each atom forms only one monatomic ion. What is the charge on that ion?

S ____________ Mg ____________ Sc ____________

P ____________ Ag ____________ Zn ____________

What are the electron configurations of the following ions? Use noble gas cores.

Sc^{3+} ____________ N^{3-} ____________ Ni^{2+} ____________

Bi^{3+} ____________ K^{1+} ____________ Br^{1-} ____________

4.2-4. Orbital Occupancies of Ions Exercise

EXERCISE 4.3:

Substances can gain and/or lose electrons, and we will frequently have to consider the orbital energy diagrams of the resulting species. Consider the following example in which you must identify which ions of substance X (shown with brown background) are represented by Figures a–d.

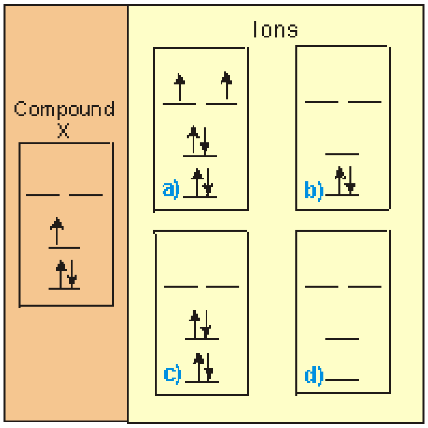


Figure a	Figure b	Figure c	Figure d
X^{4-}	X^{4-}	X^{4-}	X^{4-}
X^{3-}	X^{3-}	X^{3-}	X^{3-}
X^{1-}	X^{1-}	X^{1-}	X^{1-}
X^{1+}	X^{1+}	X^{1+}	X^{1+}
X^{2+}	X^{2+}	X^{2+}	X^{2+}
X^{3+}	X^{3+}	X^{3+}	X^{3+}

4.3 Ionic vs. Atomic Size

Introduction

We saw in the previous chapter that the size of an atom depends upon the size of its outermost orbitals, and ions form when electrons leave or enter those orbitals. Consequently, the sizes of ions are different than those of the atoms. In this section, we compare the sizes of atoms, anions, and cations.

Prerequisites

- 3.3 Relative Atomic Size (Predict relative sizes of atoms from their positions in the periodic table.)

Objectives

- Explain why cations are smaller than their atoms, but anions are larger.
- Predict the relative sizes of a series of ions.

4.3-1. Relative Ion Size

Cations are smaller than their atoms, but anions are larger than their atoms.

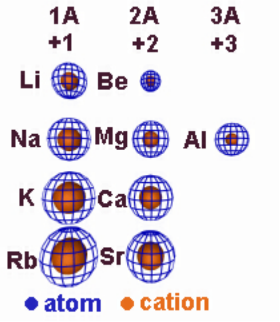


Figure 4.2 Relative Sizes of Cations and Their Atoms: A loss of electrons increases Z_{eff} and, if the valence shell is emptied, decreases the n quantum number. Consequently, cations are smaller than their parent atoms.

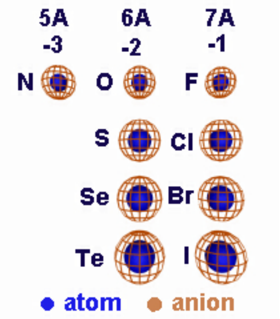


Figure 4.3 Relative Sizes of Anions and Their Atoms: A gain of electrons decreases Z_{eff}, so anions are larger than their atoms.

4.3-2. Ionic Size Exercise

EXERCISE 4.4:

Use only a periodic table to determine the **largest** ion in each group.

Cl^{1-}
F^{1-}
I^{1-}

Na^{1+}
S^{2-}
Al^{3+}

Br^{1-}
K^{1+}
Se

4.4 Oxidation States

Introduction

Electron counting (keeping track of where the electrons are in a compound) is a valuable aid in predicting the formulas of compounds, balancing certain types of chemical equations, predicting properties, and even predicting reactive centers. In this lesson, we introduce the oxidation state method for counting electrons. We then show how to determine the oxidation states of an atom in a molecule or ion and how to use oxidation states to predict formulas.

Prerequisites

- 3.4 Relative Orbital Energies (Predict relative valence orbital energies of atoms.)
- 3.5 Ionization Energy (Predict relative valence orbital energies of atoms based on their ionization energies.)
- 3.6 Electronegativity (Predict relative valence orbital energies of atoms based on their electronegativities.)
- 2.3 Bohr Model

Objectives

- Define the term "oxidation state."
- Explain how the charge on a species (compound or ion) is related to the oxidation states of its atoms.
- Determine the oxidation states of the atoms in an ion or molecule.
- Predict chemical formulas for binary compounds.

4.4-1. Oxidation States from Chemical Formulas Video

A video or simulation is available online.

4.4-2. Oxidation State Definition

The oxidation state of an atom in a compound is the charge it would have if its bonds were ionic.

The ***oxidation state*** of an atom in a compound is the charge the atom would have if its bonds were ionic. However, it is used to account for the electrons in all compounds irrespective of the bond type. **Oxidation states are obtained by assigning all bonding electrons to the more electronegative atom in each bond.** Thus, we can conclude that the oxidation state of an atom is

- negative if it is the more electronegative atom, and
- positive if it is the less electronegative atom.

4.4-3. Oxidation States of Hydrogen and Chlorine

The most common oxidation state of Cl is -1 because most of its bonds are to less electronegative elements.

Cl has a zero oxidation state when bound to itself, and it can have positive oxidation states when bound to O or F.

As shown in Figure 4.4, the valence orbitals of hydrogen lie between those of the metals and the nonmetals. Thus, the electrons in a Metal–Hydrogen bond are assigned to the hydrogen, so it adopts a -1 oxidation state. However, in a Nonmetal–Hydrogen bond, the electrons are assigned to the lower energy nonmetal, and the hydrogen adopts a $+1$ oxidation state. In the H–H bond of H_2, both orbitals have the same energy, so the electrons must be shared to give each H an oxidation state of 0.

The valence orbitals of chlorine lie below those of all other elements except those of oxygen and fluorine. Consequently, chlorine adopts a -1 oxidation state when bound to most elements. Like hydrogen, it has a zero oxidation state when bound to itself in Cl_2. However, it can adopt positive oxidation states when bound to O or F. In its binary compounds OCl_2 and FCl, it is assumed to lose the unpaired electron to adopt a $+1$ oxidation state, but if it is bound to more than one F or O, the appropriate number of electron pairs are also assigned to the O or F, so Cl can then adopt $+3$, $+5$, and $+7$ oxidation states. See Table 4.3 for some examples.

Ox State of Cl	Examples
-1	CCl_4O, NCl_3, KCl
0	Cl_2
$+1$	ClF, Cl_2O, ClO^{1-}
$+3$	ClF_3, $ClO_2{}^{1-}$
$+5$	$ClO_3{}^{1-}$
$+7$	$ClO_4{}^{1-}$

Table 4.3

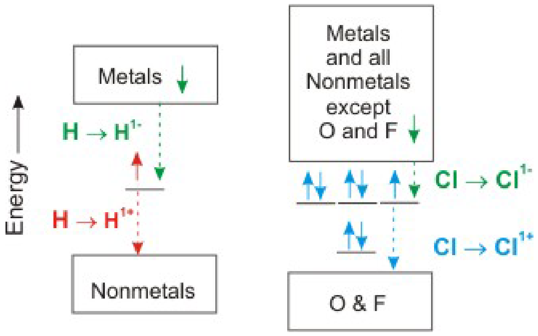


Figure 4.4 Oxidation States of Hydrogen and Chlorine

4.4-4. Oxidation State Sum

The oxidation states of all of the atoms in a chemical species must sum to the charge on the species.

The oxidation states of the atoms in a molecule or ion represent the charge they would have if all of the bonds were ionic. Consequently,

- the oxidation states of all the atoms in an ion must sum to the charge of the ion, and
- the oxidation states of all the atoms in a molecule must sum to zero.

EXAMPLE:

For example, let us determine the charge on the carbonate ion ($CO_3{}^x$) given that the oxidation states of C and O are +4 and −2, respectively. The charge on the ion equals the sum of the oxidation states, so we write

$$\text{charge} = (1\text{C})(+4/\text{C}) + (3\text{O})(-2/\text{O}) = 4 - 6 = -2$$

The carbonate ion is the $CO_3{}^{2-}$ ion.

4.4-5. Oxidation State Guidelines

The oxidation state of an atom lies between its group number and its group number minus eight.

The maximum oxidation state of an atom equals the number of electrons that can be lost from its valence shell, which equals its group number. The lowest oxidation state that an atom can achieve is equal to minus the number of electrons required to fill its valence shell, which is −(8 − group number).

$$+(\text{group number}) \geq \text{ Oxidation State } \geq -(8 - \text{group number})$$

The more electronegative the element, the more likely it is to be found in its lowest (most negative) oxidation state, and the lower its ionization energy, the more likely it is to be found in its highest oxidation state.

The valence orbitals of **metals** are high in energy, so they seldom accept electrons to obtain negative oxidation states. Thus, the metal is always in a positive oxidation state in compounds with nonmetals.

- The Group 1A, 2A, and 3A metals are usually found in their highest oxidation states (+1, +2, and +3) when bound to nonmetals.
- Transition elements tend to adopt oxidation states of +2 and +3, but Ag is +1 and Cu is +1 or +2 in most of their compounds. Some transition elements can achieve oxidation states as high as their group number when surrounded by highly electronegative atoms (usually oxygen). For example, vanadium is +5 in $VO_4{}^{3-}$, chromium is +6 in $CrO_4{}^{2-}$, and Mn is +7 in $MnO_4{}^{1-}$.

The valence orbitals of **nonmetals** are much lower than those of metals, so nonmetals are usually in their lowest oxidation states when bound to metals. The more electronegative a nonmetal is, the more likely it is to assume its lowest oxidation state. However, nonmetals can achieve positive oxidation states when bound to more electronegative elements. They can obtain oxidation states as high as their group number when bound to highly electronegative elements (especially O and F). For example, P is +5 in $PO_4{}^{3-}$ and PF_5, S is +6 in SO_3 and SF_6, and Cl is +7 in $ClO_4{}^{1-}$.

4.4-6. Oxidation State Rules

The oxidation state guidelines give us ranges for the oxidation states of the elements, but many atoms have the same oxidation state in almost all of their compounds. To determine the oxidation state of an atom in a molecule or ion, use the oxidation state rules given in Table 4.4. **The oxidation state rules are listed in order of priority, so they should be used in the order given; that is, a rule takes precedence over any rule below it, or any rule can be violated only to satisfy a rule above it.**

Note that the oxidation state rules merely reflect what we already know about atomic properties: atoms with low ionization energies (Groups 1A and 2A) are generally found in the highest oxidation states, while highly electronegative atoms (F and O) are generally in their lowest oxidation states.

Rule	**Reason**
The oxidation states of the atoms in an element are all zero.	When the valence orbitals of the two atoms are the same, the bonding electrons are assumed to be shared, not transferred. For example, the oxidation state of Cu in metallic Cu is zero, both F atoms in F_2 are zero (the only time F is not −1), and all eight sulfur atoms in S_8 are zero.
F is −1.	The valence orbitals of F are lower than the valence orbitals on any other element, i.e., F is the most electronegative element. Consequently, it is always assigned the bonding electrons. There is only one compound in which an F atom is not −1. What is it? Hint: See the only rule that takes priority over this rule.
1A metals are +1, 2A metals are +2, and Al is +3.	The valence orbitals in these metals are very high in energy, i.e., these metals have low ionization energies. They also become isoelectronic with a noble gas when they form the ions.
H is +1.	The 1s orbital on H is lower in energy than the valence orbitals of most metals and higher in energy than those of most nonmetals. Therefore, H is +1 except when Rule 1 forces it to be 0 or Rule 3 (metals with higher energy valence orbitals) forces it to be −1.
O is −2.	Oxygen is the second most electronegative atom, so it is usually assigned the bonding electrons. However, it is not −2 when it is elemental O_2 (Rule 1) or bonds to F (Rule 2). In addition, it can be −1 if Rules 3 and 4 force it. Compounds in which the oxidation state of oxygen is −1 are called peroxides. Peroxides contain $O_2{}^{2-}$, which has an O–O bond. Hydrogen peroxide (H_2O_2) is a common peroxide.
7A elements are −1.	Halogens are electronegative, so they tend to fill their valence shell to attain −1 oxidation states. However, they can attain positive oxidation states when bound to more electronegative atoms, such as oxygen, or more electronegative halogens, e.g., Cl is +7 in $ClO_4{}^{1-}$, Br is +5 in $BrO_3{}^{1-}$, and I is +3 in IF_3.

Table 4.4

4.4-7. Oxidation State Exercise

EXERCISE 4.5:

Oxidation State Rules

1 Atoms in elements are zero.
2 F is −1.
3 Group 1A metals are +1, 2A metals are +2, and Al is +3.
4 H is +1.
5 O is −2.
6 Group 7A elements are −1.

Determine the oxidation state of the first element in each of the following.

$FeCl_3$ ______ $MnO_4{}^{1-}$ ______ $Cr_2O_7{}^{2-}$ ______

CaO_2 ______ NH_3 ______

4.4-8. Using Oxidation States to Determine Charge Exercise

EXERCISE 4.6:

Determine the charge on each ion. Use the following oxidation states.

$O = -2$ $Cr = +6$ $P = +5$ $Mn = +7$ $N = +5$

$CrO_4{}^x$ ______ $PO_4{}^x$ ______

$MnO_4{}^x$ ______ $NO_3{}^x$ ______

4.4-9. Chemical Formulas from Oxidation States Video

A video or simulation is available online.

4.4-10. Predicting Formulas

The likely formula of a compound can be predicted by assigning likely oxidation states to each of the atoms.

Compounds carry no net charge, so the total positive charge must equal the negative of the total negative charge. The total positive charge equals the positive oxidation state (OX_{pos}) times the number of atoms with that oxidation state (N_{pos}), and the total negative oxidation state equals the negative oxidation state (OX_{neg}) times the number of atoms that have that oxidation state (N_{neg}). We can therefore write the following:

$$N_{pos}OX_{pos} = -N_{neg}OX_{neg}$$

Rearranging, we obtain

$$\frac{N_{pos}}{N_{neg}} = \frac{OX_{neg}}{OX_{pos}}$$

Thus, the subscripts of the atoms in a chemical formula are inversely proportional to their oxidation state.

To determine the formula of a binary compound (only two elements) follow these steps:

1 Assign oxidation states to the two elements. If the elements are not listed in the oxidation state rules, assign +Group number to the less electronegative element and −(8 − Group number) to the more electronegative element. However, recall that nonmetals can empty only their p sublevel, leaving two s electrons. In this case, $\mathrm{OX}_{\mathrm{pos}}$ = Group number − 2.

2 Determine the ratio of oxidation states as a ratio of smallest whole numbers.

3 The ratio of the subscripts in the formula varies inversely with the ratio of oxidation states, so the whole numbers in step 1 are the subscripts.

4 Write the formula, but be sure to always write the less electronegative element first.

4.4-11. Predicting Formulas Exercise

EXERCISE 4.7:

Predict the formula of the compound formed between each pair of elements below.

oxidation state of 1st element

Na and O ______________

Zn and Cl ______________

Al and S ______________

C and O ______________

oxidation state of 2nd element

Na and O ______________

Zn and Cl ______________

Al and S ______________

C and O ______________

LCM of the two oxidation states

Na and O ______________

Zn and Cl ______________

Al and S ______________

C and O ______________

formula of compound

Na and O ______________

Zn and Cl ______________

Al and S ______________

C and O ______________

4.4-12. Writing Formulas of Binary Compounds Exercise

EXERCISE 4.8:

Use the highest and lowest oxidation states of nonmetals and common oxidation states of metals to predict the formulas of the compounds that would form between each pair of elements.

phosphorus and chlorine

____

carbon and fluorine

____

calcium and oxygen

____

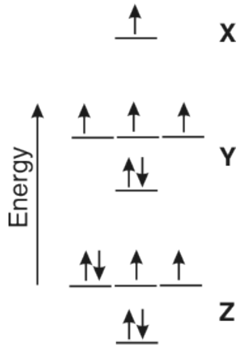
copper and sulfur

____

4.4-13. Orbital Diagrams and Oxidatation State Exercise

EXERCISE 4.9:

Use the energy level diagram for the valence electrons of X, Y, and Z to determine each answer. Always write the more electronegative element last.



oxidation state of X when it bonds to Y or Z ________________

oxidation state of Y when it bonds to X ________________

oxidation state of Y when it bonds to Z ________________

oxidation state of Z when it bonds to Y ________________

formula of the compound formed between X and Y ________________

formula of the compound formed between X and Z ________________

formula of the compound formed between Y and Z ________________

What are the identities (symbols) of X, Y, and Z if they are all in the second period?

X = ________________ Y = ________________ Z = ________________

4.5 Polyatomic Ions

Introduction

So far, we have considered only monatomic ions (ions composed of a single atom), but many ions consist of several atoms and are called polyatomic ions. The bonds between the atoms in a polyatomic ion are not ionic, but a polyatomic ion does have a net charge and bonds to other ions via an ionic bond.

Objectives

- Identify the common polyatomic ions.

4.5-1. Polyatomic Ions

A number of ionic compounds are composed of polyatomic ions, which are charged groups of covalently bound atoms. While the polyatomic ion forms ionic bonds with oppositely charged ions, the atoms within a polyatomic ion are nonmetals held together by covalent bonds. Many of the polyatomic ions are ***oxoanions***, i.e., they are negative ions that contain oxygen atoms covalently bound to another element. In the common polyatomic ions listed in Table 4.5, the only cations are ammonium and hydronium, and the only anions that are not oxoanions are hydroxide and cyanide.

Recall that ionic compounds can be identified as those that contain metals because metals represent almost all of the common monatomic cations. However, ions can also be polyatomic. Ammonium is by far the most common polyatomic cation in compounds. Thus, NH_4Cl, NH_4NO_3, and $(NH_4)_2SO_4$ are also ionic compounds. We conclude that ionic compounds are those that contain either a metal or a polyatomic cation such as ammonium.

Cations				
$NH_4{}^{1+}$	ammonium ion		H_3O^{1+}	hydronium ion
Anions				
$C_2H_3O_2{}^{1-}$	acetate ion		OH^{1-}	hydroxide ion
$CO_3{}^{2-}$	carbonate ion		$NO_3{}^{1-}$	nitrate ion
$ClO_4{}^{1-}$	perchlorate ion		$NO_2{}^{1-}$	nitrite ion
$ClO_3{}^{1-}$	chlorate ion		$MnO_4{}^{1-}$	permanganate ion
$ClO_2{}^{1-}$	chlorite ion		$O_2{}^{2-}$	peroxide ion
ClO^{1-}	hypochlorite ion		$PO_4{}^{3-}$	phosphate ion
$CrO_4{}^{2-}$	chromate ion		$SO_4{}^{2-}$	sulfate ion
$Cr_2O_7{}^{2-}$	dichromate ion		$SO_3{}^{2-}$	sulfite ion
CN^{1-}	cyanide ion			

Table 4.5: Some Common Polyatomic Ions

4.6 Naming Ionic Compounds

Introduction

Understanding how ionic compounds are named helps you better communicate about chemistry. In this section, we explain how binary ionic compounds and ionic compounds containing polyatomic ions are named.

Prerequisites

- 1.11 Dimitri Mendeleev and The Periodic Law

Objectives

- Name ions that contain one or more protons.
- Name ionic compounds containing polyatomic ions.

4.6-1. Binary Compounds

The oxidation state of the metal is given as a Roman numeral in parentheses when naming inorganic compounds that contain a metal that can attain more than one oxidation state.

The name of a binary ionic compound is simply the name of the cation (name of the metal atom) followed by the name of the anion (name of nonmetal with ending changed to -ide). If the metal has the same oxidation state in all of its compounds, the oxidation state is not indicated. The metals for which the oxidation state is usually omitted are the metals of Groups 1A and 2A, Al, Sc, Zn, Ag, and Cd. The remaining metals have more than one possible oxidation state, and so the oxidation state of the metal is indicated with a Roman numeral in parentheses after the name of the metal. Note that there is no space between the name of the metal and the Roman numeral in parentheses.

Some examples:

- $NaCl$ = sodium chloride (Group 1A are always +1.)
- Mg_3N_2 = magnesium nitride (Group 2A are always +2.)
- $ZnBr_2$ = zinc bromide (Zn is always +2.)
- AgF = silver fluoride (Ag is always +1.)
- Sc_2O_3 = scandium oxide (Sc is always +3.)
- CoO is cobalt(II) oxide to distinguish it from Co_2O_3, which is cobalt(III) oxide.
- $TlCl$ is thallium(I) chloride to distinguish it from $TlCl_3$, which is thallium(III) chloride.

4.6-2. Naming Exercise

EXERCISE 4.10:

Name the following compounds.

$AlBr_3$ ______________

Ag_2O ______________

$CuCl$ ______________

Hg_2Cl_2 ______________

$ZnBr_2$ ______________

$CoCl_3$ ______________

$ZnCl_2$ ______________

$FeCl_3$ ______________

PbO_2 ______________

MnO_2 ______________

SnO_2 ______________

K_2O ______________

4.6-3. Naming Oxoanions of the Elements of Groups 4, 5, and 6

Suffixes are used to indicate the oxidation state of the central atom in most oxoanions:

- -ate implies that the central atom is in its highest oxidation state (group number).
- -ite tells us that the oxidation state of the central atom is lower than the highest oxidation state by two because the ion has one less oxygen atom than the corresponding ion that ends in -ate.

Removing an oxygen atom from an oxoanion reduces the oxidation state of the central atom by two, but it does not change the charge on the ion. Some examples:

Group 4	CO_3^{2-} is the carbon**ate** ion because Group 4A carbon is in the +4 oxidation state.
Group 5	PO_4^{3-} is the phosph**ate** ion because Group 5A phosphorus is in the +5 oxidation state. However, NO_3^{1-} is the nitr**ate** ion. Removing a single oxygen atom produces NO_2^{1-}, the nitrite ion.
Group 6	SO_4^{2-} is the sulf**ate** ion because Group 6A sulfur is in the +6 oxidation state. Removal of one oxygen atom produces the sulf**ite** ion, SO_3^{2-}.

Table 4.6

4.6-4. Naming Oxoanions of Group 7

The oxoanions of the Group 7A elements are an exception because, unlike the others, they each form four oxoanions. Consequently, both prefixes and suffixes must be used (see Table 4.7). In the perchlorate ion ($ClO_4{}^{1-}$), the chlorine is in its highest oxidation state (+7). The chlorate ion ($ClO_3{}^{1-}$) has one less oxygen, so the oxidation state of Cl is two less, or +5. The chlorite ion ($ClO_2{}^{1-}$) has one less oxygen than chlorate, which lowers the oxidation state of Cl to +3. Finally, the hypochlorite ion (ClO^{1-}) has one less oxygen than chlorite, and the oxidation state of the Cl is reduced to +1. Similarly, perbromate is $BrO_4{}^{1-}$, bromate is $BrO_3{}^{1-}$, etc. Note, however, that fluorine is the most electronegative element, so it never has a positive oxidation state. Consequently, fluorine forms no oxoanions.

Prefix	Suffix	Oxidation State of Halogen	Formula
Per-	-ate	+7	$XO_4{}^{1-}$
	-ate	+5	$XO_3{}^{1-}$
	-ite	+3	$XO_2{}^{1-}$
Hypo-	-ite	+1	XO^{1-}

Table 4.7: Prefixes and Suffixes of the Oxoanions Formed by the Halogens

4.6-5. Protonated Ions

Ions that have charges of −2 and −3 pick up protons to produce protonated anions, which are named by placing hydrogen (or dihydrogen) and a space in front of the name of the ion. An older, but still common, method for naming some of these ions is to replace the "hydrogen and a space" with simply "bi" with no space. Thus, HS^{1-} is either the hydrogen sulfide ion or the bisulfide ion.

$HCO_3{}^{1-}$	hydrogen carbonate or bicarbonate ion
$HPO_4{}^{2-}$	hydrogen phosphate ion
$H_2PO_4{}^{1-}$	dihydrogen phosphate ion
$HSO_4{}^{1-}$	hydrogen sulfate or bisulfate ion
$HSO_3{}^{1-}$	hydrogen sulfite or bisulfite ion

Table 4.8: Common Protonated Oxoanions

4.6-6. Writing Formulas for Compounds with Polyatomic Ions Exercise

EXERCISE 4.11:

Use the fact that ***the names of the polyatomic ions are used without change when naming compounds that contain one or more polyatomic ions*** to write formulas for the following compounds.

ammonium bromide ________________

potassium chlorate ________________

cobalt(III) nitrate ________________

scandium phosphate ________________

ammonium sulfate ________________

calcium cyanide ________________

4.7 Exercises and Solutions

Links to view either the end-of-chapter exercises or the solutions to the odd exercises are available in the HTML version of the chapter.

Chapter 5 – Covalent Bond

Introduction

We saw in Chapter 4 that ionic bonds are not directional and that ionic compounds exist as extended networks rather than individual molecules. In this chapter, we begin our study of molecular substances, substances that exist as discrete molecules. Covalent bonds are directional and covalently bound atoms form molecular substances.

5.1 The Covalent Bond

Introduction

Covalent bonds result from the overlap of orbitals and involve a sharing of pairs of electrons. In this lesson, we examine the nature of the covalent bond.

Prerequisites

- 1.8 Electromagnetism and Coulomb's Law (Describe how the energy of interaction between charged particles varies with the distance between them.)
- 1.7 Energy (Predict the direction of energy change for natural processes.)
- 2.6 Orbital Shapes and Sizes

Objectives

- Explain how the energy of two nuclei varies with the distance between them.
- Define bond energy and bond length.

5.1-1. H–H Bond Video

A video or simulation is available online.

5.1-2. H–H Bond

A ***covalent bond*** results when atoms share one or more pairs of electrons. The electrons that are shared in a covalent bond are called ***bonding electrons*** or ***bonding pairs***.

In Chapters 2 and 3, we discussed the energy of interaction between a nucleus and its electrons, which reduces their potential energy and is responsible for the existence of atoms. However, valence electrons can reduce their energy ever farther by interacting with more than one nucleus. Consider Figure 5.1, which shows the energy of interaction between two hydrogen atoms as a function of their separation, r.

- At a separation of r_1, the two hydrogen atoms are too far apart to interact; i.e., they have zero energy of interaction, and the electrons are in spherical 1s orbitals.
- At a distance of r_2, each electron is attracted by the nucleus of the other atom as well as its own. There is also repulsion between the nuclei, but it is much less because the nuclei are still relatively far apart. The greater attractive force between the oppositely charged particles lowers the energy of the system. The electron density begins to concentrate in the region between the nuclei, distorting the orbitals from their spherical shape.
- At r_3, the atoms are weakly bound together, and the two orbitals overlap one another.
- At r_4, the energy of the system has reached a minimum as the electron/nuclear attraction just balances the internuclear repulsion. The bonding electrons are in an orbital that concentrates the electron density in the region between the two nuclei. The negative charge of the two electrons holds the positively charged nuclei together in an H–H covalent bond.
- At r_5, the repulsion between the nuclei is the dominating force, so the energy rises sharply.

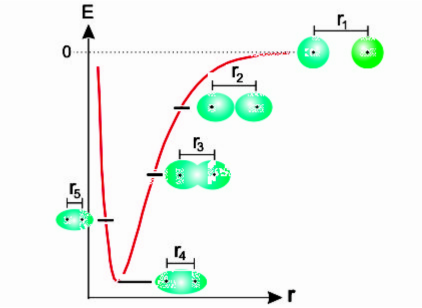


Figure 5.1: H–H Bond Formation and Length Energy of interaction between two H atoms as a function of r, the distance between the nuclei, which are represented by the small dots.

5.1-3. Bond Length and Bond Energy

The bond energy (D) is the energy required to break a mole of bonds in the gas phase.

The bond length is the separation between two bound atoms at the position of minimum energy.

The equilibrium distance between two bound nuclei in a molecule defines the ***bond length*** of their bond. The H–H bond length, which is 0.74 Å or 74 pm ($p = 1 \times 10^{-12}$), is a very short bond because the two atoms are so small that they must get very close to interact. The I–I bond length, which is 2.7 Å (270 pm), is very long because the two atoms are so large. Most bond lengths lie between 1 and 3 Å (100 and 300 pm).

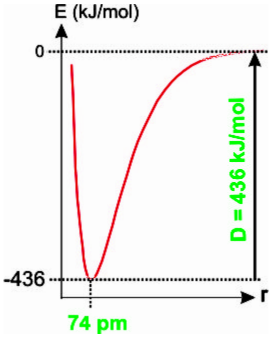


Figure 5.2

The energy of two bound atoms is lower than that of the separated atoms because the bonding electrons on each atom interact with both nuclei. Thus, energy is released when atoms bond. In the case of the H–H bond, 436 kJ is released when two moles of hydrogen atoms combine to form one mole H–H bonds. This means that the minimum energy of two interacting hydrogen atoms is −436 kJ/mol. Separating the two bound atoms requires breaking the bond, which requires an input of the same amount of energy that was released when the bond formed. The energy required to break or dissociate a bond in the gas phase is called the bond or dissociation energy and given the symbol D. The H–H bond energy in H_2 is $D = 436$ kJ/mol and is an average bond energy, as most bond energies lie between 100 and 1000 kJ/mol. The I–I bond is very weak with a bond energy of only 151 kJ/mol.

5.2 Bond Polarity

Introduction

Although the bonding electrons are shared in a covalent bond, electronegativity differences between the bound atoms can result in unequal sharing. Bonds in which the electrons are not shared equally are said to be polar bonds, the topic of this section.

Prerequisites

- 2.7 Electron Configurations
- 2.3 Bohr Model
- 3.6 Electronegativity (Predict the relative electronegativities of two atoms.)

Objectives

- Define the bond dipole and represent it with an arrow.
- Distinguish between *purely covalent*, *polar covalent*, and *ionic* bonds.

5.2-1. Polar vs. Nonpolar Bonds

If the electronegativities of two atoms in a bond are different, then the bond is polar.

A video or simulation is available online.

- The presence of a positive and a negative pole in a covalent bond produces a ***bond dipole***.
- A covalent bond with a bond dipole is said to be a ***polar covalent bond***.
- A covalent bond with no bond dipole is a ***purely covalent bond***.

5.2-2. Polar Bonds and Bond Dipoles

Polar bonds have bond dipoles, which are represented with arrows pointing from the positive pole (less electronegative atom) toward the negative pole (more electronegative atom) with a line through the positive end.

In H_2 the bound atoms have identical electronegativities, so the bonding electrons are shared equally. Such bonds are ***purely covalent bonds***. However, if the electronegativities of the bound atoms differ, as in the case of HF, the bonding electrons are not shared equally as the more electronegative fluorine becomes electron rich and the less electronegative hydrogen becomes electron poor. The result is that negative charge is produced on the more electronegative atom and positive charge on the less electronegative atom. The charge that is produced in a covalent bond is only a part of what it would be if the bond were ionic, so it is said to be a partial charge, which is represented with a δ (delta). Thus, a covalent bond involving atoms of different electronegativities has two electrical poles ($\delta-$ and $\delta+$) and is said to have a ***bond dipole*** and is called a ***polar covalent bond***.

Bond dipoles are frequently represented with arrows pointing from the positive pole toward the negative pole. A line is then drawn through the arrow so as to make a plus sign at the positive end. Although the length of the arrow is normally related to the strength of the dipole, we will use the arrow to show direction only, so relative lengths are not meaningful. No bond dipole exists for nonpolar molecules, so no arrow is used with them.

Figure 5.3 The direction of the bond dipole in HF is shown with the red arrow. Note that a line through the arrow makes a plus sign at the positive end of the dipole.

5.2-3. Charge Distribution

Although molecules are neutral, they do contain regions of charge due to the asymmetric charge distribution in polar bonds. We will use the convention of indicating regions of negative charge as red and regions of positive charge as blue. Regions of no charge will be shown as white. Consider the examples below.

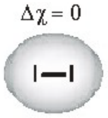


Figure 5.4a: Charge Distribution of an I–I Bond Two iodine atoms have the same electronegativities, so the I–I bond is not polar and there is no asymmetric charge distribution. Consequently, the electron cloud is shown as white.

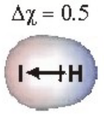


Figure 5.4b: Charge Distribution of an I–H Bond Iodine is more electronegative than hydrogen, so the bonding electrons reside nearer the iodine. The increase in electron density is shown in red. The electrons move away from the hydrogen, giving it a slight positive charge shown in blue. The electronegativity difference is only 0.5, so the intensities of the colors are not very great. The bond dipole points from the positive (blue) region toward the negative (red) region.

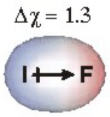


Figure 5.4c: Charge Distribution of an I–F Bond Iodine is less electronegative than fluorine, so the bonding electrons reside nearer the fluorine. Thus, F carries a partial negative charge, which is represented by the red color. The I atoms carries a partial positive charge as shown by the blue color. $\Delta\chi = 1.3$, so the colors are slightly more intense than in HI.

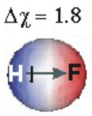


Figure 5.4d: Charge Distribution of an H–F Bond Fluorine is much more electronegative than hydrogen ($\Delta\chi = 1.8$) so the regions are intensely colored.

5.2-4. Bond Type and Electronegativity Differences

Bond types vary continuously from purely covalent to polar covalent to ionic. There is no clear distinction between a polar covalent bond and an ionic one.

The value of δ in $^{\delta+}$X–Y$^{\delta-}$ ranges from 0 to 1 for a compound like H–Cl, depending upon the electronegativity difference between X and Y. As δ increases, the charge separation in the bond increases, and it gains ionic character. When δ is 0, the bond is purely covalent, and when δ is 1, the bond is purely ionic. Thus, we refer to the ***percent ionic character*** of a bond, which increases as the electronegativity difference between the bound atoms increases. There are no clear lines separating ionic and covalent bonds; they gradually merge into one another as shown in Figure 5.5. However, we will use the following for discussion.

- **covalent bonds**: Bonds with $\Delta\chi \leq 0.4$ have less than 5% ionic character and behave like nonpolar bonds. Consequently, we will refer to them as covalent bonds. The C–H and P–H bonds are covalent bonds.
- **ionic bonds**: Bonds with $\Delta\chi \geq 1.8$ are over 50% ionic, so we will refer to them as ionic bonds. K–Br and Na–Cl are ionic bonds.
- **polar covalent bonds**: Bonds that lie between the covalent and ionic limits given above will be called polar covalent bonds. The P–O and H–Cl bonds are polar covalent bonds.

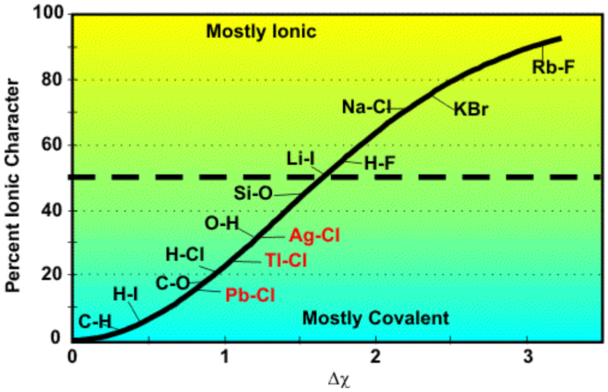


Figure 5.5 Percent Ionic Character of a Bond as a Function of the Electronegativity Difference Between the Bound Atoms

Bond types change continuously from covalent to polar covalent to ionic with no clear boundaries between the bond types. However, ionic bonds are favored by large differences in electronegativity, while covalent bonds are favored by small differences. Consequently, we will use the following generalizations in this course:

- **Ionic bonds form between metals (low χ) and nonmetals (high χ).**
- **Covalent bonds form between nonmetals because they have similar χs.**

5.2-5. Exceptions

Assume that metal-nonmetal bonds are ionic and nonmetal-nonmetal bonds are covalent, but it is not always true.

The generalization that metal-nonmetal bonds are ionic and nonmetal-nonmetal bonds are covalent will aid our discussions, but it is not a hard and fast rule. As a result, metal-nonmetal bonds are often more covalent than ionic. For example, $\Delta\chi = 1.1$ for the Ag–Cl bond, so it is only about 30% ionic, and $\Delta\chi = 0.7$ for the Pb–Cl bond, so it is less than 15% ionic. Thus, not all metal-nonmetal bonds are ionic. In addition, the H–F bond is between nonmetals, so it will be referred to as covalent, but $\Delta\chi = 1.9$ for the bond, which makes it about 60% ionic. Thus, not all nonmetal-nonmetal bonds are very covalent.

Metal	χ
Ag	1.9
Sn	2.0
Hg	2.0
Tl	2.0
Pb	2.3

Table 5.1

5.2-6. Bond Type Exercises

EXERCISE 5.1:

Use only a Periodic Table to answer the following questions.

- Which is the most polar bond?
  - H–N
  - H–C
  - H–O
- The C–Cl bond is which of the following?
  - purely covalent
  - polar covalent
  - ionic
- The Cl–Cl bond is which of the following?
  - purely covalent
  - polar covalent
  - ionic
- Which is the most polar bond?
  - S–F
  - O–F
  - F–F
- The Na–Cl bond is which of the following?
  - purely covalent
  - polar covalent
  - ionic
- The Sn–Cl bond is which of the following?
  - purely covalent
  - polar covalent
  - ionic

5.3 Naming Binary Covalent Compounds

Introduction

In this lesson, you will learn how to name binary covalent molecules.

Objectives

- Convert between the name and formula of a covalent molecule.

5.3-1. Naming Binary Compounds

Prefixes are used in the names of covalent compounds to indicate the number of each atom present.

Binary compounds are compounds that contain only two different elements. The name of a binary covalent compound consists of the name of the less electronegative element followed by the name of the more electronegative element with its ending changed to -ide. The number of atoms of each element present in a molecule is given by a Greek prefix except that the prefix "mono" is not used for the first atom in the formula. Thus, CO is carbon monoxide (not monocarbon monoxide), but N_2F_4 is dinitrogen tetrafluoride.

Many compounds have common names. For example, H_2O is water, NH_3 is ammonia, and NO is nitric oxide.

By convention, **the less electronegative element is written first in the formula except if one of the elements is hydrogen**. Many hydrogen-containing compounds are acids, and, by convention, hydrogens at the beginning of the formula are considered to be acidic hydrogens. Ammonia is written NH_3 even though hydrogen is the less electronegative element, but dihydrogen sulfide is written as H_2S because it is an acid.

The following Greek prefixes indicate the number of each type of atom that appears in the formula of covalent compounds.

Number	Prefix	Example
1	mono	CO - Carbon monoxide
2	di	CO_2 - Carbon dioxide
3	tri	SO_3 - Sulfur trioxide
4	tetra	CCl_4 - Carbon tetrachloride
5	penta	PF_5 - Phosphorus pentafluoride
6	hexa	SF_6 - Sulfur hexafluoride
7	hepta	Cl_2O_7 - Dichlorine heptaoxide*
8	octa	
9	nona	
10	deca	

*An 'a' at the end of a prefix is frequently omitted when it is followed by a vowel, so the name may also appear as 'Dichlorine heptoxide.'

Table 5.2: Prefixes Used in Naming Covalent Compounds

5.3-2. Naming Binary Covalent Compounds Exercise

EXERCISE 5.2:

Name each of the following compounds.

PF_3 ________________ IF_5 ________________ N_2O_3 ________________

$CuCl_2$ ________________ $SiCl_4$ ________________ P_2O_5 ________________

NO ________________

5.3-3. More Naming Compounds Exercises

EXERCISE 5.3:

Name the following compounds.

N_2F_4 ________________ SO_3 ________________ PbO_2 ________________

CS_2 ________________ SF_6 ________________ N_2O_4 ________________

5.4 Lewis Symbols of the Elements

Introduction

A ***Lewis structure*** shows the placement of the valence electrons around each of the atoms in a molecule. They are important because they allow us to predict the shapes of molecules, the types and relative strengths of the bonds, and regions of high and low electron density within the molecule. In this section, we introduce Lewis symbols for the elements.

Prerequisites

- Valence Electrons (Determine the number of valence electrons in an atom.)

Objectives

- Write the Lewis symbol for an atom.

5.4-1. Lewis Symbols

The structures of covalently bound molecules and ions depend upon the distribution of the valence electrons. The distribution of valence electrons can be represented by Lewis structures. The ***Lewis symbol*** **of an atom shows the valence electrons spread in four different regions and remaining unpaired until each region has at least one electron**. Lewis symbols represent the bonding atom, not the isolated atom. The number of valence electrons for a main group element is simply the element's group number, so the electron distribution given in the Lewis symbols is the same for all atoms in a group.

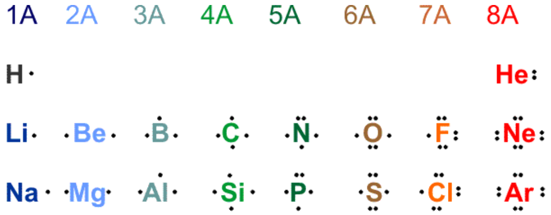


Figure 5.6: Lewis Symbols Lewis Symbol representation of the main group elements.

5.5 Lewis Structures of Diatomic Molecules

Introduction

We use diatomic molecules to introduce Lewis structures of molecules and to introduce some new terms.

Objectives

- Explain the *octet rule*.
- Determine the number of shared pairs in a Lewis formula.
- Distinguish between the bonding pairs and the lone pairs of electrons.
- Define *bond order* and determine the bond order of a bond from a Lewis formula.
- Relate the lengths and strengths of several bonds between the same two elements to the bond orders of the bonds.

5.5-1. Octet Rule

Lewis structures almost always show eight valence electrons around each atom. An exception is hydrogen, which has only two.

Filled or closed shells are very stable and atoms strive toward these configurations when they bond. In Chapter 4, we saw that atoms can attain these configurations by becoming ions: metals lose their valence electrons to obtain the closed shell configuration of the preceding noble gas, while nonmetals gain electrons to obtain the closed shell configuration of the following noble gas.

Nonmetals can also achieve closed shells by sharing electrons. A closed shell for a nonmetal consists of eight electrons (2 s and 6 p electrons). Thus, nonmetals strive to obtain eight electrons, which is called an **octet**, in their valence shell. This tendency is summarized by the ***octet rule***.

- **Lewis structures of molecules formed from nonmetals almost always show eight valence electrons around each atom**.

The octet rule provides a guide to drawing the Lewis structures of compounds.

As indicated by "almost always," there are some exceptions. The most common exception is the hydrogen atom. A closed shell for hydrogen consists of two, not eight, electrons, so **hydrogen atoms attain only a *duet* of electrons**. Thus, one and only one bond is drawn to a hydrogen atom. Other exceptions occur, but they are rare and usually result when the molecule has an odd number of electrons or contains an atom of low electronegativity such as boron.

5.5-2. Chlorine

- Chlorine is in Group 7A, so chlorine atoms each have 7 valence electrons. Consequently, chlorine atoms need one more electron to obtain an octet.
- Chlorine atoms react with one another to form Cl_2 molecules.
- The Cl atoms in a Cl_2 molecule each attain an octet by sharing their unpaired electrons.
- There is one bonding pair in Cl_2, which lies in the region of overlap of the two octet circles.
- Each Cl atom in Cl_2 also has three pairs of electrons that are not involved in the bonding. These nonbonding pairs are called ***lone pairs***.
- The two atoms have identical electronegativities, so the Cl–Cl bond is a nonpolar covalent bond.

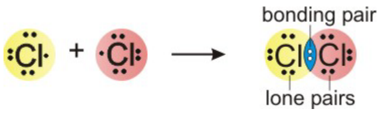


Figure 5.7: Lewis Structure of Cl_2 The yellow and red circles are not part of the Lewis structure and are used here only to distinguish between the two sets of valence electrons and to highlight the bonding pair shown in blue.

5.5-3. Shared Pairs

The number of shared pairs in a molecule can be determined from the number of valence electrons available from the atoms.

The number of shared pairs (bonding pairs) in a molecule is an important property of a molecule because it gives us information about how the atoms bond to one another. Thus, we will have occasion to determine it frequently. The number of electrons that must be shared equals the number of electrons required to satisfy the octet rule for every atom without sharing minus the number of valence electrons that are available. The number of shared pairs is half of the number of shared electrons. Mathematically, the relationship is expressed as

$$\mathrm{SP}=\frac{1}{2}(\mathrm{ER}-\mathrm{VE})$$

- **SP** is the number of shared pairs in the molecule.
- **ER** is the number electrons required to give each atom an octet (or duet for H). It is equal to the number on nonhydrogen atoms times 8 (octet) plus the number of hydrogen atoms times 2 (duet).
- **VE** is the sum of the valence electrons on all of the atoms in the molecule.

EXERCISE 5.4:

Determine the number of shared pairs in each of the following.

F_2	O_2	N_2
ER = ____________	ER = ____________	ER = ____________
VE = ____________	VE = ____________	VE = ____________
SP = ____________	SP = ____________	SP = ____________

5.5-4. Lewis Structures of Three Molecules

Bonding pairs are shown as lines in a Lewis structure, but lone pairs are shown as two dots.

In the previous exercise, we determined the number of shared pairs (SP) in three diatomic molecules (F_2, O_2, and N_2). Each atom obeys the octet rule, so the Lewis structures are drawn by first placing the correct number of shared pairs, then placing enough lone pairs around each atom to assure that each has an octet. In addition, **bonding (shared) pairs of electrons are normally shown as lines rather than dots**. Thus, the Lewis structures of these three diatomic molecules would be represented as follows:

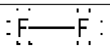
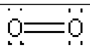
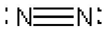
Molecule	F_2	O_2	N_2
SP	1	2	3
Lewis Structure			

Table 5.3: Lewis Structures of H_2, O_2, and N_2

Thus, each F atom has three lone pairs, each O atom has two, and each N atom has only one lone pair.

5.5-5. Bond Order

The number of bonding pairs in a bond is called its bond order.

The ***bond order*** of a bond is the number of shared pairs of electrons in the bond (the number of lines). The bond order is frequently given by indicating a single, double, or triple bond.

Bond	**Bond Order**	**Name**
F–F	1	single bond
O=O	2	double bond
N≡N	3	triple bond

Table 5.4

5.5-6. Some Bond Lengths and Strengths

Bonds get shorter and stronger as their bond order increases.

The number of electron pairs in a bond dictates the strength and length of the bond. Thus, **increasing the X–Y bond order strengthens and shortens the X–Y bond**. This is evident in the table of average bond energies and bond lengths of bonds involving C, N, and O that is shown below. The bond length also depends on the bound atoms, so **this generalization can be applied only to bonds between the same two atoms**. That is; X–Y bonds can be compared to one another as can X–Z bonds, but X–Y bonds cannot be compared with X–Z bonds.

Bond	Bond Energy (kJ/mol)	Bond Length (Å)
C–O	358	1.43
C=O	799	1.23
C≡O	1072	1.13

Bond	Bond Energy (kJ/mol)	Bond Length (Å)
C–C	347	1.54
C=C	612	1.33
C≡C	820	1.20

Bond	Bond Energy (kJ/mol)	Bond Length (Å)
N–N	163	1.47
N=N	418	1.24
N≡N	941	1.10

Table 5.5: Bond Strength and Length as a Function of Bond Order

5.6 Determining Lewis Structures

Introduction

We now extend the previous lesson to include molecules other than diatomic molecules.

Objectives

- Draw Lewis structures.

5.6-1. Determining Lewis Formulas

To determine the Lewis structure of a molecule:

1 Determine the number of shared pairs as before: $\mathrm{SP}=\frac{1}{2}\,(\mathrm{ER}-\mathrm{VE})$ where

- ER = electrons required = 8 times the number of nonhydrogen atoms + 2 times the number of hydrogens.
- VE = valence electrons = sum of the valence electrons on all of the atoms in the molecule and any charge on an ion. The number of valence electrons is increased by the negative charge of an anion and decreased by positive charge on a cation. VE is the number of electrons that must be shown in the final Lewis structure.

2 Draw the skeleton of the molecule (connect all of the atoms with single lines), then determine how many more shared pairs must be added and add them.

3 Add lone pairs to atoms to assure that each nonhydrogen atom has an octet.

4 Check your structure to be certain that each atom has an octet and that the number of electrons shown in the structure is the same as the number of valence electrons determined above.

Lewis structures should never show double or triple bonds to hydrogen or to a halogen. More than one single bond must be drawn to a halogen when it is the central atom as in $\mathrm{ClO_4}^{1-}$, but a double or triple bond should not be used. We explain why in the section on formal charge.

5.6-2. Determining Shared Pairs and Lone Pairs Exercise

EXERCISE 5.5:

Determine the number of shared pairs (SP) and the number of lone pairs (LP) around the central atom (the atom that appears first in the formula) in each of the following.

SO_2	NH_3	OF_2
ER = ____________	ER = ____________	ER = ____________
VE = ____________	VE = ____________	VE = ____________
SP = ____________	SP = ____________	SP = ____________
LP = ____________	LP = ____________	LP = ____________

$CO_3{}^{2-}$	$SO_3{}^{2-}$
ER = ____________	ER = ____________
VE = ____________	VE = ____________
SP = ____________	SP = ____________
LP = ____________	LP = ____________

5.6-3. Lewis Structure of CO Exercise

EXERCISE 5.6:

Draw the Lewis structure for carbon monoxide, CO.

1. Determine the number of electrons required with no sharing (ER).

   ____

2. Determine the number of valence electrons (VE).

   ____

3. Determine the number of shared pairs (SP).

   ____

4. What is the C–O bond order in CO?

   ____

5.6-4. Lewis structure of CO_2 Exercise

EXERCISE 5.7:

Draw the Lewis structure for carbon monoxide, CO_2.

1. Determine the number of electrons required with no sharing (ER).

____

2. Determine the number of valence electrons (VE).

____

3. Determine the number of shared pairs (SP).

____

4. What is the C–O bond order in CO_2?

____

5.7 Resonance

Introduction

In some instances, more than one Lewis structure can be drawn for a molecule. The different structures are called resonance structures.

Objectives

- Define the term *resonance* and use curved arrows to indicate how the electrons can be moved to convert one resonance form into another.
- Determine the bond order of a bond involved in a resonance structure.

5.7-1. Resonance Structures

Resonance structures are Lewis structures that differ only in the placement of the electron pairs.

Resonance structures are Lewis structures that differ only in the placement of the electron pairs. **Curved arrows** are used to show how the electrons can be moved to convert from one resonance structure into another. We will also use curved arrows in Chapters 12 and 13 to show how acid-base reactions take place, so take a moment to familiarize yourself with their meaning. As shown in the table, they are used in only two ways.

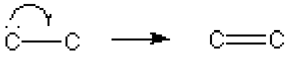
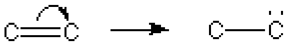
Representation	Direction	Action
	lone pair → bond	the lone pair becomes a bonding pair
	bond → atom	a bonding pair becomes a lone pair

Table 5.6

5.7-2. Resonance forms of CO_2

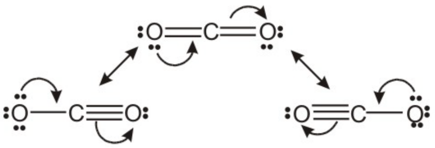


Figure 5.8

View the animation to see how curved arrows are used to explain the electron movement required to attain the three resonance structures of CO_2.

A video or simulation is available online.

5.7-3. The Number of Resonance Structures

The most common form of resonance is one in which a multiple bond can be drawn in any of several positions. Follow these steps to determine the number of such resonance forms that are possible.

Determine the number of shared pairs.

1 Determine the number of electrons required with no sharing (ER).

2 Determine the number of valence electrons (VE).

3 Determine the number of shared pairs (SP).

Resonance structures form when the number of shared pairs exceeds the number of identical bonding regions in which they can be placed. Resonance structures for molecules or ions having a single central atom occur when the number of shared pairs exceeds the number of regions by one. In this case, the number of structures equals the number of bonding regions in which the extra shared pair can be placed. The example of SO_2 is examined in the following exercise.

5.7-4. Resonance in SO_2 Exercise

EXERCISE 5.8:

ER = ______________ VE = ______________ SP = ______________

Based on the bonding regions, how many resonance structures can be drawn for SO_2?

____

5.7-5. Bond Orders in Bonds Involved in Resonance

When more than one identical resonance structures can be drawn for a molecule, they all contribute equally to the bonding picture. Fractional bond orders result in these cases as one bonding pair is shared in more than one region.

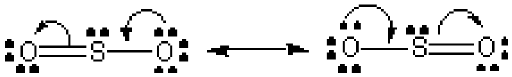


Figure 5.9: Resonance in SO_2 Note that a line with arrows on both ends is used to indicate resonance structures.

When the different resonance forms are equivalent, as is the case in SO_2, each form contributes equally to the bonding. **When more than one resonance form is important in the bonding, then the bonding in the molecule is the average of the resonance forms.** The most common cases of resonance arise when a multiple bond can be placed in more than one equivalent position. When resonance is important, one bonding pair is shared by (spread over) more than one bond, and the bond order is determined as the following:

$$\text{bond order} = \frac{\text{number of shared pairs}}{\text{number of bonding regions}} \tag{5.1}$$

where only the bonding regions in which the double bond can be placed are considered.

The two resonance structures of SO_2 are equivalent, so the bonding is the average of both forms and the double bond is shared equally by the two S–O bonds. The result is that neither bond is a single bond and neither is a double bond. The two sulfur-oxygen bonds in sulfur dioxide are of equal length, both being shorter than a S–O single bond but longer than a S=O double bond.

EXAMPLE:

The bond order of each of the bonds in SO_2 involved in the resonance is

$$\text{BO} = \frac{\text{(3 shared pairs)}}{\text{(2 bonds)}} = 1.5$$

Bonding electrons that are shared among more than two atoms are sometimes represented by dotted lines in the Lewis structure. The following shows that the two bonds are identical and have bond orders of 3/2.

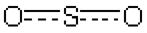


Figure 5.10

5.7-6. Bond Order is a Bond Property, Not a Molecular Property

Bond orders apply to bonds, not molecules.

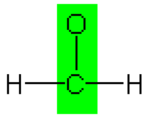
A common misconception among students is that molecules have bond orders. They do not; bonds have bond orders. This misconception arises because all of the bonds are identical in so many of our examples. Thus, it is incorrect to state that the bond order of SO_2 is 1.5; rather, it should be stated that the bond order of each bond in SO_2 is 1.5.

Resonance is important when a multiple bond can be placed in more than one position. In these cases, the bond order of each bond that is affected by the resonance is given by Equation 5.1. However, Equation 5.1 applies only to the bonding regions involved in the resonance. This distinction is the focus of the following exercise.

5.7-7. Bond Order Exercise

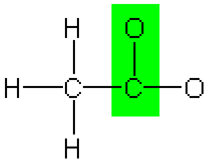
EXERCISE 5.9:

The Lewis structure of each of the following skeletal structures requires one more shared pair. Decide how to place the shared pair and then determine the bond order of the highlighted bond.



CH_2O

____



CH_3COO^{1-}

____

5.8 Formal Charge and Oxidation State

Introduction

In Chapter 4, we showed how to determine oxidation states of the atoms in a substance without knowledge of the Lewis structure of the substance. However, electron counting can be facilitated with a Lewis structure. By comparing the number of electrons around an atom in a Lewis structure with the number of valence electrons in the unbound atom, we can assign a charge to the atom in a molecule or ion. Oxidation states assign charge by assuming that the bonds are ionic. In this section, we introduce formal charge, which assigns charge by assuming that the bonds are covalent.

Prerequisites

- 3.1 Valence Electrons (Determine the number of valence electrons that an atom has.)

Objectives

- Distinguish between formal charge and oxidation state.
- Predict the formal charge on an atom by counting the number of bonds to the atom.
- Use formal charge to predict the preferred Lewis structure from several resonance forms.
- Determine oxidation states by electron counting.
- Distinguish between the oxidation states determined from Lewis structure and those determined by the oxidation state rules given in Chapter 4.

5.8-1. Regions of Charge in Molecules

The charge on an atom in a molecule lies between its formal charge and its oxidation state. It lies closer to the oxidation state when the bonds are very polar, but closer to the formal charge if they are not.

The charge distribution in bonds is usually asymmetric because the bonds are polar. This asymmetry introduces regions of charge in the molecule. These regions greatly influence both the physical and chemical properties of the molecule. Determining where the charge resides is an important challenge to the chemist. In this section, we show how to determine those regions in the two extremes of purely ionic and purely covalent bonding. The actual situation depends upon the polarity of the bonds and will lie somewhere between the two limits.

The charge that is assigned to an atom in a molecule equals the number of valence electrons in the free atom minus the number of valence electrons assigned to the atom in the molecule. The number of valence electrons in the free atom (VE) is given by the atom's group number. The number of electrons assigned to the atom in the molecule is the number of nonbonding electrons (NB) plus those bonding electrons (BE) that are assigned to it. Thus, the charge on atom A is given as

$$q_{\mathrm{A}} = \mathrm{VE} - (\mathrm{NB} + \mathbf{aBE})$$

where (NB + **a**BE) is the number of electrons (nonbonding and bonding) that are assigned to the atom. The manner in which **a** is determined and the name of the resulting charge depend upon the type of bonding that is assumed.

- The ***formal charge*** **(FC)** on an atom is the charge that the atom would have if the bonds were assumed to be purely covalent, so each atom is assigned half of the bonding electrons. In this case, $a = 1/2$ for each bond. Note that non-zero formal charges are shown within circles to distinguish them from actual charges.
- The *oxidation state* **(OX)** of an atom is the charge that the atom would have if the bonds were assumed to be ionic, so each atom is assigned all or none of the bonding electrons in each bond. In this case, $a = 0$ for those bonds in which the atom is the less electronegative atom or $a = 1$ for those bonds in which it is the more electronegative.

5.8-2. Oxidation State vs. Formal Charge Videos

A video or simulation is available online.

5.8-3. Formal Charge

Formal charge is the charge an atom would have if the bonds were purely covalent. It can be determined by electron counting.

The **formal charge** is the charge an atom would have if the bonds were purely covalent. This means that one electron from each bonding pair is assigned to each atom in the bond. Consequently, only half of the bonding electrons around an atom are assigned to it. That is, $\mathbf{a} = \frac{1}{2}$, and the formal charge on atom A is

$$\mathrm{FC_A} = \mathrm{VE} - \left(\mathrm{NB} + \frac{1}{2}\mathrm{BE}\right)$$

Each bond contains two electrons, so one-half of the bonding electrons equals the number of bonds (B). Thus, the formal charge on atom A can also be expressed by

$$\mathrm{FC_A} = \mathrm{VE} - (\mathrm{NB} + \mathrm{B}) = \mathrm{VE} - \mathrm{NB} - \mathrm{B}$$

The formal charge on an atom is placed in a circle near the atom. Zero formal charges are not shown. Thus, formal charges of +1, −1, +2, and −2 would be represented by the following.

Figure 5.11

EXERCISE 5.10:

Assign electrons to each of the following and determine their formal charge.

Valence Electrons

Non-Bonding

Bonding

Formal Charge

The Lewis structure of SO_2 that includes the formal charge is shown in the following section.

5.8-4. Lewis Structure of SO_2 with Formal Charge

In the previous exercise, we showed that the sulfur atom in SO_2 has positive formal charge, the oxygen with the single bond had negative formal charge, and the oxygen with the double bond had no formal charge. Thus, the Lewis structures of the two resonance forms that show formal charge are shown in Figure 5.12.

Figure 5.12: Formal Charge in SO_2

5.8-5. Formal Charge and the Number of Bonds

Zero formal charge results when the number of bonds to an atom equals the number of unpaired electrons in its Lewis symbol.

The formal charge of an atom depends upon the number of bonds to the atom—the greater the number of bonds, the more positive the formal charge. Note that when counting bonds, double and triple bonds count as two and three bonds, respectively. The following figures give the formal charge of some common elements as a function of the number of bonds in which it is involved. The number of bonds resulting in zero formal charge is bolded.

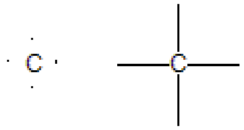


Figure 5.13

Sharing the unpaired electrons in the Lewis symbol results in zero formal charge for an atom. The Lewis symbol of carbon shows four unpaired electrons, so **carbon has zero formal charge when it is involved in four bonds**. Nonzero formal charge is hardly ever assigned to carbon, so a very good rule to use in drawing Lewis structures is that carbon atoms always have four bonds.

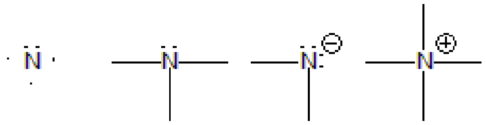


Figure 5.14

The Lewis symbol of nitrogen shows three unpaired electrons, so **nitrogen has zero formal charge when it is involved in three bonds**. Thus, nitrogen usually has three bonds to it, but it is also frequently found with four bonds and positive formal charge, e.g., $NH_4{}^{1+}$, the ammonium ion. Occasionally, it has only two bonds, in which case it carries a negative formal charge.

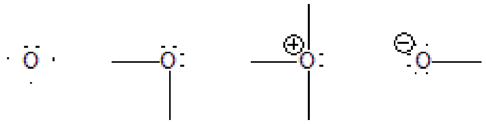


Figure 5.15

The Lewis symbol of oxygen shows two unpaired electrons, so **oxygen has zero formal charge when it is involved in two bonds**. Thus, oxygen usually has two bonds to it, but it is also frequently found with one bond and negative formal charge, e.g., OH^{1-}, the hydroxide ion. Occasionally, it has three bonds (H_3O^{1+}), in which case it carries a positive formal charge.

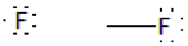


Figure 5.16

The Lewis symbol of fluorine shows only one unpaired electron, so **fluorine has zero formal charge when it is involved in only one bond**. Adding a second bond to a fluorine atom would produce a positive formal charge, but F is the most electronegative atom, so positive formal charge is never placed on it. Thus, F has one and only one bond in all of its compounds.

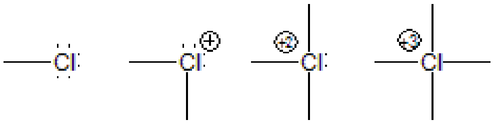


Figure 5.17

The other halogens can have more than one bond in situations where they are bound to a number of more electronegative atoms (O or F). However, a good rule to follow is that **double and triple bonds are not drawn to halogens because they place positive formal charge on these relatively electronegative elements**.

5.8-6. Structure and Formal Charge

Lewis structures that minimize formal charge are preferred.

Formal charge can be used to determine the best Lewis structure in cases where more than one Lewis structure can be drawn because charge separation (creating centers of positive and negative charge) requires energy (Coulomb's law). Thus, Lewis structures with no formal charge are favored over those that do contain formal charge.

The best Lewis structure is the one in which

- all formal charges are closest to zero and
- negative formal charge resides on the more electronegative atoms.

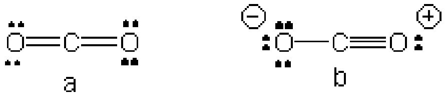


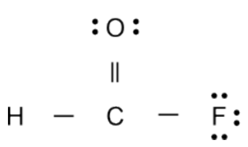
Figure 5.18: Using Formal Charge to Choose between Resonance Structures of CO_2
Although two Lewis structures can be drawn for CO_2, only structure a is important because it contains less formal charge.

5.8-7. Formal Charge Exercise

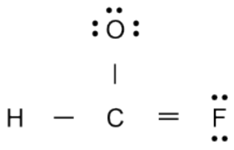
EXERCISE 5.11:

Determine the formal charges on each atom in the following Lewis structures of FCHO.

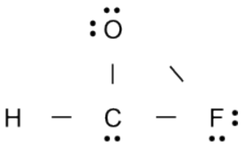
Structure a



Structure b



Structure c



Structure a

O = ______________

H = ______________

C = ______________

F = ______________

Structure b

O = ______________

H = ______________

C = ______________

F = ______________

Structure c

O = ______________

H = ______________

C = ______________

F = ______________

Note that the oxygen atom in the last structure has both an C–O and an O–F bond.

Based on the formal charges, the preferred structure is which of the following?
Structure a
Structure b
Structure c

5.8-8. Oxidation States

Oxidation state is the charge the atom would have if the bonds were ionic. It can be determined by electron counting.

The **oxidation state** is the charge the atom would have if the bonds were ionic. This means that **all of the bonding electrons** in each bond are assigned to the more electronegative atom. That is, **a** = 0 or 1, and the oxidation state of atom A is

$$\mathrm{OX_A} = \mathrm{VE} - (\mathrm{NB} + \sum \mathbf{a}\mathrm{BE})$$

where the sum is over all of the bonds to atom A and **a** is either 0 or 1 for each bond depending upon whether atom A is less or more electronegative than the other atom in the bond. In the case where the two atoms are identical, neither atom is more electronegative, so $\mathbf{a} = \frac{1}{2}$ in this special case; i.e., the bond must be assumed to be covalent when the two electronegativities are identical. Thus, the value of a in each bond is determined as follows:

- $a = 1$ if the atom is the more electronegative atom in the bond.
- $a = 0$ if the atom is the less electronegative atom in the bond.
- $a = \frac{1}{2}$ if the atoms in the bond are identical, which means that the bond cannot be ionic.

Oxidation states determined with the method outlined above may differ from those determined using the guidelines presented in Section 4.4 because the latter method yields the average oxidation state of all of the atoms if the element being considered, while the method above applies only to the one atom being considered.

5.8-9. Counting Electrons for Oxidation State Exercise

EXERCISE 5.12:

Determine the oxidation state of each atom in CO_2.

Valence Electrons ______________________

Non-Bonding ______________________

Bonding ______________________

Oxidation State ______________________

5.8-10. Difference in Oxidation State Methods

The oxidation state of an atom, determined from the rules in Chapter 4, yields the average oxidation states of all the atoms of the element be considered, while the electron counting procedure outlined in this section produces the oxidation states of the individual atom being considered.

The oxidation states determined for the carbon and oxygen atoms in CO_2 are the same whether the method used in Section 4.4 or electron counting is used because the oxidation states of the two oxygen atoms are identical. In cases where the oxidation states of two or more different atoms of the same element are different, the two methods may yield different results because the oxidation state determined by the method given in Section 4.4 is the average of the oxidation states, while that determined by electron counting applies only to the individual atom being considered. Two examples where the two methods differ are given in the following exercise.

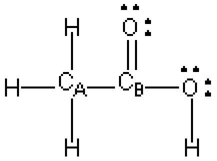
5.8-11. Differences in Oxidation State Methods Exercise

EXERCISE 5.13:

What is the average oxidation state of the C atoms in $C_2H_4O_2$ as determined by the rules outlined in Section 4.4?

OX_C = ______________

Use the method described in this chapter to determine the oxidation state of each carbon atom in acetic acid, which has the following Lewis structure:

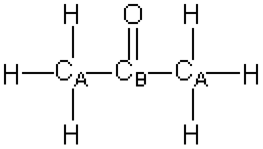


OX_{CA} = ______________ OX_{CB} = ______________

What is the average oxidation state of the C atoms in C_3H_6O? Express your answer in decimal form.

OX_C = ______________

Use the method described in this chapter to determine the oxidation state of each carbon atom in C_3H_6O, which has the following Lewis structure:



OX_{CA} = ______________ OX_{CB} = ______________

5.9 Practice with Lewis Structures

Introduction

Practice drawing Lewis structures in this section.

5.9-1. Lewis Structure of SO_3 Exercise

EXERCISE 5.14:

Draw the Lewis structure of SO_3, and indicate all nonzero formal charge.

ER = ______________ VE = ______________ SP = ______________

How many resonance structures are there?

____

What is the formal charge on the sulfur atom?

____

5.9-2. Lewis Structure of $SO_3{}^{2-}$ Exercise

EXERCISE 5.15:

Draw the Lewis structure of the following molecules and ions. Indicate all nonzero formal charge.

When dealing with ions, remember that negative charge increases the number of valence electrons, while positive charge decreases the number of valence electrons.

ER = ______________ VE = ______________ SP = ______________

What is the formal charge on the sulfur atom?

____

5.9-3. Lewis Structure of $N_3{}^{1-}$ Exercise

EXERCISE 5.16:

Draw the Lewis structure of $N_3{}^{1-}$, indicating the formal charge on each atom.

ER = ______________ VE = ______________ SP = ______________

What are the formal charges on the central and terminal N atoms?

central ______________ terminal ______________

5.9-4. Lewis Structure of H_2O Exercise

EXERCISE 5.17:

Draw the Lewis structure of H_2O, indicating the formal charge on each atom.

ER = ______________ VE = ______________ SP = ______________

What is the formal charge on the O atom?

____

5.9-5. Lewis Structure of SO_2 Exercise

EXERCISE 5.18:

Draw the Lewis structure of SO_2, indicating the formal charge on each atom.

ER = ______________ VE = ______________ SP = ______________

What is the formal charge on the S atom?

____

5.9-6. Lewis Structure of NO_3^{1-} Exercise

<u>EXERCISE 5.19</u>:

Draw the Lewis structure of NO_3^{1-}, indicating the formal charge on each atom.

ER = ______________ VE = ______________ SP = ______________

What is the formal charge on the N atom?

____

5.10 Exercises and Solutions

Links to view either the end-of-chapter exercises or the solutions to the odd exercises are available in the HTML version of the chapter.

Chapter 6 – Molecular Structure

Introduction

A method for constructing Lewis structures of simple molecules and ions was presented in Chapter 5. In this chapter, we show how to use Lewis structures to determine the structural and bonding properties of molecules and ions with covalent bonds.

6.1 Molecular Shapes

Introduction

A molecule is a three-dimensional structure, and many of its properties, both chemical and physical, are dictated by that structure. The Lewis structure of a molecule is a two-dimensional representation that can be used to obtain information about its three-dimensional structure. Determining the shape of a molecule from its Lewis structure is the topic of this lesson.

Prerequisites

- 1.8 Electromagnetism and Coulomb's Law
- 2.6 Orbital Shapes and Sizes
- 5.6 Determining Lewis Structures (Draw Lewis structures.)

Objectives

- Determine the number of electron regions around an atom.
- Rate the relative strengths of lp-lp, lp-bp, and bp-bp interactions.
- Name the molecular shapes of simple molecules that contain a single central atom.
- Use lines, wedges, and dashes to represent the 3D structure of an atom with four electron regions.
- Distinguish between a ball-and-stick model and a space-filling model.

6.1-1. Electron Regions

One electron group or region can be either a lone pair, a single bond, a double bond, or a triple bond.

Just as a two-dimensional blueprint provides information about a three-dimensional building, the Lewis structure of a molecule provides information about the three-dimensional structure of a molecule. The transition from a two- to a three-dimensional structure is accomplished with the valence-shell electron-pair repulsion (VSEPR) model. VSEPR is based on the premise that the 'electron groups' or 'electron regions' around an atom adopt positions that minimize the repulsions between them.

Each of the following is one electron group or region.

- lone pair
- single bond
- double bond
- triple bond

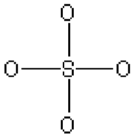
Double and triple bonds each represent a single electron group because the electron pairs in the bonds are all restricted to the region of space between the bound atoms. Thus, the electron pairs in a bonding region cannot move apart, but they can move as a single electron group to minimize their interactions with other electron groups.

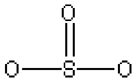
Atoms obeying the octet rule can have only two, three, or four electron groups.

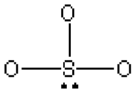
6.1-2. Counting Electron Regions Exercise

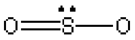
EXERCISE 6.1:

What is the number of electron regions around the sulfur atom in each of the following?









6.1-3. VSEPR Video

A video or simulation is available online.

6.1-4. VSEPR Summary

In summary, the three possible orientations of electron groups around an atom that obeys the octet rule are the following.

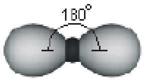
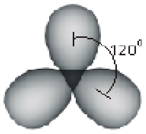
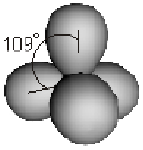
Number of Groups	Angle Between Groups	Image
2	180°	
3	120°	
4	109°	

Table 6.1

6.1-5. Bond Angles

If all of the electron groups around a central atom are not identical, the predicted bond angles are only approximate.

The angles between electron groups shown in Figure 6.1 apply only to situations where all four electron groups are the same, which is not all that common. Thus, the angles between electron groups around an atom that obeys the octet rule will be exactly 180° for two groups, but it will only be close to 120° or 109° for three or four groups unless all of the groups are the same. Deviation from the predicted angles can be caused by differences in the size of the bound atoms as large atoms tend to move apart to avoid ‘bumping’ one another, and from differences between the interactions of lone pairs and bonding pairs as lone pairs are more diffuse than lone pairs, so they are larger and other electron regions tend to move away from them. The following gives the relative strengths of the interactions.

lone pair-lone pair > lone pair-bonding pair > bonding pair-bonding pair

The ***bond angle*** is the angle formed by the intersection of two bonds. They are generally reduced from the values given in Figure 6.1 by interaction with lone pairs. As a result, the bonding pairs move away from the lone pairs by moving closer to one another. The deviation from the predicted angles increases with the number of lone pairs. Use the following to predict relative bond angles.

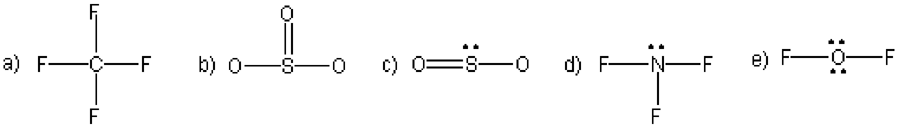
1. Determine the number of electron groups around the atom where the angle forms.
2. If there are no lone pairs and the atoms are nearly the same size, the angle will be 180°, 120°, or 109°.
3. If there are lone pairs, the angles decrease from the values predicted in step 2. The deviation is greater for two lone pairs than for one.

We will indicate that the bond angle deviates from the predicted value with a '∼' in front of the angle. Thus, all bond angles around atoms with lone pairs are preceded by a '∼'.

6.1-6. Ordering Bond Angles Exercise

EXERCISE 6.2:

Consider the Lewis structures of CF_4, SO_3, SO_2, NF_3, and OF_2, which are given below. Note, only lone pairs around the central atom are shown.



Indicate the molecule with the greater bond angles in each pair.

SO_3 or CF_4	SO_3 or SO_2	NF_3 or OF_2
SO_3	SO_3	NF_3
CF_4	SO_2	OF_2

6.1-7. Molecular Shapes

The locations occupied by the lone pairs are not used when describing the shape of a molecule.

The shapes shown in Table 6.1 show the orientations that can be adopted by the electron groups surrounding a central atom that obeys the octet rule. However, we can determine the positions of only the atoms, not the lone pairs, so a molecular shape describes the shape adopted by only the atoms not the electron groups. The **lone pairs help establish what that shape is, but the name of the shape applies only to that taken by the atoms**. We consider the shapes of some generic molecules in the following sections. Our analysis will follow three steps.

1. Determine the number of electron groups around the central atom.
2. Determine which of the shapes shown in Table 6.1 applies.
3. Name the molecular shape adopted by the **atoms**.

6.1-8. The Common Shapes

Three atoms can be either linear or bent and four atoms can be planar or pyramidal; which geometry is adopted depends upon the presence of lone pairs.

Our discussion concerns molecules with two, three or four atoms (X) attached to one central atom (A), which may have one or more lone pairs (E). Thus, AX_2E indicates that central atom A is bound to two X atoms and has one lone pair. In the molecular representations below, the atoms are shown as spheres, bonds as cylinders, and lone pairs as green balloons. In the table, br = bonding regions and lp = lone pair. The possibilities for molecules in which A obeys the octet rule are the following.

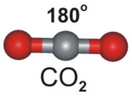
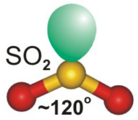
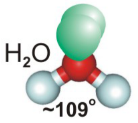
Formula	Groups	Shape	Angle	Example	Comments
AX_2	2 (2br)	linear	180°		Two bonding pairs are always 180°, not ~180°
AX_2E	3 (2br + lp)	bent	~120°		The lone pair forces the angle down slightly from 120°
AX_2E_2	4 (2br + 2lp)	bent	~109°		The two lone pairs force the angle down to 104° in water.

Table 6.2

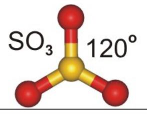
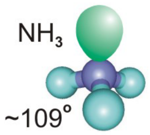
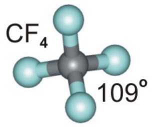
Formula	Groups	Shape	Angle	Example	Comments
AX_3	3 (3br)	planar	120°		The three groups are identical due to resonance
AX_3E	4 (3br + lp)	pyramidal	~109°		One lone pair forces the angle down to 107° in ammonia
AX_4	4 (4br)	tetrahedral	109°		All four regions are identical so no ~ is required in bond angles

Table 6.3

6.1-9. Molecular Representations

Ball-and-stick representations are better for showing bond angles, but space-filling representations are closer to how we envision molecules.

Making drawings that demonstrate the geometry around atoms with only two and three electron regions is easy because they require only one and two dimensions. However, in cases where the central atom has four or more electron regions, you must be able to represent the three-dimensions in a 2D drawing. This is often done by using lines to represent regions in the plane of the paper, solid wedges for regions that extend out from the plane of the paper, and dashed wedges for regions that extend behind the plane of the paper. The use of lines and wedges is demonstrated in the following example of a central atom with four different bonding regions.

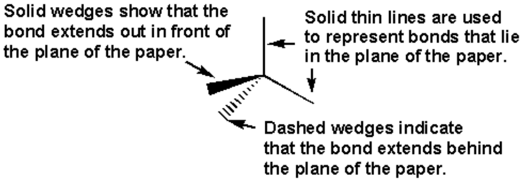


Figure 6.4: Line-Wedge-Dash Representation of a Tetrahedral Geometry

There are two other representations that give a better three dimensional view of molecules, especially larger ones. They are the ball-and-stick and space-filling models. These two models, which will be used frequently to represent molecules, are demonstrated below for an ammonia molecule. Note that **lone pairs are not shown in ball-and-stick or space-filling models**.

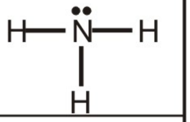
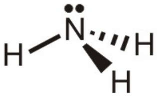
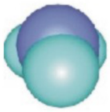
Model Name	Description	Representation
Lewis structure	Bonding pairs are shown as lines. Bonds are usually drawn at right angles.	
line-wedge-dash	A Line-wedge-dash representation attempts to show the three-dimensional structure of the molecule.	
ball andstick	Atoms are represented as spheres and bonds as cylinders. Ball-and-stick models are the better representation for discussing bond angles, but they do not represent the relative sizes of the atoms.	
space filling	Atoms are shown as spheres and bonds as the penetration of two spheres into one another, Space-filling models give a truer picture of the molecule. The relative diameters of the spheres represent the relative sizes of the atoms.	

Table 6.5

6.1-10. Structure Exercise

EXERCISE 6.3:

Draw the Lewis structure to describe the shape and give the approximate bond angles of the following ions.

$ClO_2{}^{1-}$ shape
- linear
- bent
- planar
- pyramidal
- tetrahedral

$ClO_2{}^{1-}$ approximate bond angle
- 90°
- 109°
- 120°
- 180°

$N_3{}^{1-}$ shape
- linear
- bent
- planar
- pyramidal
- tetrahedral

$N_3{}^{1-}$ approximate bond angle
- 90°
- 109°
- 120°
- 180°

$PO_3{}^{3-}$ shape
- linear
- bent
- planar
- pyramidal
- tetrahedral

$PO_3{}^{3-}$ approximate bond angle
- 90°
- 109°
- 120°
- 180°

$NO_3{}^{1-}$ shape
linear
bent
planar
pyramidal
tetrahedral

$NO_3{}^{1-}$ approximate bond angle
90°
109°
120°
180°

$BrO_4{}^{1-}$ shape
linear
bent
planar
pyramidal
tetrahedral

$BrO_4{}^{1-}$ approximate bond angle
90°
109°
120°
180°

6.2 Central Atoms With More Than Four Electron Regions

Introduction

The octet rule applies rigidly only to C, N, O and F, and even nitrogen violates it occasionally because it has an odd number of electrons in some of its molecules. Atoms with more than eight valence electrons are said to have expanded valence shells or expanded octets. Transition metals and the heavier p block elements frequently use expanded octets. In this section, we discuss the shapes of molecules in which the central atom has five and six electron regions.

Objectives

- Name the shapes adopted around atoms with five and six electron regions.

6.2-1. Shapes of Five and Six Electron Regions

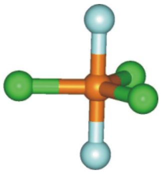


Figure 6.6a: Five Electron Regions

Five groups around a central atom adopt a trigonal bipyramidal structure, which contains two distinctly different types of positions: two positions are axial (blue spheres) and three are equatorial (green spheres). Interactions with other groups are less in the equatorial positions, so lone pairs are always in the equatorial plane.

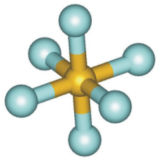


Figure 6.6b: Six Electron Regions

Six groups assume an octahedral structure. All six positions of an octahedron are identical, so lone pairs can be placed in any position. However, two lone pairs are always situated opposite to one another.

6.2-2. Determining Structures of Expanded Octets with Lone Pairs

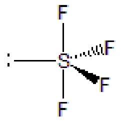
The number of lone pairs around a central atom (LP) can be determined from its group number and its oxidation state as follows.

$$\text{LP} = \frac{1}{2}(\text{group number} - \text{oxidation state}) \tag{6.1}$$

Atoms with expanded valence shells can be identified because the predicted number of shared pairs is always too small to accommodate all of the bonds. See the following example.

EXAMPLE:

We determine for SF_4: ER = 5(8) = 40 electrons; VE = 6 + 4(7) = 34 electrons; SP = 1/2(40 − 34) = 3 shared pairs. However, a minimum of 4 shared pairs is required for the four S-F bonds, so the three shared pairs cannot be correct and the octet rule cannot be obeyed. The group number of sulfur is 6 and its oxidation state in SF_4 is +4, so the number of lone pairs around the sulfur atom is LP = 1/2(6 − 4) = 1 lone pair. Thus, there are five electron groups around the sulfur: four S-F bonds and one lone pair. As shown below, the five groups adopt the trigonal bipyramidal structure with the lone pair in the equatorial plane.



6.2-3. Expanded Octet Structure Exercise

EXERCISE 6.4:

Determine the number of lone pairs on the central atom in and the structures of XeF_2 and $BrF_4{}^{1-}$.

XeF_2

group number ______________

oxidation state ______________

lone pairs ______________

number of electron regions ______________

Are the three atoms linear or bent?
linear
bent

$BrF_4{}^{1-}$
group number ______________

oxidation state ______________

lone pairs ______________

number of electron regions ______________

Do the five atoms lie in a plane?
Yes
No

6.3 Larger Molecules

Introduction

Groups connected by single bonds can rotate relative to one another about the bond, so VSEPR cannot be used to predict the exact structure of complicated molecules, but it can be used to look at the geometry around individual atoms. In this section, we examine the structure of three common molecules: acetic acid (the active ingredient in vinegar), benzene, and aspirin.

Objective

- Predict bond angles in larger molecules.

6.3-1. Acetic acid

We deduce the following bond angles in acetic acid from its Lewis structure.

1 α ~109° because there are four electron regions around the carbon 1.

2 β ~120° because the C at 2 is surrounded by three electron regions.

3 γ ~109° because there are four electron regions around the oxygen atom at 3.

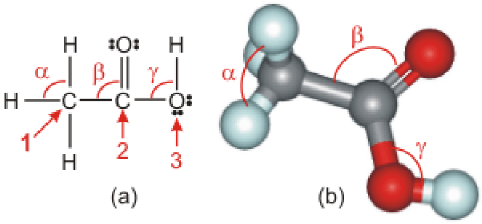


Figure 6.7: Acetic Acid

6.3-2. Benzene

Benzene has the formula C_6H_6 and is a six-membered ring (the six carbon atoms bond so as to form a hexagon). The Lewis structures of its two resonance forms that are shown in Figure 6.8a. We conclude the following based on these Lewis structures.

1 Each carbon has three regions, so each is trigonal planar and all bond angles are 120°.

2 The double bonds require that the molecule is planar.

3 As a result of resonance, all of the carbon atoms are identical as are all six of the bonds between them. The measured C-C bond lengths are all 1.4 Å. Thus, the bond lengths all lie between the 1.5 Å of a single C-C bond and the 1.3 Å of a C=C double bond, which is consistent with a bond order of 1.5. The three double bonds are threfore shared equally between the six bonding regions in the ring. Indeed, the double bonds are frequently represented as a circle rather than three lines (Figure 6.8b) to emphasize the equivalence of the carbon-carbon bonds. We will revisit this important bonding characteristic of benzene in our discussion of molecular orbital theory at the end of the chapter.

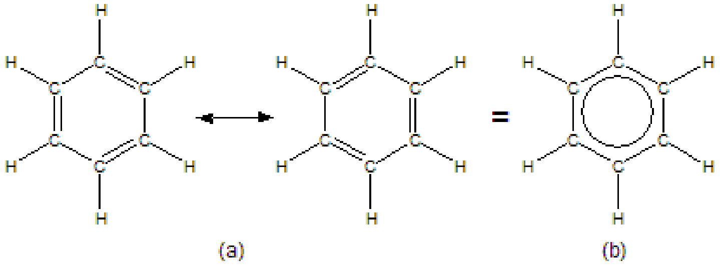


Figure 6.8: Benzene

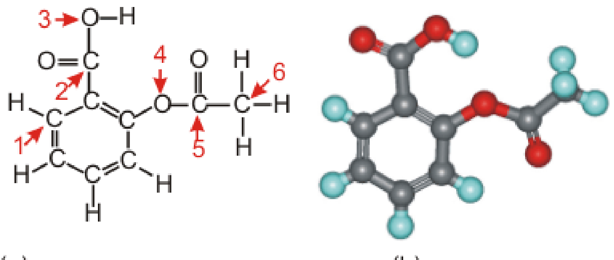
6.3-3. Aspirin

1 Carbon atoms at positions 1, 2, and 5 all have three regions, so their bond angles are ~120°.

2 The carbon at position 6 has four regions, so the bond angles there are ~109°.

3 Oxygen obeys the octet rule, but only four electrons (two bonding pairs) are shown in the Lewis structure. Consequently, two lone pairs must be added to each to produce four regions, which requires bond angles of ~109°.

4 Aspirin contains the same structural features that are found in acetic acid and benzene.



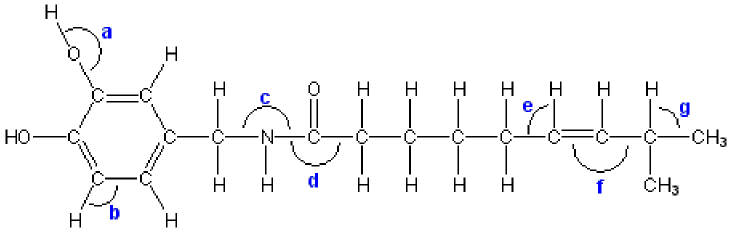
(a) (b)

Figure 6.9: Aspirin

6.3-4. Predicting Bond Angles Exercise

EXERCISE 6.5:

The structure below is that of capsaicin, the molecule responsible for the heat in chili peppers. Estimate each of the labeled bond angles. Note that lone pairs are not drawn, but C and O both obey the octet rule. Enter only the number, not the degree sign (°).



a ______________ °
b ______________ °
c ______________ °
d ______________ °
e ______________ °
f ______________ °
g ______________ °

6.4 Valence Bond Theory and Hybridization

Introduction

In valence bond theory, each bond results from the overlap of two atomic orbitals on adjacent atoms. The bonding electrons in such bonds are localized in the region between the two atoms. A single bond is composed of two bonding electrons, so the total number of electrons in the two overlapping atomic orbitals used to produce a bond cannot exceed two. In most cases, each orbital contains one electron, and the two electrons pair when the orbitals overlap. However, both electrons can reside in one of the atomic orbitals (a lone pair), but, in this case, the other orbital must be empty. A bond in which a lone pair is converted into a covalent bond is called a coordinate covalent bond. Coordinate covalent bonds are produced in Lewis acid-base reactions, which are discussed in Chapter 12. We limit our discussion here to cases where each overlapping orbital has one electron.

Objective

- Define the term *hybridization* and name the types of hybrid orbitals used by atoms that obey the octet rule.

6.4-1. Sigma Bonds

The bonding in diatomic molecules can be explained with the overlap of the atomic orbitals that contain unpaired electrons. Bonds formed from the end-on overlap of orbitals place electron density on the internuclear axis (shown as the dotted line in the figures) and are called sigma (σ) bonds. As examples of σ bond formation, we consider the cases of H_2, F_2, and HF. Note that the electrons are shown as arrows and the overlap region is shown in yellow in the figures.

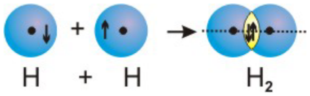


Figure 6.10a: Bond from Overlap of Atomic Orbitals

The H-H bond discussed in Section 5.1 is produced when the distance between the two H atoms is so small that their 1s orbitals overlap to form the H-H covalent bond.

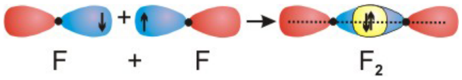


Figure 6.10b: Bond from Overlap of Atomic Orbitals

The valence electron configuration of a fluorine atom is $2s^2$ $2p^5$, so an unpaired electron resides in one of the 2p orbitals. An F-F bond is then viewed as resulting from the overlap of two p orbitals as shown in the Figure 6.10b. Note that this bond results from the end-on interaction of two p obitals.

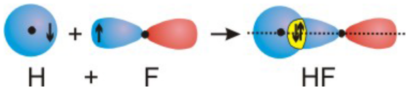


Figure 6.10c: Bond from Overlap of Atomic Orbitals

In the two previous examples, the bonding atoms were the same, so the overlapping orbitals were the same type (both s or both p orbitals). However, the overlapping orbitals do not have to be the same type. The H-F bond is the result of overlap between the 1s orbital of H and the 2p orbital of F. The lone pairs on fluorine would then reside in its s and remaining p orbitals.

In all of the examples shown in Figures 6.10a, 6.10b, and 6.10c, the overlap region lies on the line between the two atoms, which is called the ***internuclear axis***. **Bonds in which the bonding electron density falls on the internuclear axis are called *sigma (σ) bonds*.** Thus, the H-H, F-F, and H-F bonds are all sigma bonds. Indeed, all single bonds are sigma bonds.

6.4-2. Pi Bonds

A video or simulation is available online.

The sigma bonds in F_2 are formed when p orbitals overlap end-on. However, p orbitals can also overlap in a side-on fashion to form pi bonds as shown in Figure 6.11. The electron density in a pi bond lies above and below the internuclear axis, not on it. Thus, σ bonds result from end-on overlap of s or p orbitals and place electron density on the internuclear axis, while ***pi (π) bonds*** are produced from side-on overlap of p and/or d orbitals, which places the internuclear axis on a nodal plane.

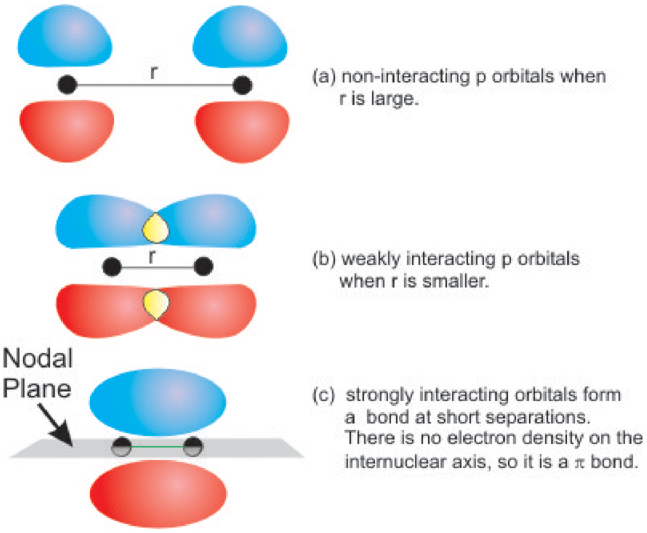


Figure 6.11: Pi Bond

6.4-3. Valence Bond Description of O_2 Bonding

O_2 is a diatomic molecule that contains both σ and π bonds. The valence electron configuration of an oxygen atom is $2s^2\ 2p^4$, so there are paired electrons in the 2s and one of the 2p orbitals. The unpaired electrons in an oxygen atom lie in the other two p orbitals. In Figure 6.12, the unpaired electrons are assumed to be in the p_z and p_y orbitals. As the atoms approach along the z-axis, the p_z orbitals of the two oxygen atoms overlap in an end-on fashion (orange line) to produce an σ bond, while the p_y orbitals overlap side-on (both violet lines) to produce a π bond. Thus, the O=O double bond consists of one σ and one π bond. All bonds contain one and only one σ bond. Double bonds contain one σ and one π bond, and triple bonds contain one σ and two π bonds. The bond order of a bond is simply the sum of the number of σ and π bonds that it contains.

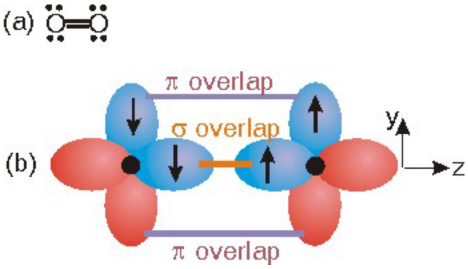


Figure 6.12: Valence Bond Picture of O_2 Bonding

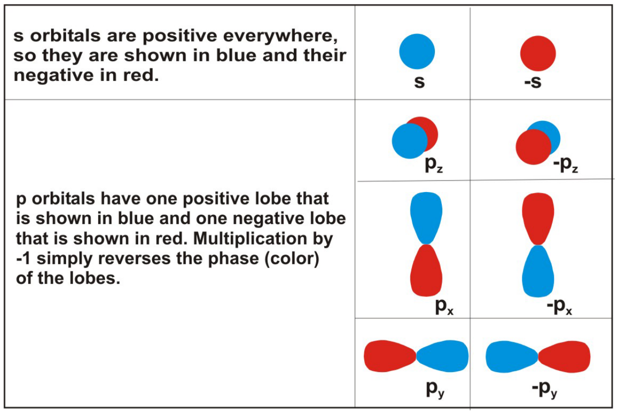
6.4-4. Hybrid Orbitals

The simple overlap of atomic orbitals used for diatomic molecules cannot be used for larger ones. Consider the molecule formed between a carbon atom and hydrogen atoms. Carbon has a valence electron configuration of $2s^2 2p^2$, so it has two unpaired electrons in its p orbitals. If carbon used only atomic orbitals with one electron, its compound with hydrogen would be CH_2, and the H-C-H bond angle would be 90° (the angle between two p orbitals). However, the simplest compound involving carbon and hydrogen is CH_4, which has the 109° bond angles predicted from VSEPR.

In order to account for molecular geometries in the valence bond model, orbitals on a central atom must be combined to produce new orbitals before they overlap with the orbitals of another atom. By choosing the appropriate combination of the atomic orbitals, we can create orbitals that have the geometries required by VSEPR. Orbitals produced by combining two or more atomic orbitals on the same atom are called ***hybrid orbitals***, and the process by which they are formed is called ***hybridization***. However, before we can understand hybridization, we must examine how orbitals combine.

6.4-5. Orbital Phase

To understand the process of combining orbitals, we must first review the nature of atomic orbitals. Recall from Chapter 2 that atomic orbitals describe algebraic functions that are solutions to an atom's wave equation, and that the phase or algebraic sign of an orbital in a particular region is frequently indicated with shading (Section 2.6). In Figure 6.13, we adopt the convention of using blue to indicate regions where the function is positive and red for regions where it is negative.



s orbitals are positive everywhere, so they are shown in blue and their negative in red.

p orbitals have one positive lobe that is shown in blue and one negative lobe that is shown in red. Multiplication by -1 simply reverses the phase (color) of the lobes.

Table 6.13

6.4-6. An Example of Mixing Two Functions

Mixing orbitals is the mathematical combination of these functions by addition and/or subtraction. Consider the two combinations of the functions P and Q shown in the Figure 6.14. Regions where the functions are positive are shaded in blue, while negative regions are shown in red. This is consistent with our use of these colors to describe the sign of orbital functions. In Figure 6.14a, the two functions are added to produce function $R = P + Q$. R is amplified on the ends because both P and Q have the same phase (sign) there, but it is reduced dramatically in the center because the phases of P and Q are opposite there. We conclude the following.

Adding regions of the same phase (blue + blue) is constructive and produces a region of increased amplitude, while adding regions of opposite phase (blue + red) is destructive and produces a region of decreased or even annihilated amplitude.

To obtain the difference $S = P - Q$ in the Figure 6.15b, the phase of Q is reversed (its sign is changed) to produce $-Q$ and then the two waves are added to produce S. The ends of P and $-Q$ have different phases, so they add destructively to nearly annihilate one another, while the regions in the middle have the same phase and add constructively to produce an amplified region in S.

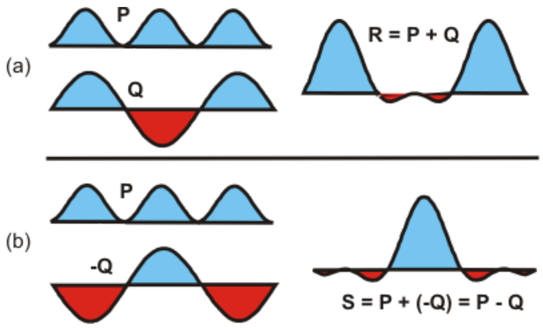


Figure 6.14: Mixing Two Functions

6.4-7. Rules for Mixing

Use the following rules when mixing orbitals.

1 The number of orbitals produced must always equal the number of atomic orbitals used to construct them.

2 Regions in which the atomic orbitals have the same sign (shading) add constructively, which makes the produced orbital larger in that region, but regions where the orbitals have opposite phases add destructively, which makes the combined orbital smaller in that region.

6.4-8. Hybridizing an s and a p Orbital

A video or simulation is available online.

The orbitals constructed from the addition and subtraction of one s and one p orbital are called sp hybrid orbitals. The sp hybrid orbitals are formed from s + p and s − p.

In (a) in Figure 6.15, the s and p orbitals are added to produce s + p, one sp hybrid orbital. Both atomic orbitals are positive (blue) to the right, but they have opposite phases to the left. Thus, they add constructively to the right to produce a large lobe, but they add destructively to the left to produce a small negative lobe. The other hybrid is produced by taking the difference between the atomic orbitals in (b). To obtain s − p, we change the phase of the p orbital and then add it to the s orbital. Now, the regions to the left have the same phase and add constructively and those on the right add destructively. The two sp hybrid orbitals are centered on the same atom, so they would look like (c). However, the small negative lobes are not used in bonding and are usually omitted. Thus, the two sp hybrid orbitals are normally represented as in (d). Note that forming the two sp hybrid orbitals required the use of only one p orbital, so an sp hybridized atom would have two p orbitals available to form bonds.

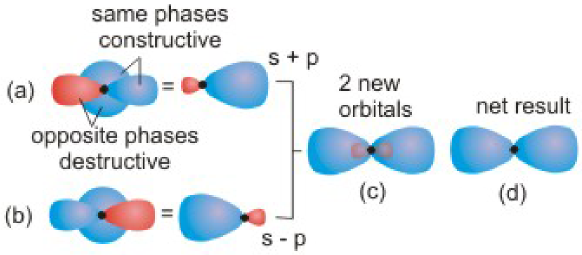


Figure 6.15: Mixing an s and a p Orbital on the Same Atom

6.4-9. Hybrid Orbital Descriptions

The number of hybrid orbitals used by an atom equals the number of electron groups around the atom.

Two ***sp*** hybrid orbitals are produced by combining one s and one p orbital as shown in the previous video. They are oriented 180° from one another. Only one p orbital is used to construct the hybrid orbitals, so two p orbitals are available to form π bonds. Thus, sp hybridized atoms form two π bonds (one triple bond or two double bonds) and have bond angles of 180°. Note that the sp hybrid orbitals lie along the axis of the p orbital used to construct them, so if the σ bonds are directed along the z-axis, then the s and the p_z orbitals would be used to make the hybrid orbitals, and the p_x and p_y orbitals would be used to form π bonds.

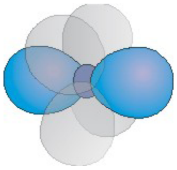


Figure 6.16a: A Hybridization Used by Atoms Obeying the Octet Rule

Three ***sp^2*** (spoken "sp two") hybrid orbitals are produced by combining one s and two p orbitals. The three hybrid orbitals lie in the plane defined by the two p orbitals used to construct them and are oriented 120° from one another. Two p orbitals are used in the hybridization, so only one p orbital remains to form a π bond. Thus, sp^2

hybridized atoms have one double bond and 120° bond angles. If the hybrids lie in the xy-plane, then the p_x and p_y orbitals must be used to construct them, which leaves the p_z orbital available for π bonding.

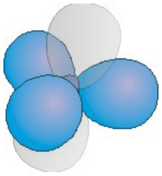


Figure 6.16b: A Hybridization Used by Atoms Obeying the Octet Rule

Four ***sp³*** (spoken "sp three") hybrid orbitals are produced by combining the s and all three p orbitals. There are no p orbitals available to form π bonds, so sp^3 hybridized atoms form only single bonds and have bond angles of 109°.

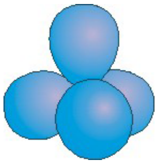


Figure 6.16c: A Hybridization Used by Atoms Obeying the Octet Rule

6.4-10. Using Valence Bond Theory to Explain the Structure of Allene

We conclude our discussion of valence bond theory by using it to explain why the planes of the two CH_2 groups of allene are perpendicular.

A video or simulation is available online.

We start by determining the hybridization of each carbon atom. The central atom is surrounded by two electron groups and is involved in two bonds, so it is sp hybridized. If the bonding axis is the z-axis, then the p_z orbital must be used to construct the hybrid orbitals, which leaves the p_x and p_y orbitals available to form the two bonds. Each of the terminal carbon atoms (C_A and C_B) is surrounded by three electron groups and is involved in one bond, so each is sp^2 hybridized. The sp^2 hybrid orbitals of C_A lie in the xz-plane because that is the plane defined by the C-H bonds, so the s, p_x and p_z orbitals are used to construct them.

This leaves the p_y orbital available to form a bond with the central carbon. If the central carbon uses its p_y orbital to bond to C_A, then it must use its p_x orbital to bond with C_B. If C_B uses its p_x orbital to form a bond, then it must use its s, p_y, and p_z orbitals to form the sp^2 hybrid orbitals, which lie in the yz-plane and are perpendicular to the sp^2 plane of C_A. Thus, the two CH_2 groups must be perpendicular if the central atom is to bond to both terminal carbon atoms because each bond requires a different p orbital. Figure 6.17 shows the bonding geometry in allene.

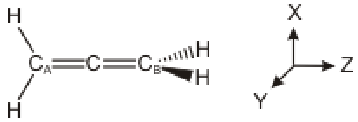


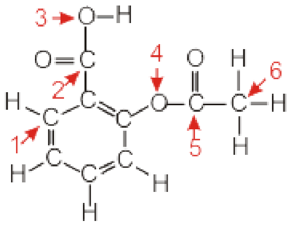
Figure 6.17: Coordinate System Used in Allene

Bonding and Hybridization Examples

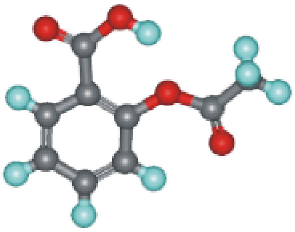
6.4-11. Aspirin

EXERCISE 6.6:

Indicate the hybridization as sp, sp^2, or sp^3 at each of the labeled atoms in the Lewis structure of the aspirin molecule shown below. Note that the lone pairs have been omitted, but C and O do obey the octet rule.



(a)



(b)

C_1
- sp
- sp^2
- sp^3

C_2
- sp
- sp^2
- sp^3

O_3
- sp
- sp^2
- sp^3

O_4
- sp
- sp^2
- sp^3

C_5
- sp
- sp^2
- sp^3

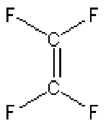
C_6
- sp
- sp^2
- sp^3

6.4-12. C_2F_4

EXERCISE 6.7:

Lewis structure and bonding in **tetrafluoroethylene (C_2F_4)**:
- ER = 6(8) = 48 electrons required with no sharing
- VE = 2(4) from C + 4(7) from F = 36 valence electrons
- SP = 1/2(48 - 36) = 6 shared pairs

The Lewis structure is the following.



The double bond must go between the carbon atoms because double bonds are never drawn to fluorine as that places positive formal charge on the fluorine atom. Note that each fluorine atom has three lone pairs, which are not shown.

Determine the following for C_2F_4.

C-C bond order ______________

the hybridization of each carbon atom:
- sp
- sp^2
- sp^3

the number of σ bonds ______________

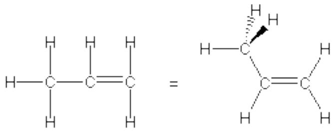
the number of π bonds ______________

6.4-13. C_3H_6

EXERCISE 6.8:

Lewis structure and bonding in **propene (C_3H_6)**:

- ER = 3(8) + 6(2) = 36 electrons required with no sharing
- VE = 3(4) from C + 6(1) from H = 18 valence electrons
- SP = 1/2(36 - 18) = 9 shared pairs



The six C-H bonds must all be single bonds, two more bonds are required to connect the three carbon atoms for a total of eight shared pairs. The Lewis structure requires nine shared pairs, so one C-C double bond is required.

Determine the following for C_3H_6.

left C-C bond order ______ right C-C bond order ______

the hybridization of the leftmost carbon atom
sp
sp^2
sp^3

the hybridization of the rightmost carbon atom
sp
sp^2
sp^3

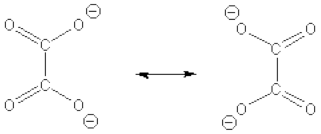
the number of σ bonds ______ the number of π bonds ______

6.4-14. $C_2O_4{}^{2-}$

EXERCISE 6.9:

Lewis structure and bonding in the **oxalate ion ($C_2O_4{}^{2-}$)**:

- ER = 6(8) = 48 electrons required with no sharing
- VE = 2(4) from C + 4(6) from O + 2 from charge = 34 valence electrons
- SP = 1/2(48 - 34) = 7 shared pairs



Five shared pairs are required for the sigma bonds, but seven shared pairs are required, so there must be two double bonds. This can only be accomplished while obeying the octet rule with one C=O double bond to each carbon.

Determine the following for $C_2O_4{}^{2-}$.

C-C bond order ______ C-O bond order ______

the hybridization of each carbon atom
sp
sp^2
sp^3

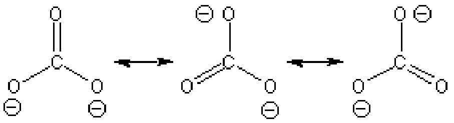
the number of σ bonds ______ the number of π bonds ______

6.4-15. $CO_3{}^{2-}$

EXERCISE 6.10:

Lewis structure and bonding in the **carbonate ion ($CO_3{}^{2-}$)**:

- ER = 4(8) = 32 electrons required with no sharing
- VE = 4 from C + 3(6) from O + 2 from charge = 24 valence electrons
- SP = 1/2(32 - 24) = 4 shared pairs



The lone pairs on the O atoms have been omitted, but each O obeys the octet rule.

Determine the following for $CO_3{}^{2-}$.

C-O bond order ______________

the hybridization of the carbon atom
sp
sp^2
sp^3

the number of σ bonds ______________

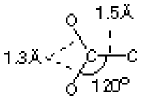
the number of π bonds ______________

6.4-16. Bonding from Structure

EXERCISE 6.11:

X-rays are scattered from the atoms in molecules, and the manner in which they are scattered can be used to determine the relative positions of the atoms. Indeed, the structures of many molecules have been determined with this technique. However, x-rays are not scattered by electrons, and H atoms are usually too small to be seen. Consequently, lone pairs and H atoms must be added by the chemist.Determine the number of hydrogen atoms that must be added to the central carbon atom and the hybridization of the central atom of the structures given in the activity area. Hint:

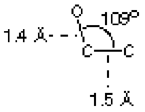
- use bond lengths (see table in the Resources) to determine bond orders and bond angles to determine hybridizations, and
- recall that C usually has no formal charge, which is the case when there are 4 bonds to it.



What is the hybridization on the central carbon atom?
sp
sp^2
sp^3

How many hydrogen atoms must be added to the central carbon atom?

____



What is the hybridization on the central carbon atom?

sp
sp^2
sp^3

How many hydrogen atoms must be added to the central carbon atom?

____

6.5 Molecular Orbital Theory and Delocalized Bonds

Introduction

In valence bond theory, orbitals on the same atom are combined to produce hybrid orbitals, which are then used to overlap an orbital on an adjacent atom to produce a bond that is localized between the two atoms. In ***molecular orbital theory***, atomic orbitals on different atoms are mixed to produce bonds that can be localized between two atoms but are frequently ***delocalized*** over several. The rules presented in the previous section for mixing atomic orbitals that we used in the construction of hybrid orbitals will now be used to construct molecular orbitals.

Valence bond theory allows us to make predictions about bonding and structure from relatively simple considerations, but hybridization and resonance had to be invoked to account for some structural features. MO theory is more powerful in its predictive power, but it is somewhat more difficult to use. Thus, chemists use both theories, choosing the one that is easier to use while still providing sufficient predictive power. In this section, we present a qualitative introduction to molecular orbital theory; one that will introduce some important terms, present a more satisfying picture of delocalization, and explain the electronic structure of molecules.

Prerequisites

- 5.7 Resonance (Describe resonance and determine the bond order of bonds involved in resonance structures.)
- 2.6 Orbital Shapes and Sizes

Objectives

- Explain the difference between bonding and antibonding orbitals and show how s orbitals combine to produce MO's.
- Show how p orbitals can be used to construct σ and σ^* MO's.
- Show how p orbitals can be used to construct π and π^* MO's.
- Predict the relative energies the bonding MO, the antibonding MO, and the atomic orbitals used to construct them.
- Define HOMO and LUMO.
- Use an MO diagram to predict whether a diatomic molecule can form.
- Determine the bond order of a bond from the number of bonding and antibonding pairs of electrons.
- Use an MO diagram to predict the number of unpaired electrons in a molecule.
- Explain how to determine the relative phases of the atomic orbitals used to construct the molecular orbitals for molecules with more than two atoms.
- Determine whether a molecular orbital is bonding, nonbonding, or antibonding from the phases of the atomic orbitals used to construct it.

- Explain how MO theory explains resonance.
- Show how MO theory explains delocalized pi systems.

6.5-1. Bonding Versus Antibonding Orbitals

Bonding MO's increase the electron density between the nuclei, while antibonding MO's contain nodal planes perpendicular to the internuclear axis.
A video or simulation is available online.

In MO theory, atomic orbitals (AO's) are combined to form molecular orbitals (MO's). The number of MO's created is always equal to the number of AO's used to create them. Thus, combining two AO's produces two MO's, which differ in the way in which the AO's are combined.

1 **Bonding MO's**: A combination of two AO's that have the same phase in the region between the two nuclei results in a bonding MO. Bonding MO's are characterized by an accumulation of electron density between the two atoms.

2 **Antibonding MO's**: A combination of two AO's of opposite phase in the region between the two nuclei results in an antibonding MO. Antibonding MO's are characterized by an annihilation of electron density between the two atoms. That is, antibonding interactions contain nodal planes perpendicular to the bonding axis. Antibonding MO's are designated with a star (*). For example, the σ^* and π^* (pronounced "sigma star" and "pi star") are the antibonding combinations that contain nodal planes perpendicular to the bonding axis.

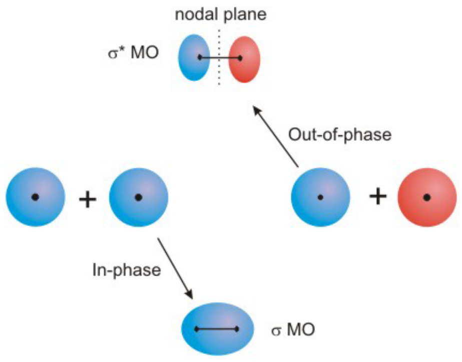


Figure 6.18: Combining Two s Orbitals

6.5-2. End-on Interactions of p Orbitals Produce σ and σ^* MO's

Head-on combination of two p orbitals results in electron density on the bonding axis, so both combinations are classified as σ. The combination of orbitals of the same phase increases electron density on the bonding axis, so it is the bonding σ orbital. The combination of opposite phases produces a nodal plane perpendicular to the bonding axis, so it is the antibonding σ^* orbital.

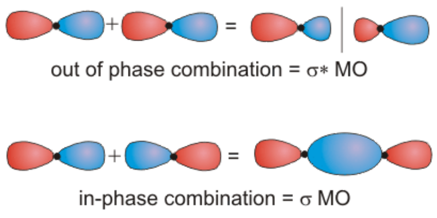


Figure 6.19: Head-on Combination of Two p Orbitals

6.5-3. Side-on Interactions of p Orbitals Produce π and π^* MO's

A video or simulation is available online.

The side-on combination of two p orbitals results in no electron density on the bonding axis, so both combinations are classified as π. The combination of orbitals of the same phase increases electron density between the bound atoms, so it is the π bonding orbital. The combination in which lobes of opposite phase interact produces a nodal plane perpendicular to the bonding axis, so it is an antibonding π^* orbital.

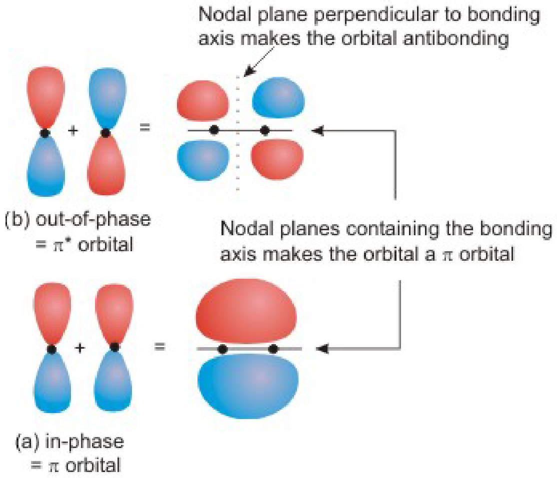


Figure 6.20: Side-on Combinations of Two p Orbitals

6.5-4. Energy

Each molecular orbital is characterized by an energy level, and the electrons in a molecule fill the molecular energy levels in the same manner that they fill atomic orbitals. That is, the electrons fill the molecular energy levels at lowest energy while obeying both Hund's Rule and the Pauli Exclusion Principle.

The energy changes resulting from the combinations of two s orbitals are shown in an MO diagram like the one shown in Figure 6.21. Three important characteristics of these diagrams are:

- the energy of bonding interactions is lower than that of the atomic orbitals by ΔE.
- the energy of antibonding orbitals is higher than that of the atomic orbitals by (ΔE^*).
- $\Delta E^* > \Delta E$.

Many of the properties of a molecule are dictated by the nature of and energy difference between the occupied MO that is highest in energy and the unoccupied MO that is lowest in energy. These two orbitals are referred to as the HOMO and LUMO.

- ***HOMO***; The **H**ighest **O**ccupied **MO**
- ***LUMO***; The **L**owest **U**noccupied **MO**

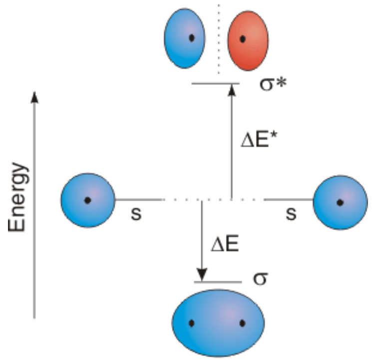


Figure 6.21: An MO Energy Diagram An MO diagram for the combination of two s orbitals of the same energy. Note that $\Delta E^* > \Delta E$.

Electrons that occupy bonding orbitals lower the energy of the system and make the MO more bonding, while those occupying antibonding orbitals raise the energy and make the MO less bonding. Indeed the bond order (BO) is defined in terms of the difference between the number of bonding and antibonding electrons in the bond as follows.

$$\text{BO} = \frac{1}{2}(\text{number of bonding electrons} - \text{number of antibonding electrons})$$

6.5-5. MO Diagrams for H_2 and He_2

As an example of the use of a diagram such as the one shown in Figure 6.21, we examine the differences predicted for the H_2 and He_2 molecules.

$H + H \rightarrow H_2$: Each H atom has one electron in the 1s orbital, so the two-atom system has two electrons to place in the MO diagram. Both electrons would enter the σ bonding orbital. Their energy in a sigma orbital of H_2 is less than that of two electrons in two 1s orbitals of separated H atoms, so H_2 is a stable molecule. The bond order of the H-H bond is $1/2(2-0) = 1$, a single bond.

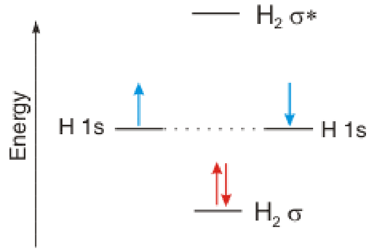


Figure 6.22a: MO Diagram for H_2

$He + He \rightarrow He_2$: Each He atom has two electrons in its 1s orbital, so the two-atom system has four electrons. Two electrons would be placed in the σ orbital and two would be placed in the σ^*. However, $\Delta E^* > \Delta E$, so the energy of four electrons in He_2 is greater than in two separated He atoms. The bond order of the He-He bond would be $1/2(2-2) = 0$, no bond. Consequently, He_2 does not form.

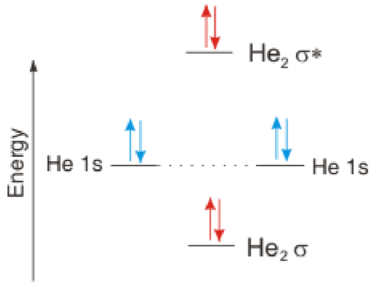


Figure 6.22b: MO Diagram He_2

6.5-6. Relative Orbital Energies in O_2

Consider the interaction of the valence orbitals of two oxygen atoms to form an oxygen molecule.

- The 2s orbitals interact to form σ and σ^* orbitals as shown in the Combining Two s Orbitals video. We use the notation σ (2s) and σ^* (2s) to show that these MO's are derived from the 2s interaction. The 2s orbitals are the lowest energy valence orbitals in an oxygen atom, so the two MO's are also low in energy.
- The 2p orbitals that are directed along the bonding axis interact in a head-on manner similar to that shown in Figure 6.19 to produce the σ (2p) and σ^* (2p) orbitals. Head-on interactions are stronger than side-on interactions, so the σ (2p) is the lowest energy MO derived from the 2p interactions, while the σ^* (2p) is the highest energy MO.
- The remaining 2p orbitals interact in a side-on fashion as shown in the Side-on Combinations of Two p Orbitals video to produce a pair of π (2p) and a pair of π^* (2p) orbitals. Note that the members of each pair have the same energy because there the two π (2p) orbitals are identical except for their orientation relative to one another.

The energy level diagram for the MO's in O_2 is shown in Figure 6.23.

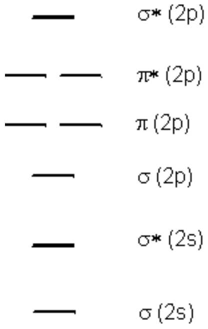


Figure 6.23

6.5-7. Predictions for O_2

Each oxygen atom has six valence electrons, so a total of 12 electrons must be placed into the energy diagram. The electrons are placed in the same manner as they are into the orbitals of an atom: lowest energy orbitals are occupied first and the Pauli Exclusion Principle and Hund's Rule are obeyed. The result of placing 12 electrons in the diagram is shown in Figure 6.24. Note that the π^* MO constructed from the 2p orbitals is the HOMO, while the σ^* MO constructed from the 2p is the LUMO. Two important predictions can be made based on this diagram:

1 **O-O bond order is 2**. Recall that the bond order of a bond is determined as BO = 1/2(number bonding electrons − number antibonding electrons), so the O-O bond order is 1/2(8 − 4) = 2, which is the same conclusion we made from the Lewis structure.

2 **Oxygen molecules are paramagnetic**. Oxygen molecules are paramagnetic (deflected in a magnetic field), which means that O_2 must have unpaired electrons. The Lewis structure we drew in Section 5.5 had no unpaired electrons, which indicates a flaw in the bonding theory used in the previous chapter. However, paramagnetism in O_2 is readily explained with MO theory. The two highest energy electrons must be placed into the two π^* orbitals, and, since they must obey Hund's Rule, they must be unpaired. The presence of two unpaired electrons in O_2 makes it paramagnetic. This prediction was a major success for the MO theory.

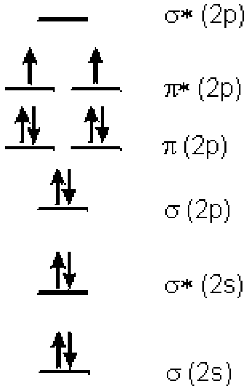


Figure 6.24: Molecular Orbital Occupancy for an O_2 Molecule

6.5-8. Heteronuclear Diatomic Molecules

The two nuclei in heteronuclear diatomic molecules are nuclei of different elements, so the AO's that mix to form the bonding MO are at different energies. Whereas the two atoms of a homonuclear diatomic molecule like H_2 and O_2 make equal contributions to each MO in the molecule, the energy difference between the AO's in a heteronuclear diatomic molecule results in MO's that are not composed of equal amounts of the AO's. Instead, the AO's mix in the ratio that achieves the lowest energy possible for the bonding MO. The lowest energy MO is produced when the AO at lower energy contributes more to the MO than does the AO at higher energy. We now examine the bonding between an s orbital on atom X with the s orbitals on atoms A, B, and C, which are at different energies.

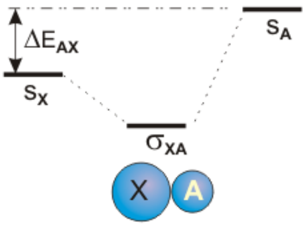


Figure 6.25a: Mixing AO's of Different Energy

The energy of s_X (the s orbital on atom X) is less than that of s_A by an amount ΔE_{XA}. s_X is the lower energy AO, so it contributes more to the bonding MO (σ_{XA}) than does s_A, which is shown by the relative sizes of the spheres describing the MO. The larger sphere on X means that there is more electron density on atom X in the bond, so the XA bond is polar with atom X carrying the negative charge.

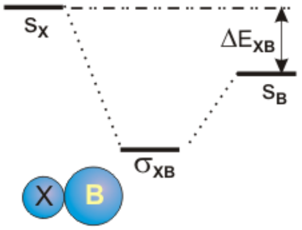


Figure 6.25b: Mixing AO's of Different Energy

s_B is lower in energy than s_X by an amount ΔE_{XB}. s_B is the lower energy orbital, so it contributes more to the bonding MO (σ_{XB}). The XB bond is therefore polar with atom B carrying the negative charge.

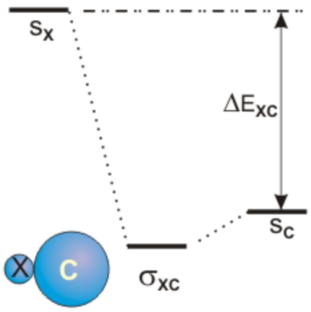


Figure 6.25c: Mixing AO's of Different Energy

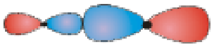
s_C is lower in energy than s_X by an amountΔE_{XC}. $\Delta E_{XC} > \Delta E_{XB}$, so s_C contributes even more to the XC bond than did s_B to the XB bond. The small sphere representing the contribution of s_X to the σ_{XC} MO indicates that only a small amount of the electron density in the bond resides on atom X. The result is that the XC bond is more polar than the XB bond.

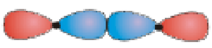
Recall that electronegativity is a measure of how well an atom attracts the bonding electrons, but, as shown in the preceding figure, the electron density in a bond is greater around the atom with the lower energy orbital; i.e., the atom with the lower energy orbital attracts the electrons more, so it is the more electronegative atom. This is why we used the energy of the unfilled orbitals to predict relative electronegativities in Chapter 3! Using the relative energies of atoms X, A, B, and C in Figures 6.25a, 6.25b, and 6.25c, we conclude that atom C is the most electronegative atom and atom A is the least electronegative. The bond dipole of the AX bond points toward atom X because X is more electronegative than A, but it points toward atom C in the XC bond because atom C is more electronegative than atom X.

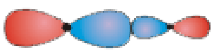
6.5-9. Heteronuclear Bonding MO Exercise

EXERCISE 6.12:

Indicate which representation (a, b, or c) best describes the interaction of p orbitals in each of the following O-X bonds. Assume the oxygen orbital is on the left in each case.


(a)


(b)


(c)

an O-F bond	an O-N bond	an O-O bond
a	a	a
b	b	b
c	c	c

6.5-10. Rules for MO Construction of Simple Systems

MO's can be bonding, nonbonding, or antibonding.

So far we have discussed the MO's formed by interacting only two atoms, but all of the atoms in a molecule can be involved in a single MO. Computers are used to determine the MO's of complicated molecules, so we will limit our discussion to the MO's of simple systems, which can be constructed with the following rules.

1. The number of MO's equals the number of atomic orbitals used to construct them.
2. Each MO contains one more nodal plane than the MO that it is immediately beneath it in energy. There are no nodal planes in the lowest energy MO, and there is a nodal plane between each pair of atoms in the highest energy MO.
3. The nodal planes are placed symmetrically even if it means placing them on an atom.
4. Nodal planes cannot be placed on adjacent atoms.

5 Nodal planes are not placed on terminal atoms.

The bonding character of an MO spread over several atoms depends upon the relative number of bonding and antibonding interactions. In the following discussion, we use **B** = number of bonding interactions and **A** = number of antibonding interactions.

- **B > A**: The MO is bonding, and its energy is lower than the energy of the AO's used to construct it.
- **B < A**: The MO is antibonding, and its energy is higher than the energy of the AO's used to construct it.
- **B = A**: The MO is nonbonding, and its energy is close to the energy of the AO's used to construct it.

A common way to draw MO's, and the one used in the following discussion, is to show only the relative phases of the AO's used to construct them. Thus, we will not be drawing the σ and π orbitals shown in the Combining Two s Orbitals video or the Side-on Combinations of Two p Orbitals video. Rather, we will represent them by the phases of the interacting orbitals.

6.5-11. Constructing the MO's for a Three-Atom System

A video or simulation is available online.

There are three atomic orbitals, so there must be three MO's. All of the atomic orbitals must be of the same phase in the lowest energy orbital, which produces an MO with two bonding interactions and no anti-bonding interactions. This orbital is a bonding orbital. The next highest orbital must contain one nodal plane placed in the center. This orbital contains no bonding or antibonding interactions between adjacent atoms, so it is nonbonding. The highest energy orbital requires one more nodal plane. The two nodal planes must be placed symmetrically. The resulting MO contains no bonding and two antibonding interactions, so it is an antibonding orbital. If we assume the system contains four electrons and place them the two lowest energy orbitals, then the nonbonding orbital is the HOMO and the antibonding orbital is the LUMO.

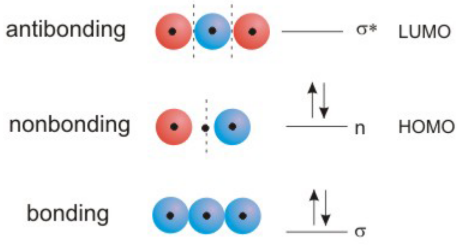


Figure 6.26

6.5-12. SO_2

The structural features that could only be explained by invoking resonance in Chapter 5 are readily understood in terms of delocalized MO's. Consider the case of SO_2 shown in Figure 6.27. Although the bond angles are 120° not 180°, the atomic orbitals are p orbitals not s orbitals, and the interactions are pi not sigma, the relative phases of the AO's are the same for SO_2 as for the three-atom system discussed above.

Two resonance structures (shown at the top of the figure) were used to account for the fact that the two S-O bonds are of equal length. The two structures differ in the position of the π bond, which is shared between the two bonds, and the location of one of the lone pairs, which appears to be shared by the oxygen atoms. The σ bonds and the lone pairs except the one that appears in different locations in the Lewis structure lie in the molecular plane and will be ignored in the following MO description discussion, which centers on the π system. Note that the term resonance is not required in the MO description.

The π system contains four electrons: the two in the π bond and two in the lone pair that appears to move in the two resonance forms. The AO's used to construct the π MO's are p orbitals that are perpendicular to the molecular plane. Placing four electrons into the system fills the π and n (nonbonding) orbitals. Note that there is one bonding orbital (the π bond) and one lone pair (nonbonding orbital) as shown in the Lewis structures. However, the π bond is delocalized over all three atoms, with no difference between the two S-O bonding regions, and the lone pair is delocalized over both oxygen atoms. Thus, all of the features that caused us to invoke resonance with the earlier bonding theory are explained with molecular orbital theory.

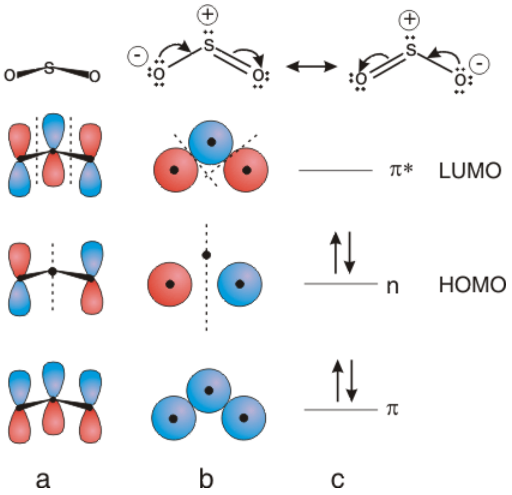
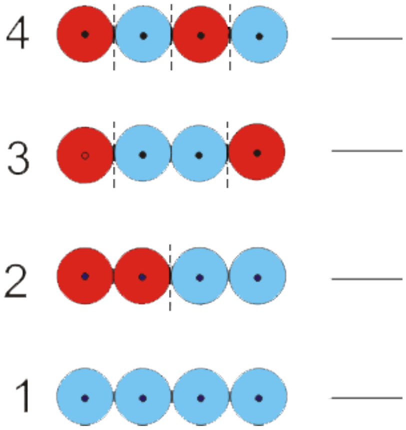


Figure 6.27: π MO's for Sulfur Dioxide (a) Viewing the p orbitals from the side; (b) Viewing the p orbitals from above so that only the top of the p orbitals can be seen; (c) Energy diagram showing two occupied MO's and identifying the HOMO and LUMO.

6.5-13. Orbital Types in a Delocalized Four-Atom System - Exercise

EXERCISE 6.13:

Use the MO diagram in the figure to determine the number of bonding interactions, the number of antibonding and orbital type for each of the four MO's of a delocalized four-atom system.



Orbital Number 4:

bonding interactions ____________

antibonding interactions ____________

orbital type:
bonding
antibonding
nonbonding

Orbital Number 3:

bonding interactions ____________

antibonding interactions ____________

orbital type:
bonding
antibonding
nonbonding

Orbital Number 2:

bonding interactions ____________

antibonding interactions ____________

orbital type:
bonding
antibonding
nonbonding

Orbital Number 1:

bonding interactions ____________

antibonding interactions ____________

orbital type:
bonding
antibonding
nonbonding

Assume a four-electron system to identify the orbital number of the HOMO and LUMO.

HOMO ____________

LUMO ____________

6.5-14. Four-atom Example: Butadiene

The Lewis structure of butadiene (Figure 6.28) shows two C=C double bonds and one C-C single bond, so we would expect two bond lengths of about 130 pm and one of about 150 pm. Experimentally, we find that there are two bonds of 134 pm and one of 135 pm, the approximate length of a C=C double bond. We now use an MO treatment of the π system to explain this observation. The relative phases of the p orbitals are the same as the s orbitals in the above exercise. Figure 6.28a views the molecule from the top so that only the top lobe of each orbital is shown, while Figure 6.28b shows the side-on view. There is one electron in each p orbital, so there are a total of four electrons in the π system, which are distributed into MO's as shown. Note that both pairs of electrons reside in π bonding orbitals, which is consistent with the two double bonds predicted by the Lewis structure. However, the π orbitals are delocalized over all four carbon atoms not localized between two atoms as shown in the Lewis structure, which explains why the bond lengths are nearly the same.

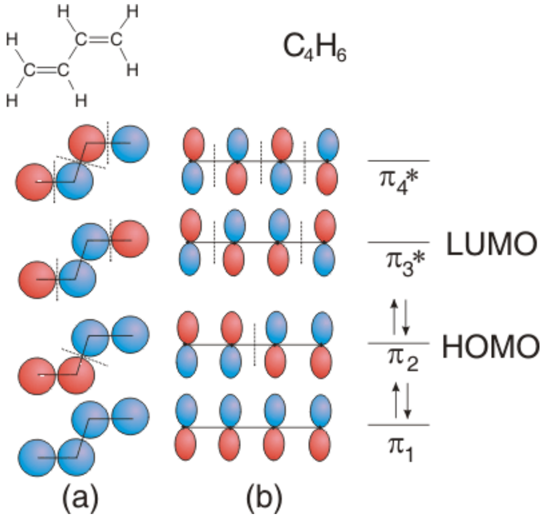


Figure 6.28: MO's for Butadiene (a) The circles represent the relative phases of the p orbitals (the orbitals viewed from the top). (b) Each p orbital represented by the traditional 'figure 8'.

6.5-15. Benzene

As our last example, we examine the delocalized π system in benzene (C_6H_6) shown in Figure 6.29. Recall that the double bonds in benzene are sometimes represented by a circle in Figure 6.8 due to resonance in the molecule. Although the construction of the MO's is beyond the scope of this text, an examination of them demonstrates the rules for construction and provides a better understanding of the bonding in this very important molecule. There are six carbon atoms and six p orbitals, so there are six π MO's. The lowest energy MO has no nodal planes and is a bonding orbital delocalized over all six atoms. The highest energy orbital has a nodal plane between each pair of atoms, but, due to the symmetry of benzene, this requires only three nodal planes. Thus, the four remaining MO's must contain either one or two nodal planes. In fact, two MO's have one nodal plane, and two MO's have two nodal planes. The π system has six electrons, so only the three bonding MO's are occupied, which gives rise to the three double bonds in the Lewis structure. The three MO's are delocalized over all six carbon atoms, so, consistent with representing the double bonds with a circle, the π electron density is spread over the entire molecule with no localized double bonds.

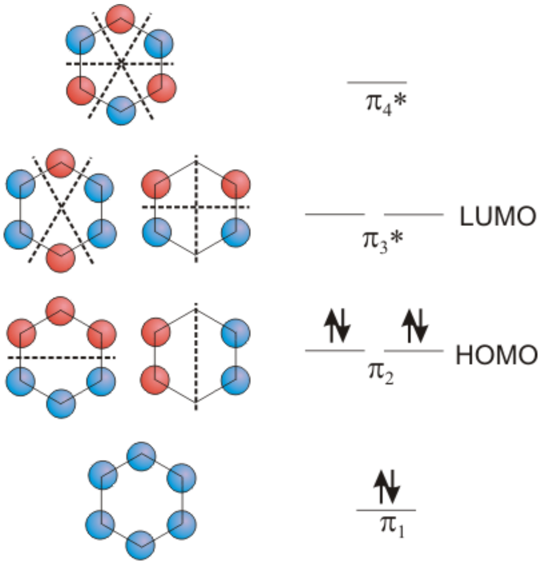


Figure 6.29: MO's for the π System of Benzene

6.5-16. Summary

Molecular orbital theory is a very powerful tool, and we will refer to the concepts and terms introduced here in subsequent chapters. However, the simple predications about geometry and bonding that we made in the previous chapter and most of this chapter are correct, and they are much easier to make using the bonding theory presented earlier. Thus, chemists often use a combination of the two theories when discussing molecular structure and bonding.

6.6 Exercises and Solutions

Links to view either the end-of-chapter exercises or the solutions to the odd exercises are available in the HTML version of the chapter.

Chapter 7 – States of Matter and Changes in State

Introduction

The materials we deal with every day exist in one of three states of matter: solid, liquid, or gas. The molecules in the liquid and solid phase are much closer to one another than are the molecules in the gas state. Consequently, the solid and liquid states are often called the *condensed states*. Some substances, such as water, are found in all three states under normal conditions (ice, water, and steam). However, most other substances are found in only one state under normal conditions. Thus, most of us have only encountered elemental iron as a solid, helium as a gas, and table salt as a solid. In this chapter, we examine the properties of the states of matter.

7.1 Gases

Introduction

Gases are characterized by their volume (V), pressure (P), temperature (T), and the number of moles of particles (n). In this section, we discuss how the volume of a gas is affected by changes in its pressure, temperature, and number of moles. Finally, we consider mixtures of gases.

Objectives

- Explain how a barometer is used to determine atmospheric pressure.
- Determine the pressure of a gas with a manometer reading and atmospheric pressure.
- Explain how the volume of a gas varies with its pressure (sketch V vs. P for an amount of gas at constant T).
- State Boyle's Law and use it to determine the volume of a gas at one pressure from its volume at a different pressure but at the same temperature.
- Explain how the volume of a gas varies with its temperature (sketch V vs. T for an amount of gas at constant pressure).
- Convert a temperature from the Celsius scale to the Kelvin scale and vice versa.
- State Charles's Law and use it to determine a volume of a gas at one temperature given its volume at a different temperature.
- State the Ideal Gas Law.
- Use the Ideal Gas Law.
- Define *partial pressure*.
- Determine the pressure of a mixture of gases from the partial pressures of the component gases.
- Define *molarity* and determine the molarity of a gas from its pressure and temperature or the number of moles of gas and its volume.

Boyle's Law and Pressure

7.1-1. Boyle's Law and Pressure

Barometric pressure is usually given by the height of a mercury column that the atmosphere will support.

As shown in Figure 7.1, a ***barometer*** is a glass tube, which is closed at one end and open at the other, that is filled with mercury and immersed with the open end down into a pool of mercury. Only part of the mercury drains from the tube, and the resulting column has a height that depends upon the atmospheric pressure. The column, which is supported by the molecules in the atmosphere, has a height of 760 mm at sea level at normal conditions. Gas pressures can be determined by measuring the height of the mercury column that they support. The height is usually given in mm, and the pressure is given in mm of Hg or ***torr*** (1 torr = 1 mm Hg). The following are common ways of expressing the normal pressure at sea level.

$$1\ \text{atm} = 14.7\ \text{lb/in}^2 = 760\ \text{mm Hg} = 760\ \text{torr} = 1.01 \times 10^5\ \text{Pa} \qquad (7.1)$$

Pa is the ***pascal***, the SI unit of pressure.

$$1\ \text{Pa} = 1\ \text{kg} \cdot \text{m}^{-1} \cdot \text{s}^{-2}$$

Note that the barometric pressures given in weather reports are given in inches of Hg. The median barometric pressure at sea level is 760 mm = 29.9 in. Some extreme barometric pressures observed in the U.S. are given below.

- High: 809 mm = 31.9 in = 1.06 atm (Alaska, 1969)
- Low: 670 mm = 26.3 in = 0.88 atm (Florida, 1935)

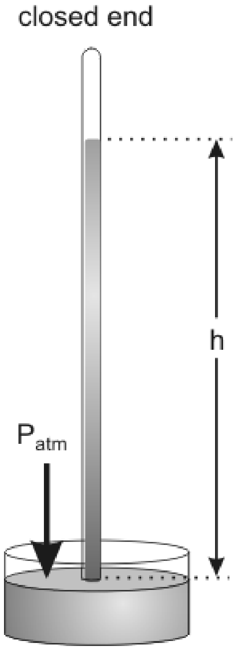


Figure 7.1: A Barometer The pressure exerted by the weight of the mercury column of height h equals the pressure exerted by the weight of the atmosphere.

7.1-2. Measuring Pressure with a Manometer

The pressure of a gas in the laboratory is often found as the difference in heights of two columns of a liquid (most often mercury) in a manometer.

The device used to measure the pressure of a gas in the laboratory is called a ***manometer***. One side of the manometer shown in Figure 7.2 is open to the atmosphere, while the other is attached to the gas whose pressure is to be measured. Consequently, the atmospheric pressure (P_{atm}) is pushing on the right side, and the unknown gas pressure (P) is pushing on the left. When the two pressures are the same, the two mercury columns in the manometer are at the same height, and $h = 0$. However, when the two pressures are not the same, the side with the greater pressure exerts the greater force, which causes the mercury column on that side to drop, and the column on the other side to rise. The difference in the pressures of the two sides is given by the difference in the two mercury levels, h, as described below.

- $P_{\text{gas}} = P_{\text{atm}} + h$ if mercury level is higher on atmosphere side
- $P_{\text{gas}} = P_{\text{atm}} - h$ if mercury level is higher on gas side

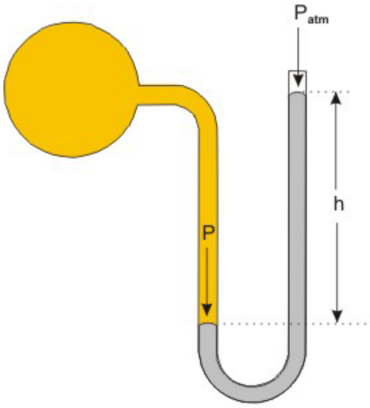
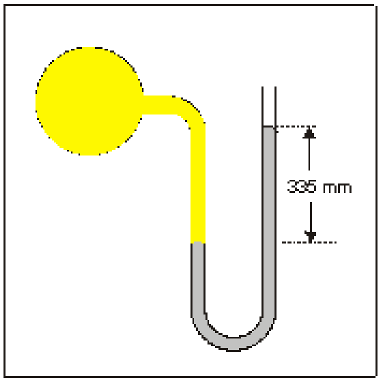


Figure 7.2: Determining Pressure with a Manometer A manometer, which is used to measure the pressure of a gas: In the above experiment, the pressure of the gas (P) is greater than barometric pressure (P_{atm}) by h mm of Hg, i.e., $P = P_{\mathrm{atm}} + h$.

7.1-3. Barometer Exercise

EXERCISE 7.1:



What is the pressure of the yellow gas in torr (mm Hg) if barometric pressure is 762 torr?

______________ torr

What is the pressure of the yellow gas in atmospheres?

______________ atm

7.1-4. Boyle's Law

$PV = k$, where k is a constant that depends only upon the amount and temperature of the gas.

The volume of a given amount of gas at a constant temperature varies with its pressure. The graph in Figure 7.3 shows the volume of one mole of gas as a function of its pressure at 0 °C. The relationship between pressure and volume

$$PV = k(n, T) \qquad \text{Boyle's Law} \tag{7.2}$$

is known as ***Boyle's Law***. The constant, $k(n,\ T)$, is a function of the number of moles of gas (n) and its temperature (T). Boyle found that the product of the pressure of a gas and its volume is constant as long as the number of moles of the gas and the temperature of the gas are held constant. The following equation is often used for Boyle's Law.

It indicates that the PV product is unchanged in processes that involve no change in temperature or amount of gas. Thus, the following form of Boyle's Law is also commonly used.

$$P_\mathrm{f}V_\mathrm{f} = P_\mathrm{i}V_\mathrm{i}$$

where $P_\mathrm{f}V_\mathrm{f}$ is the final PV product and $P_\mathrm{i}V_\mathrm{i}$ is the initial product.

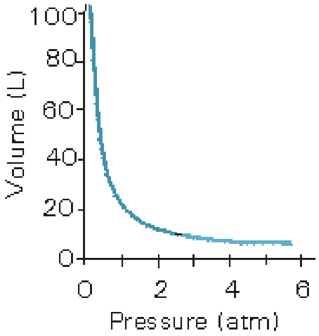


Figure 7.3: Volume of Gas vs. Pressure of Gas The volume of one mole of a gas at 0 °C vs. the pressure of the gas is shown.

7.1-5 Boyle's Law Exercise

EXERCISE 7.2:

The pressure on 5.2 L of a gas is decreased from 1.0 to 0.75 atm at constant temperature. What is the new volume?

initial volume in liters ______________ L

initial pressure in atmospheres ______________ atm

final pressure in atmospheres ______________ atm

final volume in liters ______________ L

Temperature and Charles's Law

7.1-6. Charles's Law

$V = kT$, where k is a constant that depends on the amount and pressure of the gas, and T is the temperature in kelvins.

Experiments with gases in the late 1700s and early 1800s determined the relationship between the volume of a gas and its temperature. As shown in Figure 7.4, the volume of a given amount of gas at constant pressure increases linearly with its temperature. Although the slope of the straight line varies with the number of moles and pressure of the gas, extrapolation of all lines to the temperature of zero volume yields the same temperature, −273.15 °C (degrees Celsius). At lower temperatures, the volume of the gas would be negative, which is not possible, so we conclude that temperatures can be no lower than −273.15 °C. The absolute temperature, or Kelvin, scale was defined based on this absolute minimum in temperature.

$$\mathrm{K} = {}^\circ\mathrm{C} + 273.15 \tag{7.3}$$

Note that the word "degrees" is not used with Kelvin temperatures, so 273 K is said "273 kelvins." Equation 7.3 shows that you add 273.15 to a temperature in degrees Celsius to convert it to the absolute scale. For example, water freezes at 0 °C, which is 273 K, and boils at 100 °C, which is 373 K. Room temperature is usually assumed to be 25 °C, which is 298 K. The absolute temperature must be used in all equations involving the temperature of a chemical system. However, either the Celsius or absolute scales can be used in equations involving a change in the temperature of a system because the unit size is the same in both scales. Once the new temperature scale was defined, the volume of a gas was found to be directly proportional to its temperature expressed in kelvins, which is known as **Charles's Law**.

$$V = k(n, P)T \qquad \text{Charles's Law} \tag{7.4}$$

Charles's Law indicates that the V/T ratio of a gas is constant as long as n and P are unchanged, so Charles's Law can also be given as follows.

$$\frac{V_\mathrm{f}}{T_\mathrm{f}} = \frac{V_\mathrm{i}}{T_\mathrm{i}}$$

The above shows that the final V/T ratio equals the initial V/T ratio as long as the amount of gas and its pressure are unchanged.

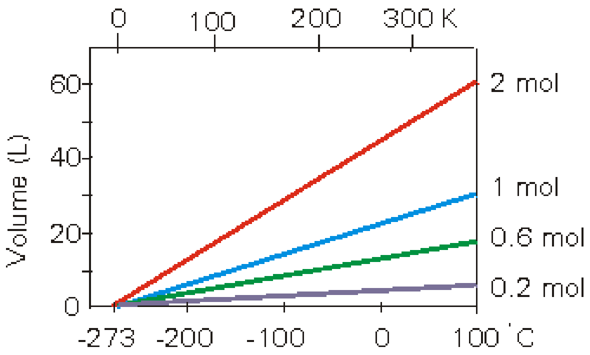


Figure 7.4: Charles's Law The volume of the specified number of moles of gas as a funtion of temperature: The bottom scale is in degrees Celsius, and the top scale is the Kelvin scale.

7.1-7. Charles's Law Exercise

EXERCISE 7.3:

What is the volume of gas at 0 °C if the volume is 250 mL at 100 °C?

initial volume in milliliters ________________ mL

initial temperature in kelvins ________________ K

final temperature in kelvins ________________ K

final volume in milliliters ________________ mL

The Ideal Gas Law

7.1-8. Ideal Gas Law

$PV = nRT$ is the ideal gas law.

Avogadro's Law states that equal volumes of gases measured under the same conditions of temperature and pressure contain equal numbers of molecules. The volume of a gas at constant temperature and pressure is directly proportional to the number of moles of gas,

$$V = k(P, T)n \qquad \text{Avogadro's Law} \tag{7.5}$$

where n is the number of moles of gas, and $k(P, T)$ is a proportionality constant that depends upon the pressure and the temperature of the gas.

We now have three equations that relate the volume of a gas to its pressure, its temperature, and to the number of moles of the gas. These three relationships can be combined into the ***ideal gas law***.

$$PV = nRT \qquad \text{Ideal Gas Law} \tag{7.6}$$

P	V	$=$	n	R	T
Pressure expressed in **atmospheres**: It can be expressed in other units, but that would change the value of R.	Volume of the gas expressed in **liters**: It can be expressed in other units, but that would change the value of R.		**Number of moles of gas**	$R = 0.0821$ L · atm · K^{-1} · mol^{-1}: It is the **gas law constant**.	T is the absolute temperature in **kelvins**.

Table 7.1

7.1-9. Ideal Gas Law Exercise

<u>EXERCISE 7.4</u>:

The ideal gas law can be used to solve for any one of the variables (P, V, n, or T) if the others are known. Things to remember when using $R = 0.0821$ L · atm · K^{-1} · mol^{-1}:

- T is in kelvins.
- P is in atmospheres.
- V is in liters.

What is the pressure in a 280-mL container that contains 1.8 g He at 330 °C?

$n =$ ______________ mol

$R =$ ______________ L · atm · K^{-1} · mol^{-1}

$T =$ ______________ K

$V =$ ______________ L

$P =$ ______________ atm

Mixtures of Gases

7.1-10. Molarity

The molar concentration, or molarity, of a gas is the number of moles of gas present in 1 L.

Mixtures of gases are the same throughout, i.e., they are *homogeneous mixtures*, and homogeneous mixtures are called solutions. The molecules in a mixture (solution) of ideal gases do not interact, so they can be treated independently. This means that we can apply the ideal gas law to each component of a mixture as if the other components were not present. Each gas in a mixture is at the same temperature, and each has the same volume (the volume of the container). Thus, only the number of moles and the pressure of each component differ. The pressure exerted by gas A in a mixture is called the ***partial pressure*** of A and given the symbol P_A. If A is an ideal gas, we can express its pressure with the ideal gas law as follows.

$$P_\text{A} = \frac{n_\text{A}RT}{V} \qquad \text{Partial Pressure} \tag{7.7}$$

(n_A/V) is the number of moles of A per unit volume. The amount of substance per unit volume is called the ***concentration*** of the substance. When the amount is expressed in moles and the volume in liters, it is called the molar concentration, or ***molarity***, of the substance, so n_A/V is the molarity of A in the solution. Molarity is the most common unit of concentration in a chemistry laboratory (and the only one used in this course). The molarity of A is represented as [A] and is defined as follows.

$$[\mathrm{A}] = \frac{\text{moles of A}}{\text{total volume in liters}} \qquad \text{Definition of Molarity} \tag{7.8}$$

[A] = 1 M is read as "the concentration of A is one molar, or one mole per liter." Substituting $[\mathrm{A}] = n/V$ into the expression for the partial pressure of A, we obtain the relationship between the pressure of a gas and its concentration.

$$P_\mathrm{A} = [\mathrm{A}]RT \qquad \text{Pressure and Molarity} \tag{7.9}$$

Thus, the pressure of a gas is directly proportional to its molar concentration.

EXAMPLE:

If a mixture of gases in a 9.6-L flask at 300 K contains 0.53 moles of A, we would determine that $[\mathrm{A}] = 0.53/9.6 = 0.055$ M, i.e., the solution of gases is 0.055 molar in A. In addition, the partial pressure of A would be:

$$\begin{aligned} P_\mathrm{A} &= (0.055\ \mathrm{mol/L})(0.0821\ \mathrm{L \cdot atm \cdot mol^{-1} \cdot K^{-1}})(300\mathrm{K}) \\ &= 1.36\ \mathrm{atm} \end{aligned}$$

7.1-11. Molarity Exercise

EXERCISE 7.5:

What is the concentration of fluorine (F_2) in a 4.0-L flask that contains 4.2 g of fluorine?

1. Determine the number of moles of F_2 ($M_m = 38.00$ g/mol).

$n =$ ______________ mol F_2

2. Calculate the molarity.

$[F_2] =$ ______________ M

7.1-12. Partial Pressures

The pressure of a mixture of gases equals the sum of the partial pressures of the component gases.

The total pressure in a container filled with a mixture of gases is equal to the sum of the partial pressures of the component gases.

$$P_\text{tot} = \sum_\text{all gases} P_i \qquad \text{Dalton's Law of Partial Pressures} \tag{7.10}$$

where P_i is the partial pressure of the i^th component of the gas.

Thus, the total pressure in a container that contains two gases, A and B, can be expressed as follows.

$$P = P_\mathrm{A} + P_\mathrm{B}$$

Using Equation 7.7 to evaluate P_A and P_B, we obtain the following.

$$P = \frac{n_\text{A}RT}{V} + \frac{n_\text{B}RT}{V} = \frac{(n_\text{A} + n_\text{B})RT}{V}$$

The total pressure of a mixture of gases equals the total number of moles of gas times RT/V.

7.1-13. Partial Pressure Exercise

EXERCISE 7.6:

What are the partial pressures of Ne and He in a 6.0-L flask that contains 0.12 mol Ne and 0.19 mol He at 55 °C?

$P_\text{Ne} =$ ______________ atm

$P_\text{He} =$ ______________ atm

What is the total pressure in the flask?

______________ atm

7.1-14. Gas Law Exercise

EXERCISE 7.7:

A mixture contains 15 g Ne (AW = 20) and 10 g Ar (AW = 40) in a 5.0-L container at 30 °C.

Neon:

number of moles ______________ mol Ne

molar concentration ______________ M Ne

partial pressure in atm ______________ atm Ne

Argon:

number of moles ______________ mol Ar

molar concentration ______________ M Ar

partial pressure in atm ______________ atm Ar

What is the total pressure in the container?

______________ atm

7.2 Kinetic-Molecular Theory and Thermal Energy

Introduction

The ideal gas law applies only to gases that exhibit ideal gas behavior, which can deviate from real gas behavior. In this section, we examine the properties of ideal gases.

Objectives

- Explain the meaning of *temperature* at the molecular level.
- Explain the meaning of *thermal energy* and determine the relative thermal energies of several gases.

7.2-1. Postulates

The behavior of gases is explained by kinetic-molecular theory, which is based on the four postulates provided below. Gases that obey all four postulates are called ideal gases.

1 The volume of the particles is negligible compared to the volume of the container. On average, the distances between gas particles are large compared to the size of the particles.

2 The particles are in constant, random motion. Collisions are elastic, i.e., no kinetic energy is converted into potential energy.

3 Particles in the gas phase do not interact with one another, i.e., there are no attractive forces between the particles, which is why the collisions are elastic (Postulate 2).

4 The average kinetic energy of the molecules in a gas depends only on the absolute temperature of the gas. The kinetic energy of a particle is $\frac{1}{2}mv^2$, so hot molecules move faster than cold ones. This postulate provides the molecular definition of the absolute ***temperature***:

  - The ***absolute temperature*** of a system is a measure of the *average* kinetic energy of the molecules in the system.

7.2-2. Thermal Energy

Thermal energy, which is approximated as RT, is a measure of the average kinetic energy of the molecules.

The average kinetic energy of the molecules in a system is often referred to as the ***thermal energy*** of the system. Thermal energy is an average energy because the molecules in a system do not all move at the same speed—some are moving faster and have more energy than others. All of the energies related to molecules or ions that we have encountered to this point have been potential energies arising from Coulombic interactions. The thermal energy of the molecules is energy that can be used to overcome Coulombic interactions. Thus, thermal energy can be used to break a bond or to melt a solid. Thermal energy is also required to make reactions occur. As we will see in Chapter 9, rates of reaction increase when the temperature is increased. Thus, thermal energy plays an important role in chemistry, but the thermal energy of a solid or a liquid is not easily determined. However, thermal energy is usually approximated as follows:

$$E_{\text{thermal}} \sim RT \qquad \text{Thermal Energy Approximation} \qquad (7.11)$$

where

- $R = 8.31451\ \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ or
- $R = 0.00831451\ \text{kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$

is the ideal gas law constant in J rather than L · atm.

7.2-3. Thermal Energy Exercise

EXERCISE 7.8:

What is thermal energy at room temperature (25 °C)?

____________ kJ/mol

What is thermal energy at 100 °C?

____________ kJ/mol

What is the approximate temperature at which $E_{\text{thermal}} \sim 100$ kJ/mol?

____________ K

7.3 Intermolecular Interactions

Introduction

Why are some molecules gases, while others are liquids and solids at room conditions? Why does water expand upon freezing? The answers to both questions lie in the nature of the interaction between molecules, the topic of this section.

Prerequisites

- 1.7 Energy (Distinguish between kinetic and potential energy.)
- 1.8 Electromagnetism and Coulomb's Law (Explain how the force of attraction of two opposite charges varies with their charge and the distance between them.)
- 5.2 Bond Polarity (Represent the bond dipole with an arrow.)
- 5.6 Determining Lewis Structures

Objectives

- Distinguish between intermolecular and intramolecular forces.
- Explain a temporary dipole and how it leads to dispersion forces.
- Describe a molecular dipole and represent it with an arrow.
- Use bond dipoles in a molecule to determine if there is a molecular dipole.
- Describe the hydrogen bond and state the requirements for it.
- Describe the structure of ice, explain why it has the structure it does, and use the structure to explain some physical properties of water.

7.3-1. Intermolecular Forces

Particles in the gas phase are relatively far apart, so their attractive forces are negligible compared to their thermal energy. However, the attractive forces between particles in the condensed states are strong enough to hold the particles in contact with one another. Ionic compounds are always solids at room temperature because their cations and anions are held in the solid network by strong electrostatic attractions called ionic bonds. However, molecular substances can occur as gases (O_2), liquids (H_2O), or solids (sugar) at room conditions. This diversity in states arises from a diversity in the strengths of the forces between the molecules. Whereas the strength of ionic bonds determines the physical properties of a salt crystal, the physical properties of molecular substances are not related to the strength of their covalent bonds. In molecular substances, we must distinguish between two different kinds of forces:

1. ***Intramolecular forces*** exist **within** a molecule. They are the bonds between atoms that hold the atoms together in the molecule.
2. ***Intermolecular forces*** exist **between** molecules. They are the forces between different molecules that keep the molecules in the liquid and solid states.

The N≡N bond is a very strong bond, so the intramolecular force between the nitrogen atoms in an N_2 molecule is very strong. However, N_2 is a gas at room conditions because the intermolecular forces between different N_2 molecules are very weak. Intermolecular forces, like all interactions in chemistry, are electrostatic. Thus, condensed phases in molecular substances result because there is an attraction between regions of opposite charge on the molecules. However, these charges are smaller, more diffuse, and farther apart than those in bonds, so the force of attraction between different molecules is much less than that between the atoms in a bond. Bond energies lie between 100 and 1000 kJ/mol, but the strengths of most intermolecular interactions are less than 10 kJ/mol. Consider that the bond formed with Super Glue is an intramolecular (bonding) interaction, while static cling is an intermolecular interaction.

Although molecules are electrically neutral, many have regions of nonzero charge due to asymmetric distributions of their valence electrons that produce regions with above normal electron density that are slightly negative ($\delta-$) and regions of depleted electron density that are slightly positive ($\delta+$). Such molecules contain two poles, one positive ($\delta+$) and one negative ($\delta-$). The presence of two poles in the molecule results in a molecular dipole, much like the bond dipole discussed in Chapter 5.2 Bond Polarity. In the remainder of this section, we discuss the origin of these dipoles and the forces they create.

Dispersion Forces

7.3-2. Dispersion Forces

Dispersion forces, which result from the interaction of induced dipoles, increase with molar mass.

Electrical charge in molecules is derived from asymmetrical electron distributions within the molecules, i.e., there are regions within the molecule that are electron rich and other regions that are electron deficient. These regions of excess and deficient electron density result in negatively and positively charged regions in the molecule. The center of the positive regions and the center of the negative regions form two **poles**. If the two poles do not coincide, the molecule is said to have a ***dipole***. Dipoles can be permanent or temporary.

Temporary dipoles result from random electron motion, which can create a dipole in a molecule. The resulting dipole then *induces* dipoles in surrounding molecules as the electrons in surrounding molecules move toward the positive pole and away from the negative pole. Thus, temporary dipoles are also called **induced dipoles**. The force of attraction of the opposite charges of the temporary dipoles is called a ***dispersion force***.

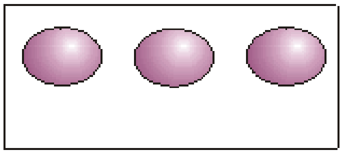


Figure 7.5a: The Dispersion Force Three molecules with no regions of charge have no way to interact.

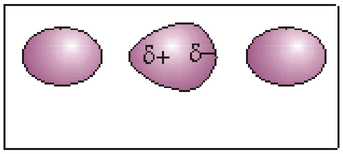


Figure 7.5b: The Dispersion Force Random electron movement in the central molecule causes more electrons to be on one side and fewer on the other, which results in two charged regions.

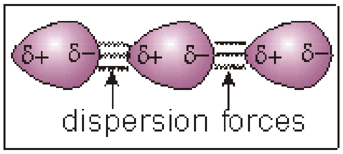


Figure 7.5c: The Dispersion Force The charged regions on the central molecule induce charged regions on the adjacent molecules. The result is that the adjacent molecules have ***induced dipoles***. The interaction of the opposite charges of the induced dipoles is called a **dispersion force**.

Dispersion forces are present in all molecular substances, but they are most important in large molecules where the electron clouds are more easily deformed. Thus, **dispersion forces increase with molar mass**.

Molecular Dipoles

7.3-3. Dipolar Interactions

Dipolar forces act in addition to dispersion forces to increase the strength of the intermolecular interaction.

Most molecules contain atoms with partial positive charge and atoms with partial negative charge as a result of the electronegativity differences that produce polar bonds. If the centers of positive and negative charge do not coincide, two poles are produced and the molecule has a permanent dipole. The magnitude of the dipole depends upon both the size and the separation of the two centers of charge; if the centers of charge coincide, their separation is zero and they have no permanent dipole. Molecules with permanent dipoles are said to be ***polar molecules***, or simply polar, while those that do not have permanent dipoles are said to be nonpolar. Interactions between the centers of opposite charge of the permanent dipoles of different molecules are called ***dipolar forces*** or dipole-dipole forces. Dipolar forces act in addition to dispersion forces. For example, the dispersion forces in HCl and F_2 are expected to be nearly the same because they have similar molar masses (38 and 37 g/mol, respectively). However, HCl is polar, and as shown in Figure 7.6, the partial positive charge on the hydrogen atom of one HCl molecule interacts with the partial negative charge on the chlorine atom of an adjacent molecule to produce a dipolar force between the molecules. This force is in addition to the dispersion forces, so the intermolecular forces are greater in HCl than in F_2, which makes HCl gas much easier to liquefy.

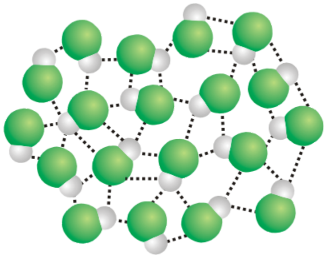


Figure 7.6: Dipolar interactions in HCl Dipolar interactions (dotted lines) are between the chlorine atom (negative end of dipole) of one molecule and the hydrogen atom (positive end of dipole) on an adjacent molecule.

7.3-4. Charge Distribution

Molecules with a permanent asymmetric charge distribution are said to be polar or to have a molecular dipole.

Recall from Chapter 5.2 Bond Polarity that bond dipoles arise in bonds due to electronegativity differences between the bound atoms. Although the total charge on a molecule is zero, some of the atoms in a molecule with polar bonds can carry some charge. The charge on an atom lies somewhere between its formal charge and its oxidation state, depending upon bond polarities.

The centers of positive and negative charge in a molecule are called poles, and a ***molecular dipole*** is defined as the product of the charge on the two poles of a molecule and the distance between them. If the centers of positive and negative charge coincide, their separation is zero, and there is no molecular dipole. Molecules with permanent dipoles are said to be ***polar***, while those without molecular dipoles are said to be nonpolar. We now compare the charge distributions in SO_3 and H_2O. In Figures 7.7a and 7.7b, regions of negative charge are shown in red and regions of positive charge are shown in blue, with a deeper color used to depict more charge.

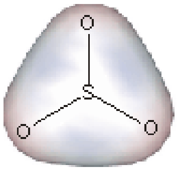


Figure 7.7a: Charge Distribution in SO_3

O is more electronegative than S, so the three S–O bonds in SO_3 are polar. As a result, negative charge resides on the O atoms (red regions in Figure 7.7a), while positive charge is found around the S atom (blue regions in Figure 7.7a). The geometric centers of the negative and positive charge both lie on the sulfur atom. Although SO_3 has regions of charge, the centers of positive and negative charge coincide, so SO_3 does not contain a molecular dipole and is a nonpolar molecule.

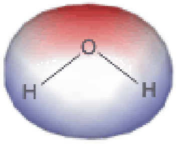


Figure 7.7b: Charge Distribution in H_2O

O is more electronegative than H, so the two O–H bonds in H_2O are polar. Increased electron density on the oxygen produces a partial negative charge there (red region in Figure 7.7b), while decreased electron density on the hydrogens results in positive charge on both hydrogen atoms (blue regions in Figure 7.7b). The coloring is more intense in H_2O than in SO_3 because O–H bonds are more polar than S–O bonds. The center of negative charge (near the O atom) does not coincide with the center of positive charge (between H atoms), so water is a polar molecule (has a molecular dipole).

7.3-5. Representing Molecular Dipoles

A molecular dipole is represented by an arrow that points from the positive pole toward the negative pole. A line is drawn through the arrow at the positive end to make "+" sign.

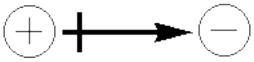


Figure 7.8 A molecule's permanent dipole is indicated by an arrow pointing from the center of positive charge toward the center of negative charge. A short line crosses the arrow forming a "+" at the positive end.

7.3-6. Effect of Geometry on Molecular Polarity

Molecular dipoles also depend upon molecular shape.

The strength of the dipole depends on both the charge on the poles and their separation.

- **Charge**: The charge depends upon the electronegativity differences (strengths of the bond dipoles).
- **Structure**: The separation between dipoles depends upon the structure of the molecule. If the structure is such that the centers of negative and positive charge coincide, i.e., the separation is zero, the molecule is not polar.

Consider the examples of CO_2 and SO_2.

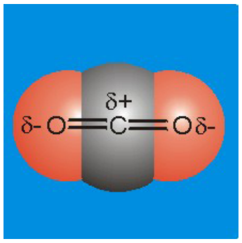


Figure 7.9a: Charge Distribution in CO_2

CO_2

- **Charge**: Oxygen ($\chi = 3.5$) is more electronegative than carbon ($\chi = 2.5$), so the oxygen atoms will carry some negative charge, while the carbon carries some positive charge.
- **Structure**: CO_2 is linear, so the centers of positive and negative charge both reside on the carbon atom.
- **Polarity**: Since the centers of charge coincide, CO_2 is not polar.

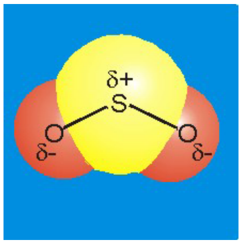


Figure 7.9b: Charge Distribution in SO_2

SO_2

- **Charge**: The electronegativity of sulfur is identical to that of carbon, so the charges carried by S and O in SO_2 are identical to those carried by C and O in CO_2.

- **Structure**: There is a lone pair on the sulfur atom, so sulfur dioxide is bent with an O–S–O bond angle of about 120°.

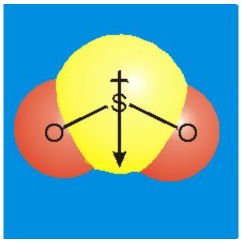


Figure 7.9c: Polarity in SO_2

- **Polarity**: The center of positive charge is on the sulfur atom, but the center of negative charge lies at the midpoint of the line connecting the two oxygen atoms. Thus, the centers of positive and negative charge do not coincide, so SO_2 is a polar molecule. The dipole points from the positive sulfur toward the center of negative charge between the two oxygen atoms.

7.3-7. Molecular Dipole of H_2O

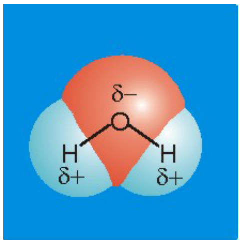


Figure 7.10a

- **Charge:** Oxygen is more electronegative than hydrogen, so it carries a partial negative charge, and the hydrogen atoms each carry a partial positive charge.
- **Structure:** There are two lone pairs on the oxygen atom, so water is bent with an H–O–H bond angle of about 109° (actually it is 104° due to a strong lp-lp interaction).

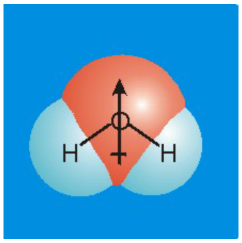


Figure 7.10b

- **Polarity**: The center of negative charge resides on the oxygen, while the center of positive charge resides on the line between the two hydrogen atoms. The two centers do not coincide, so water is a polar molecule (it contains a dipole). In fact, water is a very polar molecule. Its strong dipole plays an important role in its ability to dissolve ionic substances such as table salt.

7.3-8. Molecular Dipoles from Bond Dipoles

Molecular dipoles are the vector sum of the bond dipoles in a molecule.

Recall that the bond dipole (5.2 Bond Polarity) points from the less electronegative atom to the more electronegative atom in the bond. It is a vector that indicates the charge distribution in the bond. The molecular dipole can be determined as the vector sum of the bond dipole vectors.

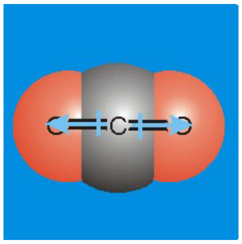


Figure 7.11a: Molecular dipoles are the sums of bond dipoles. The bond dipole of each CO bond points from the carbon toward the oxygen. Because they point in opposite directions, they cancel one another, and CO_2 does not have a molecular dipole, i.e., it is a nonpolar molecule.

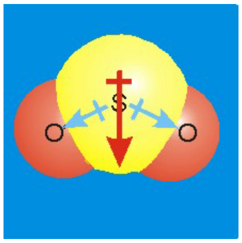


Figure 7.11b: Molecular dipoles are the sums of bond dipoles. Each SO bond has a bond dipole pointing from the sulfur toward the more electronegative oxygen. The sum of the two bond dipoles results in the molecular dipole represented by the red arrow.

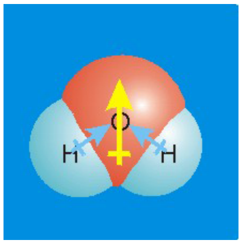


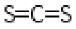
Figure 7.11c: Molecular dipoles are the sums of bond dipoles. The OH bond dipoles (blue arrows) are at 104° angles. The resultant molecular dipole (yellow arrow) points from the center of the line connecting the hydrogens toward the oxygen.

7.3-9. Predicting Dipoles Exercise

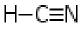
<u>EXERCISE 7.9</u>:

Predict whether each of the following molecules is polar or nonpolar.

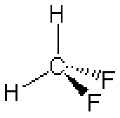
polar
nonpolar



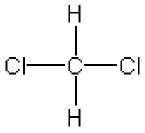
polar
nonpolar



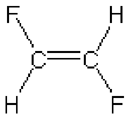
polar
nonpolar



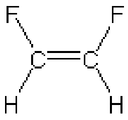
polar
nonpolar



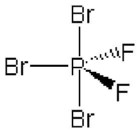
polar
nonpolar



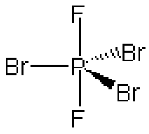
polar
nonpolar



polar
nonpolar



polar
nonpolar



polar
nonpolar

Hydrogen Bonding

7.3-10. Hydrogen Bonding

Hydrogen bonding is a strong dipolar force that can occur between a hydrogen atom and either a nitrogen, oxygen, or fluorine atom.

The strength of a dipole-dipole interaction depends upon the distance between the two interacting poles (the positive pole of one molecule and the negative pole of a different molecule) and the magnitude of the charge on the poles. Consequently, dipole-dipole interactions can be quite strong in molecules that contain small atoms of very different electronegativities.

- Small size allows the interacting poles to get closer.
- Large electronegativity differences produce more charge on the poles.

Hydrogen is the smallest and one of the least electronegative nonmetals, so when it is bound to another small, highly electronegative element (N, O, or F), a very strong dipole-dipole interaction, the ***hydrogen bond***, is established. However, a molecule must contain one of the following bonds to participate in a hydrogen bond.

- H–F bond: HF is the only molecule that contains an H–F bond.
- H–O bond: Water is a strong H-bonder, but there are many other molecules with O–H bonds.
- H–N bond: Ammonia is a strong hydrogen bonder, but there are many other compounds with H–N bonds.

7.3-11. H-bonding in Water

An oxygen atom in water can hydrogen bond to two hydrogen atoms on different water molecules.

Hydrogen bonding in water is especially strong because each oxygen atom can bond to two different water molecules through its two lone pairs. Note that the oxygen is tetrahedral with two O–H covalent bonds that are responsible for H_2O molecules and two longer O–H hydrogen bonds that hold water molecules close to one another and are responsible for water being a liquid at room temperature.

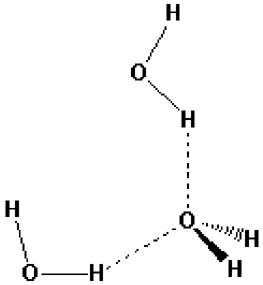


Figure 7.12

7.3-12. Ice

In order to maximize the hydrogen bonding interactions, water molecules in ice orient relative to one another so that the two lone pairs on an oxygen interact with hydrogen atoms of two different water molecules. As a result, water crystallizes in a structure containing hexagonal channels (see Figure 7.13). These channels, which are created when water freezes, result in void space. The presence of the large amount of void space makes the solid less dense than the liquid. The following properties of ice are due to these channels.

- Ice floats because the solid is less dense than the liquid.
- Pipes and radiators burst when water freezes in them because the water expands to create the channels.
- Ice crystallizes around the six-sided channels, so snowflakes are six-sided.
- Ice melts when pressure is applied because the pressure collapses the channels. One theory holds that ice skating is possible because the high pressure exerted by the skates melts the ice under them. The layer of liquid on top of the ice is what is actually slippery.

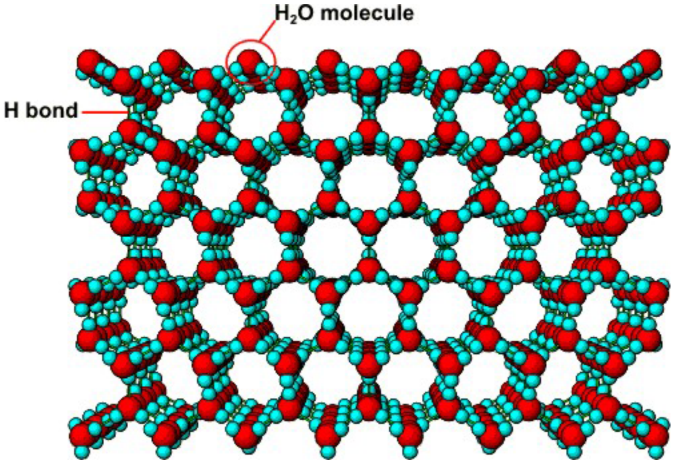


Figure 7.13: Structure of Ice

Predicting Relative Forces

7.3-13. Summary

As shown in Table 7.2, the relative strengths of the various interactions we have discussed overlap, so it is difficult to predict whether the interactions in a large nonpolar molecule are stronger or weaker than in a small polar molecule that hydrogen bonds. For example, I_2 is a solid at room condition, while H_2O is a liquid. Remember that dispersion forces are always present, so the interactions in a large polar molecule are probably stronger than in a small one. In the examples in Exercise 7.10, you will be asked to select the molecule in each pair that is expected to have the stronger interactions and the force responsible for the difference. Only one is responsible for the difference because the molecules have been chosen so that the other forces are comparable, not because they do not exist.

Type of Interaction	Energy of Interaction (kJ/mol)
Covalent Bond	100–1000
Hydrogen Bond	10–50
Dipolar Force	5–25
Dispersion	1–50

Table 7.2: Relative Strengths of Interaction

7.3-14. Predicting Relative Strengths of Interaction Exercise

EXERCISE 7.10:

Predict the compound with the stronger interaction in each pair. Then indicate the force that is most responsible for the difference.

Compound:
CH_3–O–CH_3
C_2H_5–O–H

Force:
dispersion
dipole-dipole
H-bonding
ionic bonding

Compound:
CH_3–O–CH_3
C_6H_{13}–O–C_6H_{13}

Force:
dispersion
dipole-dipole
H-bonding
ionic bonding

Compound:
NH_4Cl
PCl_5

Force:
dispersion
dipole-dipole
H-bonding
ionic bonding

Compound:
PH_3
NH_3

Force:
dispersion
dipole-dipole
H-bonding
ionic bonding

7.4 Solids

Introduction

Molecules in the solid and liquid states are much closer to one another than they are in the gas phase, so the solid and liquid states are referred to as the condensed states. Since the molecules are much closer, they interact much more strongly, and the strengths of those interactions dictate the properties of the substance.

7.4-1. Introduction to Solids

The energy of interaction between particles in the solid state is much greater than thermal energy, so the particles in a solid sit in fixed positions relative to one another that maximize their interactions. Figure 7.14 shows the structure of NaCl, which has ions in each position. Each ion interacts with six ions of opposite charge, and the arrangement that is shown is the one that maximizes those interactions. Each particle has a fixed position, so solids have their own shape and volume, which are independent of the container. The kinetic (thermal) energy of each particle is in the form of oscillations about these positions. Thus, solids are characterized by an ordered array of particles, and that order allows us to understand their structures and properties. The structure/property relationships of solids are discussed in much more detail in the next chapter.

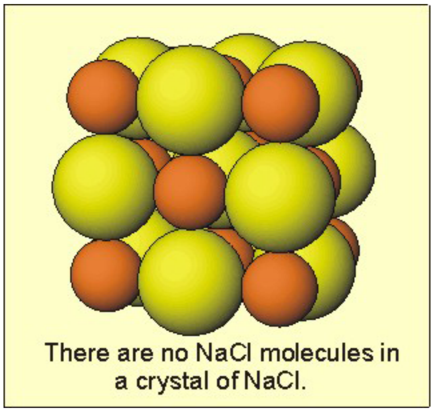


Figure 7.14

7.5 Liquids

Introduction

The intermolecular interactions in the liquid state are comparable to thermal energy, so the molecules remain relatively close to one another while undergoing random, but restricted, motion. This combination of hindered motion without fixed positions makes understanding liquids much more difficult than gases or solids. Liquids adopt the shape of the bottom of the container but maintain their own volume, which depends only slightly on the temperature. In this section, we introduce a few properties of liquids and relate them to the strengths of the intermolecular interactions.

Objectives

- Describe the differences between solids, liquids, and gases.

7.5-1. Viscosity

Viscosity, which is the resistance of liquids to flow, depends upon the energy of interaction relative to thermal energy. In order for a liquid to flow, molecules must slide past one another, breaking and forming intermolecular interactions. If thermal energy is relatively low compared to the energy of interaction, flow is retarded and the liquid is viscous because the molecules cannot readily break the interactions. Thus, viscosity decreases as the liquid is heated. Viscosity also depends upon the shape of the molecule: viscosity increases as the ease with which molecules become entangled increases.

7.5-2. Surface Tension

Molecules in a liquid minimize their energy by minimizing their surface area, and the surface tension is the energy required to increase the surface area of a liquid by a fixed amount.

Intermolecular interactions lower the energy of a molecule, so the more interactions that a molecule experiences, the lower is its energy. Molecules on the surface of a liquid cannot interact with as many other molecules as those within the bulk, which causes the liquid to "bead."

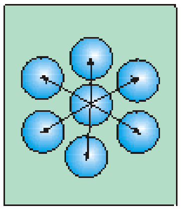


Figure 7.15a: Surface Tension Molecules in bulk of a liquid experience forces in all directions, which cancel one another. Thus, there is no net force acting on the molecule.

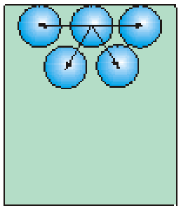


Figure 7.15b: Surface Tension There are no molecules above one at the surface so there is no upward force to cancel the downward force. Thus, there is a net inward force exerted on molecules at the surface that causes liquid to minimize its surface area.

Alternatively, molecules on the surface are at a higher potential energy (fewer interactions to lower it). Consequently, liquids minimize the number of high-energy molecules on the surface by minimizing their surface, which is why water "beads" into distorted spheres when it is placed on a surface with which it does not interact. Energy is required to increase the surface area of a liquid, and the ***surface tension*** is the energy that is required to increase the surface area of a liquid by a fixed amount. Surface tension increases with increasing intermolecular forces. Surface tension is the reason that some insects can walk on water.

7.5-3. Meniscus

A meniscus is concave when the adhesive forces between a liquid and its container are strong, but it is convex when they are weak.

Forces between like molecules are called ***cohesive forces***, while those between unlike molecules are said to be ***adhesive***. Viscosity and surface tension both result from cohesive forces. However, when a liquid is placed in a container, there may also be adhesive forces between the liquid and the walls of the container, and the balance between the cohesive forces that tend to "bead" the liquid and the cohesive forces that tend to "wet" the walls of the container dictates the curved shape of the top of the liquid, which is known as the ***meniscus***.

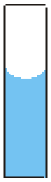


Figure 7.16a: Meniscus Glass contains many Si–O bonds, and water can hydrogen bond to the oxygens on the surface of the wall. The strong adhesive forces between water and glass tend to draw the liquid up the walls of the glass and produce the concave shape of the meniscus.

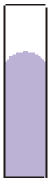


Figure 7.16b: Meniscus Mercury atoms do not interact well with glass, so the adhesive forces are very weak. Consequently, mercury forms a convex meniscus to maximize Hg-Hg interactions and minimize interactions with the walls of the container.

7.5-4. Summary of Properties

It is the interplay between thermal energy and the energy of interaction that dictates the state of a substance.

The strength of a dipole does not change with temperature, so two polar molecules do interact when they collide. However, if they are moving fast enough, their kinetic energy is sufficient to overcome the potential energy of their interaction and they do not "stick" to one another. As they are cooled, however, their kinetic energy is decreased, and, when they are cold enough, they no longer have sufficient kinetic energy to escape their interaction. Thus, it is the interplay between temperature and the strength of the intermolecular interaction that dictates the state of a substance. Table 7.3 summarizes some of the differences between the three states of matter. Note that solids are taken up in some detail in the next chapter.

	Gas	**Liquid**	**Solid**
Shape	shape and volume of the container	shape of the bottom of container, but have own volume	own shape and volume
Intermolecular Distance	great enough that intermolecular forces can be neglected	much smaller in a liquid than in a gas	similar to those in a liquid, but the molecules are oriented so as to optimize their interactions
Thermal vs. Interaction Energy	thermal >> interaction	thermal ~ interaction	thermal << interaction
Molecular Motion	straight line until a collision	random but restricted	oscillations about fixed positions

Table 7.3: A Comparison of the Gas, Liquid, and Solid States

7.6 Changes in State

Introduction

We have all seen ice melt and liquid water boil as a result of increasing the temperature, but ice can also be melted by applying pressure, and liquid water can be made to boil by reducing the pressure. Thus, ice melts under a skater's weight, and water that boils in Denver will not boil at the same temperature at sea level. In this section, we discuss the various changes in state at a molecular level.

Prerequisites

- 1.7 Energy (Distinguish between kinetic and potential energy.)
- 7.3 Intermolecular Interactions (Distinguish between intermolecular and intramolecular forces.)

Objectives

- Order the three states of matter in terms of their potential energies.
- Distinguish between the thermal energy and potential energy of interaction of a molecule.
- Define heat of fusion, heat of vaporization, and heat of sublimation.
- Define *fusion.*
- Describe melting and freezing at a molecular level.
- Define *melting point.*

- Predict whether the solid or liquid state is more dense from the slope of the solid $\rightleftharpoons$ line in a plot of P vs. T for the substance.
- Define *vapor pressure*.
- Define *boiling point* and explain what is meant by the normal boiling point.
- Use a plot of vapor pressure versus temperature to determine whether a substance is a liquid or a vapor at a given set of conditions of T and P.
- Determine which of two substances has the stronger intermolecular forces based on their vapor pressures at some temperature or their boiling points at some pressure.
- Predict which of two compounds is expected to show stronger dispersion forces.
- Predict relative boiling points based on the relative strengths of the dispersion forces of the molecules.
- Explain the effect of permanent dipoles on boiling points.
- Explain the effect of hydrogen bonding on boiling points.
- Explain why bubbles form at the boiling point.
- Define *sublimation* and *deposition*.
- Use a phase diagram to determine which state of matter a substance is in at given conditions of temperature and pressure.
- Use a phase diagram to determine the melting point, the normal boiling point, and the triple point of a substance.
- Use a phase diagram to determine the vapor pressure at a given temperature or the temperature at which the vapor pressure has a given value.

Introductory Overview

7.6-1. Video on the Molecular View of Changes in State

View a video describing **changes in state using kinetic molecular theory**.

A video or simulation is available online.

Energy Considerations

7.6-2. Heats of Change

The potential energy of a particle varies as solid < liquid << gas.

The potential energies of the particles in each of the three states are different because the strength of the intermolecular forces is different. Thus, particles in the solid are at the lowest (most negative) energy because the strength of the intermolecular forces is the strongest in the solid. There are no intermolecular interactions in an ideal gas because the particles are far apart and do not interact. In the liquid, the particles are close together, but interactions are not optimized as they are in the solid. Consequently, the potential energy of a particle varies as solid < liquid << gas. Note that, due to these relative energies,

- the interactions in a solid are so strong that the solid has its own shape;
- the interactions in the liquid are not strong enough to retain a unique shape, but they are strong enough to keep the liquid in the bottom of the container and adopting that shape; and
- the interactions in gases are so weak that the molecules fill the container.

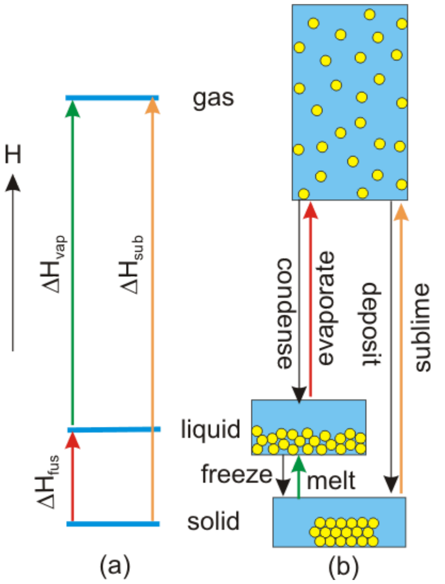


Figure 7.17: Relative Energies of the Vapor, Liquid, and Solid States The solid and liquid states have similar energies, but the energy of the vapor is much higher.

7.6-3. Heats of State Changes Defined

The heats of fusion, vaporization, and sublimation are always positive.

The energy required to melt a solid at its melting point is called its ***heat of fusion***, ΔH_{fus}. The heat of fusion is simply the difference in the potential energies of the liquid and solid states. Heats of fusion are always positive because the liquid is always at higher energy (less negative) than the solid.

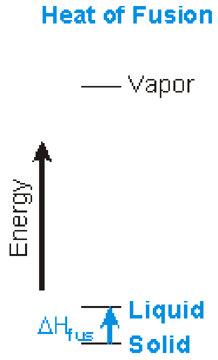


Figure 7.18a: Heat of Fusion

The energy required to vaporize a liquid at a given temperature is called the liquid's ***heat of vaporization***, ΔH_{vap}, at that temperature. The heat of vaporization is the potential energy difference between the liquid and gas. Since the potential energy of the gas is much greater than that of the liquid, a substance's heat of vaporization is always positive and greater than its heat of fusion.

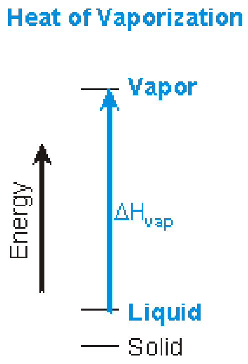


Figure 7.18b: Heat of Vaporization

The energy required to convert the solid directly to the vapor at a given temperature is called the ***heat of sublimation***, ΔH_{sub}. It is the sum of the heats of fusion and vaporization.

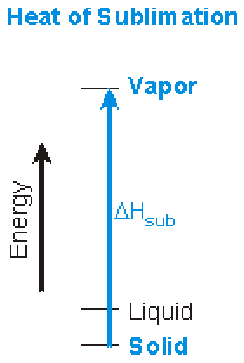


Figure 7.18c: Heat of Sublimation

Solid-Liquid Equilibria

7.6-4. Solid-Liquid Equilibria

The melting point is the temperature at which the solid and liquid are in equilibrium.

When the temperature is such that the kinetic energy of the molecules is low compared to the potential energy of interaction, the molecules arrange themselves in a rigid array that optimizes the interactions. The rigid array is the solid state. Thermal energy in the solid is in the form of oscillations of the molecules about their fixed positions in the crystal. Warming a solid causes the molecules to oscillate faster and with a greater amplitude. When the temperature reaches the point where the intermolecular interactions are no longer sufficient to keep the particles in position, the crystal melts. The ***melting point*** is the temperature at which the solid and liquid are in ***dynamic equilibrium***, i.e., it is the temperature at which the rates of melting and freezing are the same. The dynamic equilibrium is expressed as follows.

$$\text{solid} \underset{\text{freezing}}{\overset{\text{melting}}{\rightleftharpoons}} \text{liquid}$$

Figure 7.19

A high melting point means that the thermal energy required to overcome the intermolecular interactions is high, so substances with high melting points have strong intermolecular interactions.

7.6-5. Graph of Solid-Liquid Equilibrium

The more dense phase can be determined from the slope of the P vs. T line for the solid-liquid equilibrium.

A plot of the pressure versus melting point is nearly a straight line with a steep slope. The slope is steep because large changes in pressure are required to produce small changes in melting point. The slope of the line depends upon whether the solid or liquid is the more dense state because the application of pressure to a solid-liquid equilibrium shifts the equilibrium to the more dense state. Consider the two possibilities shown in Figures 7.20a and 7.20b.

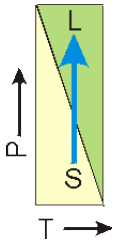


Figure 7.20a: Melting Point as a Function of Pressure The slope of the line is negative, so increasing the pressure (indicated by the arrow) on the solid-liquid equilibrium converts the solid into the liquid (melts the solid). In this case, the liquid is the more dense state, which is the situation for water.

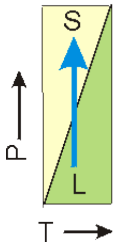


Figure 7.20b: Melting Point as a Function of Pressure The slope of the line is positive, so increasing the pressure on the solid-liquid equilibrium converts liquid into solid (freezes the liquid). In this case, the solid is more dense than the liquid. This is the more common situation.

Liquid-Vapor Equilibria

7.6-6. Liquid-Vapor Equilibria

Vapor pressure increases with temperature and decreases with the strength of the intermolecular force.

The same intermolecular forces that are responsible for the solid state are at play in the liquid state as well, but the kinetic energy of the particles is sufficient to keep the molecules from being locked into position. The molecules in the liquid can slip past one another. As a liquid is heated, its temperature rises as the molecules gain kinetic energy, but temperature is a measure of the *average* kinetic energy of the molecules. Thus, some molecules have much more kinetic energy than others. Indeed, some of the molecules have enough kinetic energy to break their intermolecular interactions completely and enter the gas or vapor state in a process known as ***evaporation***, or ***vaporization***. If the container is open, the liquid evaporates, but if it is closed, the concentration of molecules in the vapor reaches a point where some of the vapor undergoes ***condensation***. When the rate of vaporization equals the rate of condensation, the system reaches equilibrium. The pressure of vapor (gas) in equilibrium with the liquid at any temperature is known as the ***vapor pressure*** of the liquid at that temperature. Vapor pressures increase with temperature because the fraction of molecules with sufficient kinetic energy to break away increases as the temperature rises. Vapor pressures also depend upon intermolecular interactions—**strong intermolecular interactions result in low vapor pressures**. The liquid and vapor reach a dynamic equilibrium when molecules evaporate and condense at the same rate, so the process is written as shown in Figure 7.21.

$$\text{liquid} \underset{\text{condensation}}{\overset{\text{vaporization}}{\rightleftharpoons}} \text{vapor}$$

Figure 7.21

7.6-7. Vapor Pressure of Water, Dew Point, and Relative Humidity

Table 7.4 gives the vapor pressure of water at various temperatures. Note that the vapor pressure increases with temperature, as it must for all substances. Weather reports normally indicate the partial pressure of water in the atmosphere in terms of the relative humidity or dew point. The relative humidity is 100% times the ratio of the observed partial pressure of water in the atmosphere to the vapor pressure of water at that temperature. The dew point is the temperature at which the atmospheric water would begin to condense, i.e., the temperature at which the vapor pressure of H_2O equals its partial pressure in the atmosphere.

EXAMPLE:

For example, consider a day on which the temperature is 25 °C and the partial pressure of H_2O is 12.8 torr. We note from Table 7.4 that the vapor pressure of water is 12.8 torr at 15 °C, so 15 °C is the dew point. The vapor pressure of water at 25 °C is 23.8 torr, so:

$$\text{relative humidity} = \left(\frac{12.8}{23.8}\right)(100\%) = 53.8\%$$

T (°C)	**P (torr)**		**T (°C)**	**P (torr)**
0	4.6		50	92.5
5	6.5		55	118.0
10	9.2		60	149.4
15	12.8		65	187.5
20	17.5		70	233.7
25	23.8		75	289.1
30	31.8		80	355.1
35	41.2		85	433.6
40	55.3		90	525.8
45	71.9		95	633.9

Table 7.4: Vapor Pressure of Water at Various Temperatures

7.6-8. Graph of Liquid-Vapor Equilibrium

The vapor pressure of a compound at a given temperature depends upon the strengths of its intermolecular interactions. **Compounds with stronger intermolecular interactions have lower vapor pressures than those that interact only weakly** because stronger interactions favor the more condensed state. Figure 7.22 shows the vapor pressure of CCl_4 and H_2O as a function of temperature. From the graph, we can see that the vapor pressure of CCl_4 is 760 torr at 77 °C, while H_2O must be heated to 100 °C to obtain the same vapor pressure. We also note that the vapor pressure of H_2O is less than that of CCl_4 at every temperature, so the intermolecular interactions are stronger in H_2O. Although the dispersion forces are greater in CCl_4, water also has dipolar and hydrogen bonding forces, which results in its relatively low vapor pressure.

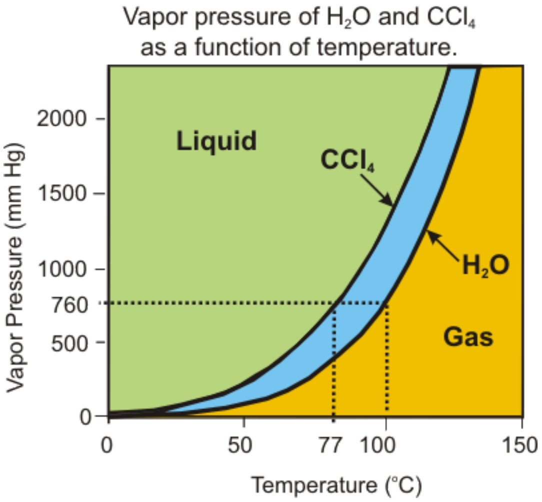


Figure 7.22: Vapor Pressure of CCl_4 and H_2O as a Function of Temperature Both substances are liquids at temperatures and pressures in the green region and both are gases at conditions in the orange region. CCl_4 is a gas while H_2O is a liquid in the blue region.

7.6-9. Boiling Points

Molecules with sufficient kinetic energy escape into the gas phase if they are on the surface of the liquid, but what about those that are not on the surface? The highly energetic molecules in the bulk of the liquid also attempt to escape into the gas by aggregating into bubbles, but the bubbles cannot withstand pressures greater than the vapor pressure of the gas at that temperature, so the bubbles cannot form if the external pressure exceeds the vapor pressure. However, the bubbles are sustained at the temperature where the vapor pressure of the liquid equals the external pressure, so we define the ***boiling point*** as that temperature at which the vapor pressure equals the external pressure. A liquid can be made to boil at other temperatures by reducing the external pressure to the vapor pressure of the liquid at that temperature, so Table 7.4 and Figure 7.22 can also be viewed as the boiling points as a function of pressure. Thus, the boiling point of water at 4.6 torr is 0 °C, and at 23.8 torr, it is 25 °C.

Typically, substances are boiled in a container open to the atmosphere, so the external pressure is 1 atm, and it is this boiling point that is assumed when a boiling point is given without reference to a pressure. We define the ***normal boiling point*** as the boiling point at 1 atm pressure. Whenever the boiling point of a substance is given without reference to an external pressure, it is assumed to be the normal boiling point. The normal boiling point of water is 100 °C.

7.6-10. Normal Boiling Points and Intermolecular Interactions

The higher the boiling point of a substance, the stronger are its intermolecular interactions.

Normal boiling points are good indicators of relative strengths of intermolecular forces because molecules with stronger intermolecular interactions have higher normal boiling points. For example, dispersion forces are the only intermolecular forces acting in the halogens and noble gases, and the fact that their normal boiling points increase with molar mass (Figure 7.23) is strong support for our conclusion that dispersion forces increase with molar mass. Fluorine is a gas at room temperature (boiling point = 85 K), while the much larger iodine molecule is a solid at room temperature (boiling point = 457 K). Helium has the weakest intermolecular interaction of any substance and the lowest boiling point (4 K).

It is more difficult to quantify dipolar interactions because they never occur in the absence of dispersion forces. However, the dispersion forces in CO and N_2 should be very similar because they are isoelectronic (they have the same number of valence electrons) and have the same molar mass, but CO is polar while N_2 is not. The normal boiling points are 77 K for N_2 and 81 K for CO, so the impact of the dipole is not very great in this case. The difference between F_2 and HCl, which have very similar molar masses, is more dramatic. The boiling point of polar HCl is over 100 K higher than that of nonpolar F_2 even though the molar mass of HCl is slightly less.

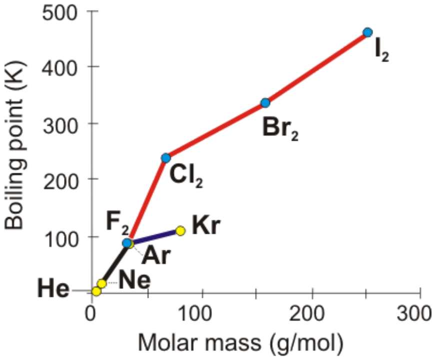


Figure 7.23: Boiling Points of the Halogens and the Noble Gases

Hydrogen bonding is a relatively strong interaction, and molecules that interact through hydrogen bonds have unusually high boiling points. The case of the boiling points of the hydrides of Groups 4, 5, 6, and 7 is considered in Figures 7.24a, 7.24b, 7.24c, and 7.24d.

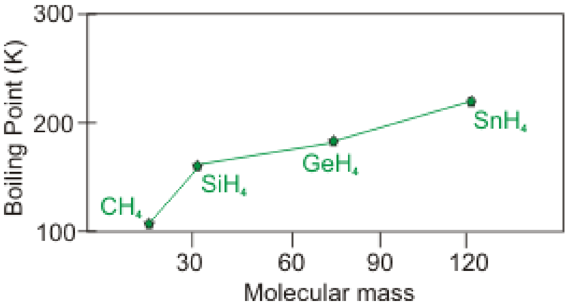


Figure 7.24a: Boiling Points of the Group 4 Hydrides as a Function of Molar Mass
Group 4A: None of the hydrides of Group 4A exhibit hydrogen bonding, so their boiling points decrease as their molar masses decrease.

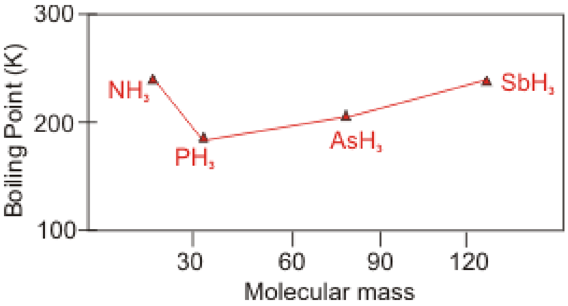


Figure 7.24b: Boiling Points of the Group 5 Hydrides as a Function of Molar Mass
Group 5A: Dispersion forces are the main differences between the intermolecular forces of SbH_3, AsH_3, and PH_3, so their boiling points decrease with decreasing molar mass. However, NH_3 exhibits hydrogen bonding, so its high boiling point is much higher than would be predicted based on the boiling points of the other members of the group.

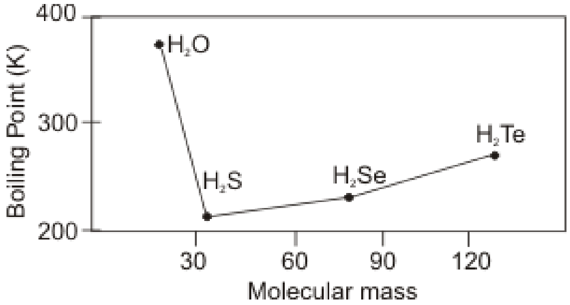


Figure 7.24c: Boiling Points of the Group 6 Hydrides as a Function of Molar Mass
Group 6A: Water can hydrogen bond through two hydrogen atoms. Consequently, its boiling point is much higher than that of H_2S, which has stronger dispersion forces. Based solely on molar mass, water would be predicted to boil around 200 K rather than 373 K. Thus, water would be a gas rather than a liquid at normal conditions on Earth if it were not for the hydrogen bond.

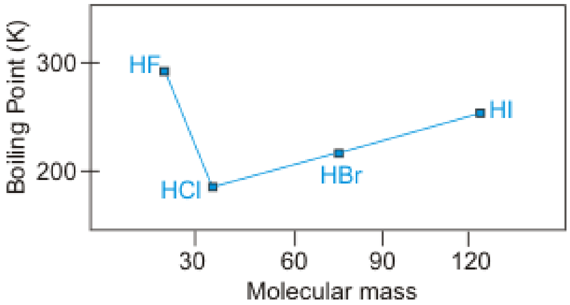


Figure 7.24d: Boiling Points of the Group 7 Hydrides as a Function of Molar Mass
Group 7A: Note that HF exhibits hydrogen bonding, but, based on the above graph, HCl does not. Chlorine is electronegative enough, but it is too large.

7.6-11. Predicting Relative Boiling Points Exercise

EXERCISE 7.11:

Indicate the molecule with the higher boiling point in each pair.

N_2	CH_2Cl_2	CS_2
CO	CF_4	CO_2

7.6-12. Critical Point

Liquid-vapor equilibria, like the one shown for CCl_4 and H_2O in Figure 7.22, are established in closed containers (the liquid would evaporate before establishing equilibrium in an open container). However, as the liquid-vapor equilibrium is heated, the density of the liquid decreases, while the density of the gas increases. At a temperature known as the ***critical temperature***, T_c, the densities are the same, there is no longer a boundary between the two phases, and the liquid-vapor line ends. The pressure at this point is called the ***critical pressure***, P_c. The point established by the critical temperature and pressure is called the ***critical point***. Thus, the critical temperature is the highest temperature at which the liquid phase can exist, and the critical pressure is the pressure required to liquefy a gas at the critical temperature. The **critical temperature is also a function of intermolecular forces and increases in the same manner as the boiling point**. Above the critical point, the substance is neither a gas nor a liquid and has properties of both phases. Under these conditions, the substance is a ***supercritical fluid***.

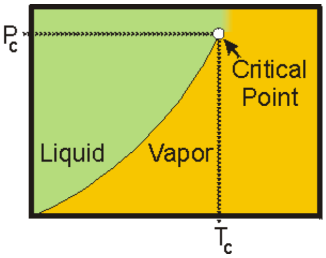


Figure 7.25

Solid-Vapor Equilibria

7.6-13. Solid-Vapor Equilibria

Under certain conditions, the vapor and solid states are in equilibrium. ***Sublimation*** is the process in which a solid is converted directly to a gas. The reverse process is called ***deposition***. Ice sublimes slowly, which is why snow can disappear without melting when the temperature does not rise above 0 °C. A dynamic equilibrium is established when the rate of sublimation equals the rate of deposition.

Figure 7.26

Dry ice, which is solid CO_2, does not exist as a liquid at pressures less than 5.1 atm, so it does not melt at 1 atm. Consequently, dry ice sublimes rapidly at room conditions. Figure 7.27 shows the temperatures and pressures at which the solid $\rightleftharpoons$ vapor equilibrium is established. Increasing the temperature increases the pressure of vapor above a solid, i.e., it causes the solid to sublime. Increasing the pressure of the gas at a point on the line causes more solid to deposit.

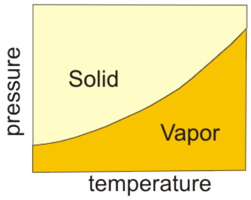


Figure 7.27: Sublimation Pressure as a Function of Temperature

Phase Diagrams

7.6-14. Phase Diagram of Water

A ***phase diagram*** shows the stable phases of a substance as a function of temperature and pressure. For example, consider the phase diagram of water shown in Figure 7.28. The lines separating the states represent the equilibria discussed in the previous sections.

- **Point A** is on the solid $\rightleftharpoons$ liquid line. The pressure is 1 atm, or 760 torr, so the temperature (0 °C) is called the normal melting point, or simply the melting point. Increasing the pressure at point A moves the system into the liquid region (melts the solid), so liquid water is more dense than ice (the reason ice floats).
- **Point B** is the ***triple point***, which is the temperature and pressure at which all three states of matter coexist. The triple point of water is 0.0098 °C and 4.58 torr (0.006 atm). Reducing the pressure at this point would cause the ice water to boil.
- **Point C** represents room conditions ($P = 760$ torr and $T = 298$ K (25 °C)). It is well within the liquid range for water, consistent with water being a liquid under these conditions. However, in a closed container there would also be 24 torr (0.031 atm) of vapor above the liquid. If the pressure over the liquid were reduced to 24 torr at this temperature, the water would boil.

- **Point D** is on the liquid $\rightleftharpoons$ vapor line. The pressure is 760 torr, so the temperature (100 °C) is the normal boiling point. Increasing the temperature or decreasing the pressure drives the system into the vapor region, while decreasing the temperature or increasing the pressure of vapor causes steam to condense.
- **Point E** is the critical point. The critical temperature is $T_c = 374$ °C, and the critical pressure is $P_c = 218$ atm. Water is a supercritical fluid above this point.

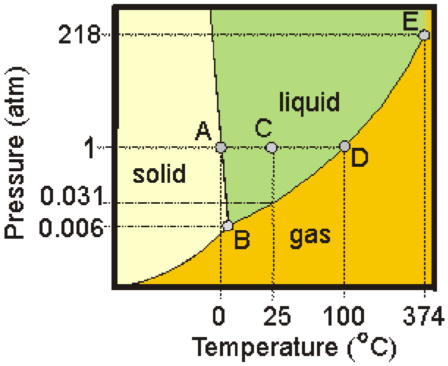


Figure 7.28: Phase Diagram of Water The above phase diagram shows how the state of matter of water varies with conditions of temperature and pressure. Water is a solid in the yellow region, a liquid in the green region, and a gas or vapor in the orange region. The temperatures and pressures are not to scale.

7.6-15. Phase Diagram of Carbon Dioxide

Consider the phase diagram of CO_2 shown in Figure 7.29.

- **Point A** is on the solid $\rightleftharpoons$ vapor line and is the point where the partial pressure of the vapor in equilibrium with the solid is 1 atm. Thus, CO_2 can be liquified at 1 atm by reducing its temperature to −78 °C.
- **Point B** is the triple point (5.1 atm and −56 °C).
- **Point C** represents room conditions. CO_2 is a gas under these conditions.
- **Point D** shows that CO_2 can be liquified at room temperature (25 °C) by increasing the pressure to 67 atm.
- **Point E** is the critical point. The critical temperature is $T_c = 31$ °C, and the critical pressure is $P_c = 73$ atm. Supercritical CO_2 is used as a dry cleaning solvent.

The slope of the solid $\rightleftharpoons$ liquid line indicates that the solid is more dense than the liquid. Finally, carbon dioxide does not have a normal boiling point because the liquid does not exist at pressures below 5.1 atm (the triple point pressure).

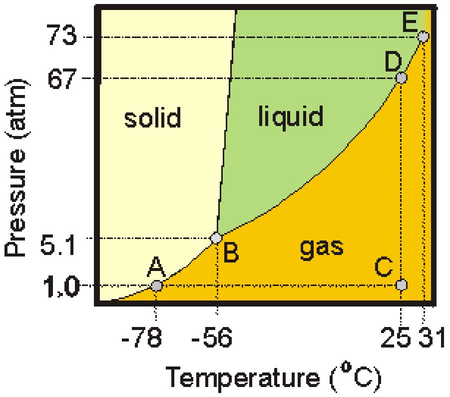
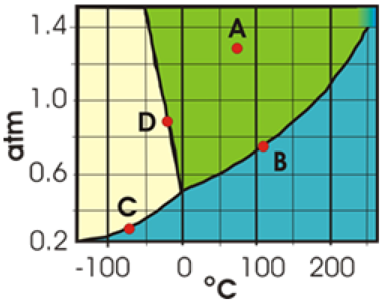


Figure 7.29: Phase Diagram of Carbon Dioxide

7.6-16. Phase Diagram Exercise

EXERCISE 7.12:

In the following exercises, give all temperatures to the nearest 25 °C and all pressures to the nearest 0.1 atm.



What is the normal boiling point of X in °C?

_______________ °C

What is the melting point of X in °C?

_______________ °C

What is the temperature in °C at the triple point?

_______________ °C

What is the pressure in atm at the triple point?

_______________ atm

What state of matter is X in at point A?
- solid
- liquid
- gas

What is the most dense state of X?
- solid
- liquid
- gas

What is the critical temperature of X in °C?

_______________ °C

What is the critical pressure of X in atm?

_______________ atm

Indicate the phase change that is caused by each of the following.

increasing T at point B
- vaporization
- condensation
- sublimation
- deposition
- melting
- freezing

increasing T at point C
- vaporization
- condensation
- sublimation
- deposition
- melting
- freezing

increasing P at point D
- vaporization
- condensation
- sublimation
- deposition
- melting
- freezing

7.7 Exercises and Solutions

Links to view either the end-of-chapter exercises or the solutions to the odd exercises are available in the HTML version of the chapter.

Chapter 8 – Solids

Introduction

Solids are characterized by an orderly arrangement of their particles. If the order is over short distances only (local order), the solid is an ***amorphous solid***. Charcoal and glass are amorphous solids. If the order exists throughout the entire solid (long range order), the solid is said to be a ***crystalline solid***. Table salt and sugar are two common examples of crystalline solids. This chapter is devoted to the study of crystalline solids. Even a small crystal contains millions and millions of particles. Thus, studying the solid state could be a formidable task.

8.1 Unit Cells

Introduction

However, the long range order that characterizes crystalline solids means that there is a small repeat unit, called the unit cell, that can be used to generate the entire crystal. Our study is simplified because, instead of studying the positions of the enormous number of particles that constitute the entire crystal, we need study only the small number of particles that comprise a unit cell. In this section, we define the unit cell and discuss how it is packed with atoms.

Objectives

- Define *unit cell* and *lattice*.

8.1-1. Definition

The unit cell is the smallest repeat unit of the crystalline lattice that generates the entire lattice with translation.

Crystalline solids are orderly, repeating, 3-D arrays of particles, which can be atoms, ions, or groups of atoms, such as polyatomic ions or molecules. The pattern of the array is called the crystal ***lattice***, and the individual positions are called **lattice sites**. The simplest portion of the lattice that makes up the repeating unit is called the ***unit cell***. When the unit cell is repeated in all three directions, it generates the entire crystalline lattice.

The figure shows two different but equivalent unit cells in a two-dimensional array. One unit cell consists of four A's on the corners and a B in the face center, while the other has B's on the corners with an A in the center. Translation by the length of one of the cell edges of either cell in any of the four directions produces an adjacent cell. Continued operations of translation generate the complete crystalline lattice. A three-dimensional lattice is formed by translation of a three-dimensional unit cell in three directions.

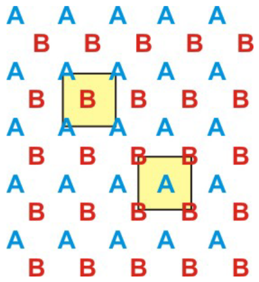


Figure 8.1: Definitions of Lattice and Unit Cell The unit cell is the smallest repeat unit of the crystalline lattice that generates the entire lattice with translation. The figure shows two different but equivalent unit cells highlighted in yellow.

8.1-2. Unit Cell Parameters

All unit cells can be uniquely characterized by their three edge lengths, (a, b, and c) and the angles (α, β, and γ) defined in Figure 8.2. They must be six-sided polygons that completely fill space; that is, no holes are present when the unit cell polygons are packed in three dimensions. As a result, there are only seven different types of unit cells. We limit our discussion to the simplest type of unit cell, the cubic unit cell. The cubic unit cell is one in which

$a = b = c$ and $\alpha = \beta = \gamma = 90°$. There are three types of cubic unit cells that differ only in the manner in which the particles fill the cell.

- simple cubic (sc)
- body-centered cubic (bcc)
- face-centered cubic (fcc)

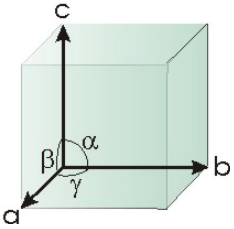


Figure 8.2: Parameters that Define the Unit Cell Type

8.2 Cubic Unit Cells and Metallic Radii

Introduction

Unit cells must be six-sided polygons that completely fill space (no space between unit cells), and there are only seven types of unit cells that fulfill this requirement. However, our discussion is limited to only one type, the cubic unit cell.

Objectives

- Distinguish between simple, body-centered, face-centered cubic unit cells.
- Determine atomic radii from the unit cell edge length or the edge length from the atomic radii.

8.2-1. The Cubic Unit Cells

There are three cubic unit cells that differ in how the particles fill the cube. In each cubic unit cell, the same atom-type occupies each of the eight corners of the cube. The unit cell type is then dictated by where else in the unit cell that atom-type is found. Note that in the images below, all spheres represent the same atom type—the color differences are used only to distinguish different positions in the cell. There are three different types of cubic unit cells.

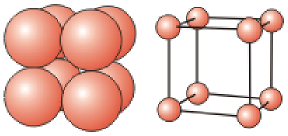
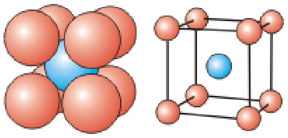
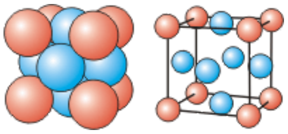
Type of Cubic Unit Cell	Location of Identical Particles	Image
simple cubic (sc)	on the corners but nowhere else in the cell	
body-centered cubic (bcc)	on the corners and in the center of the cell	
face-centered cubic (fcc)	on the corners and in the centers of the six faces of the cell	

Table 8.1: Cubic Unit Cells

8.2-2. Metallic or Atomic Radii

Atoms are not hard spheres with distinct boundaries, so their sizes are not determined directly. However, the positions of the atoms in a solid can be determined by x-ray diffraction, and the sizes of the atoms are inferred from those distances. In this method, the radius of an atom is determined from the unit cell edge length (a), which is determined from the location of the atoms, and the assumption that the atoms touch as shown in Figures 8.3a, 8.3b, and 8.3c.

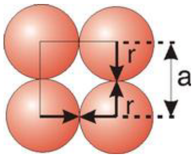


Figure 8.3a: Atom Contact in Simple Cubic Unit Cells

$$2r = a \qquad \textbf{sc}$$

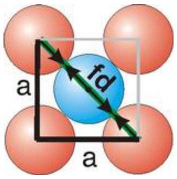


Figure 8.3b: Atom Contact in Face-Centered Cubic Unit Cells

$$\begin{aligned} fd &= 4r \\ fd^2 &= a^2 + a^2 \qquad \textbf{fcc} \\ (4r)^2 &= 2a^2 \end{aligned}$$

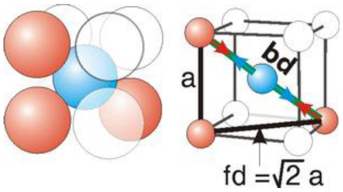


Figure 8.3c: Atom Contact in Body-Centered Cubic Unit Cells

$$\begin{aligned} bd &= 4r \\ bd^2 &= fd^2 + a^2 \qquad \textbf{bcc} \\ (4r)^2 &= 2a^2 + a^2 = 3a^2 \end{aligned}$$

Setting the edge length equal to $2r$ in the sc unit cell, and applying the Pythagorean theorem to the triangles shown in Figures 8.3a, 8.3b, 8.3c, we obtain the relationships between the atomic radius (r) of the atom and the edge length of the unit cell (a) given in Equation 8.1.

$$\begin{aligned} r &= \frac{a}{2} \quad \text{(sc)} \\ r &= \frac{\sqrt{2}a}{4} \quad \text{(fcc)} \qquad \text{Relationship of Atomic Radii and Unit Cell Edge Lengths} \qquad (8.1) \\ r &= \frac{\sqrt{3}a}{4} \quad \text{(bcc)} \end{aligned}$$

The radius obtained from the structure of a metallic solid is referred to as either the ***metallic radius*** or the ***atomic radius***.

8.2-3. Determining an Atomic Radius Exercise

EXERCISE 8.1:

γ-Iron adopts a fcc crystal structure with an edge length of 3.56 Å. What is the atomic radius of iron inferred from this structure?

$r =$ ______________ Å

8.3 Unit Cell Stoichiometry

Introduction

The number of atoms or ions in a unit cell of a compound does not have to be the same as the number of atoms in the formula of the compound, but the stoichiometry of the unit cell must be the same as the stoichiometry of the compound. Thus, a unit cell of NaCl may have many sodium and chloride ions, but the number of each ion must be the same because their stoichiometric ratio is 1:1 in the compound. However, when determining the unit cell stoichiometry, you cannot simply count all of the atoms or ions that form the unit because many of the particles may be part of more than one unit cell. In this section, we explain how to determine the stoichiometry of a unit cell.

Objectives

- Determine the fraction of an atom that lies in a unit cell given the lattice site occupied by the atom.
- Determine the number of atoms, molecules, or ions in a unit cell.

8.3-1. Unit Cells Share Particles

A particle in a face contributes 1/2 particle to each unit cell, one on an edge contributes 1/4 to a unit cell, and one on a corner contributes 1/8 per cell.

The structure of the unit cell is useful for understanding the stoichiometry of the compound. The stoichiometry of a compound can be determined by considering the number of particles (atoms, molecules, or ions) that make up the unit cell. However, most atoms in a unit cell are shared by several unit cells, so the contribution of a particle to any one unit cell is usually less than one.

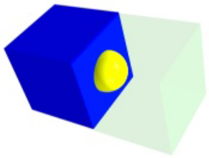


Figure 8.4a: Particle Contributions to Unit Cell Stoichiometry A particle on a **face center** is shared by two unit cells, so it contributes 1/2 particle to each.

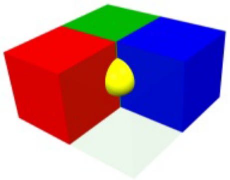


Figure 8.4b: Particle Contributions to Unit Cell Stoichiometry A particle on an **edge** is shared by four unit cells, so it contributes 1/4 particle to each.

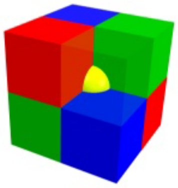


Figure 8.4c: Particle Contributions to Unit Cell Stoichiometry A particle on a **corner** is shared by eight unit cells, so it contributes 1/8 particle to each.

8.3-2. Contributions per Unit Cell

The particles on the eight corners combine to contribute 1 particle to a unit cell. Particles in the six face centers combine to contribute 3 particles to a unit cell. Those on twelve edges combine to contribute 3 particles per unit cell.

Atoms that are entirely within a unit cell each contribute a full atom to the cell stoichiometry, but the atoms in the faces, corners, and edges are shared by more than one unit cell, and the number of atoms they contribute to each unit cell is given below.

$$\frac{\text{8 corners}}{\text{unit cell}} \times \frac{\text{1 atom}}{\text{8 corners}} = \frac{\text{1 atom}}{\text{unit cell}}$$

Atoms located on the *corners* of the unit cell contribute 1 atom per unit cell.

$$\frac{\text{6 faces}}{\text{unit cell}} \times \frac{\text{1 atom}}{\text{2 faces}} = \frac{\text{3 atoms}}{\text{unit cell}}$$

Atoms located on the *faces* of the unit cell contribute 3 atoms per unit cell.

$$\frac{\text{12 edges}}{\text{unit cell}} \times \frac{\text{1 atom}}{\text{4 edges}} = \frac{\text{3 atoms}}{\text{unit cell}}$$

Atoms located on the *edges* of the unit cell contribute 3 atoms per unit cell.

8.3-3. Determining the Number of Atoms in a Unit Cell Exercise

EXERCISE 8.2:

How many atoms are in each of the three cubic unit cells?

sc = ______________ bcc = ______________ fcc = ______________

8.4 Coordination Number and Geometry

Introduction

The ***coordination number*** (CN) is the number of nearest neighbors of a given particle in the crystal lattice. It determines the nature of the bonding in a crystal. The most common coordination numbers are 4, 6, 8, and 12.

Objectives

- Define the term coordination number.
- Determine the coordination number of an atom or ion in a unit cell.

8.4-1. Common Coordination Numbers and their Geometries

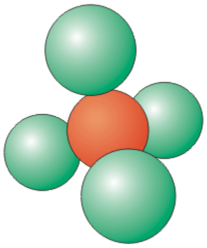


Figure 8.5a: Coordination Number of 4

Four atoms around a central atom are located at the corners of a tetrahedron.

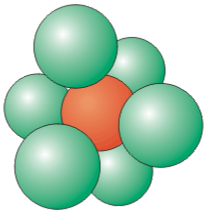


Figure 8.5b: Coordination Number of 6

Six atoms around a central atom are located at the corners of an octahedron. An atom on the corner of a simple cubic unit cell has a coordination number of six.

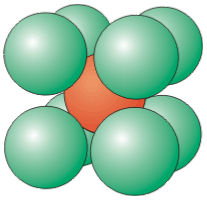


Figure 8.5c: Coordination Number of 8

Eight atoms around a central atom are located at the corners of a cube. The atom in the center of a body-centered unit cell has a coordination number of eight.

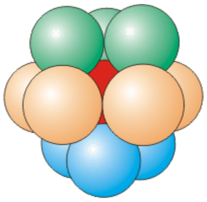


Figure 8.5d: Coordination Number of 12

Each atom in a face-centered cubic unit cell has a coordination number of 12. The 12 particles, which make up the *coordination sphere* of the red particle lie in three planes. The three planes can be seen in either of two ways:

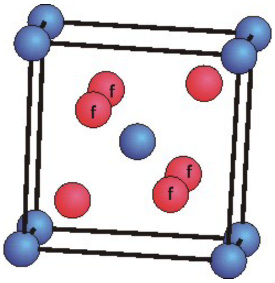
- The top and bottom planes each have three particles, while the plane in the middle contains the central particle and six others forming a belt around it.
- The top and bottom planes each have four particles, while the plane in the middle contains the central particle and four others. The central plane is the face of a face-centered cube.

The packing of equal sized particles shown for the coordination number of twelve represents the tightest possible packing arrangement and is frequently described as the *closest packed* geometry.

8.4-2. Coordination Number Exercise

EXERCISE 8.3:

The mineral rutile is an oxide of titanium that crystallizes in the tetragonal ($a = b > c$, $\alpha = \beta = \gamma = 90°$) unit cell. Use the unit cell shown below to determine the following for titanium oxide.



Ti atoms are blue and O atoms are red. The four O atoms marked "f" are in the cell face, but the other two are in the cell body.

number of Ti atoms in the uc = ________________

number of O atoms in the uc = ________________

simplest formula of titanium oxide = ________________

coordination number of Ti = ________________

8.5 Density and Packing Efficiency

Introduction

It is impossible to pack spheres without introducing some ***void space*** (space that is not occupied). How well the atoms pack a unit cell depends upon the unit cell type and is given by the packing efficiency of the unit cell. Solids with tightly packed unit cells are more dense than those with low packing efficiencies. In this section, we examine the packing efficiencies of the cubic unit cells and show how to determine the density of a solid from its crystal structure.

Objectives

- Determine relative packing efficiencies of cubic unit cells.
- Determine the density of a solid from its crystal structure.

8.5-1. Density

Density is the mass-to-volume ratio of a substance.

$$d = \frac{\text{mass of substance}}{\text{volume of substance}} \qquad \text{Density} \qquad (8.2)$$

Densities of metals range from 0.53 g/cm^3 for lithium to 22.65 g/cm^3 for iridium.

8.5-2. Packing Efficiency

Packing efficiency is the fraction of the unit cell that is occupied by particles. Closest packed spheres pack with a packing efficiency of 74%.

Spheres cannot be packed without creating some void space, but the amount of void space depends upon how well they are packed. ***Packing efficiency*** (PE) is that fraction of the unit cell volume that is actually occupied by particles, not void space.

Thus, the packing efficiency of a unit cell is

$$
\begin{aligned}
\text{Packing Efficiency} &= \frac{\text{volume of atoms}}{\text{volume of unit cell}} \times 100\% \\
\text{PE} &= \frac{N \times (4/3)\pi r^3}{a^3} \times 100\%
\end{aligned}
\tag{8.3}
$$

- a = the length of a side of the unit cell, so a^3 is the volume of the unit cell.
- r = the radius of the atoms that occupy the unit cell, so $(4/3)\pi r^3$ is the volume of a single atom in the unit cell.
- N = the number of atoms in the unit cell, so $N(4/3)\pi r^3$ is the volume occupied by all of the atoms in the unit cell.

The unit cell size (a) is directly proportional to the atom size (r), so one can be defined in terms of the other and then canceled in the above expression. Consequently, the packing efficiency depends only upon the cell type, not its size. As shown in the next sections, the relationship between a and r depends only upon the unit cell type.

8.5-3. Packing in Simple Cubes

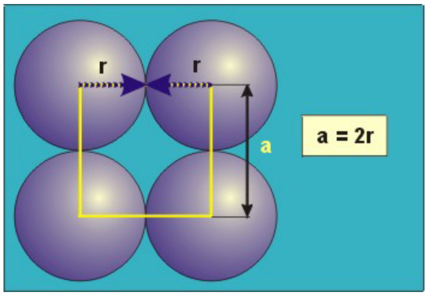


Figure 8.6

In the *simple cubic unit cell*, the spheres touch along the cell edge. Consequently, the edge length is two atomic radii ($a = 2r$).

The properties of the simple cubic unit cell:

- $r = 0.5a$
- N = 1 atom/unit cell
- packing efficiency = 52%
- coordination number = 6

8.5-4. Packing in Face-Centered Cubes

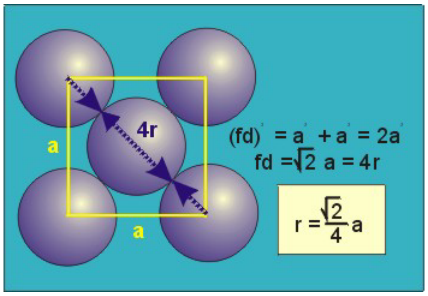


Figure 8.7

Particle contact in the *face-centered cubic unit cell* is along the face diagonal (*fd*). The face diagonal is four atomic radii ($fd = 4r$) and is related to the unit cell edge length (a) by the Pythagorean theorem.

The properties of the face-centered cubic unit cell:

- $r = \dfrac{\sqrt{2}}{4}a = 0.354a$
- $N = 4$ atoms/unit cell
- packing efficiency = 74%
- coordination number = 12

8.5-5. Packing in Body-Centered Cubes

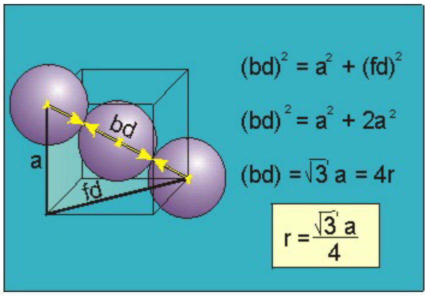


Figure 8.8

For the *body-centered cubic unit cell*, the spheres make contact along the body diagonal (bd), which is four atomic radii (each yellow arrow is one atomic radius), i.e., $bd = 4r$. The body diagonal is related to the face diagonal (fd) and the cell edge (a) by the Pythagorean theorem. The relationship between the cell edge and the face diagonal was derived in the discussion of the fcc unit cell.

The properties of the body-centered cubic unit cell:

- $r = \dfrac{\sqrt{3}}{4}a = 0.433a$
- $N = 2$ atoms/unit cell
- packing efficiency = 68%
- coordination number = 8

8.5-6. Packing Efficiency and Coordination Number

As shown in the previous sections, the packing efficiency of a unit cell depends only on the cell type; it is independent of edge length and atomic radius because both cancel in the calculation. Table 8.2 gives the packing efficiencies of the cubic unit cells and coordination numbers of the atoms in them. As might be expected, the packing efficiency increases as the number of atoms in the unit cell and the number of atoms that are packed around each atom (coordination number) increases.

Lattice Type	**Packing Number**	**Coordination Efficiency**
Simple	52%	6
Body-centered	68%	8
Face-centered	74%	12

Table 8.2: Packing Efficiencies and Coordination Numbers of Cubic Lattices

8.5-7. Packing Efficiency and Crystal Properties

Table 8.3 shows the unit cell types, metallic radii, and densities of selected metals that adopt cubic unit cells. Almost half of the volume of a sc unit cell is void space, so the sc unit cell is not a favorable way to pack and metals do not generally crystallize in sc lattices. Indeed, the only known example of a metal adopting the sc unit cell is a form of polonium. The densities of the Group 1A elements are all quite low because their atoms are not very dense (they have the greatest volume and smallest mass of any atom in their period) and because they pack in the less efficient bcc lattice. The impact of packing efficiency on the density can be seen by comparing K and Ca, which are next to one another in the periodic chart and have nearly identical metallic radii. Ca is almost 60% more dense because it crystallizes in the more efficient fcc unit cell. The effect can also be seen by comparing two forms of iron. Iron normally crystallizes with a bcc structure known as α-iron, but it also can be made to adopt a more efficiently packed fcc structure called γ-iron by adding small amounts of carbon and manganese or nickel and chromium. The tighter packing of γ-iron makes it so corrosion-resistant that it is known as stainless steel.

Metal	**Unit Cell**	**Radius** (Å)	**Density (g/cm^3)**
Ag	fcc	1.44	10.5
Al	fcc	1.43	2.70
Au	fcc	1.46	19.3
Ba	bcc	2.48	3.59
Ca	fcc	2.35	1.55
Cu	fcc	1.28	8.96
K	bcc	2.35	0.86
Li	bcc	1.55	0.53
Na	bcc	2.35	0.97
Ni	fcc	1.25	8.90
Pb	fcc	1.75	11.35
Pt	fcc	1.39	21.45
Rb	bcc	2.48	1.53
Sr	fcc	2.15	2.6

Table 8.3: Unit Cell Type, Metallic Radii, and Densities of Selected Metals with Cubic Unit Cells

8.5-8. Exercise on Determining Packing Efficiency

EXERCISE 8.4:

Rhodium (Rh, M_{m} = 102.9 g/mol) crystallizes in a face-centered cubic unit cell that is 3.79 Å on a side. Determine the atomic radius, packing efficiency, and density of the unit cell based on these data. See Section 8.5-4. for help with fcc unit cell packing. Express your answers with three digits.

The atomic radius of Rh is $r =$ ______________ Å

The volume of one Rh atom is $V =$ ______________ $Å^3$

The number of Rh atoms present in one unit cell is $n =$ ______________

The volume of all of the atoms in the unit cell is $V =$ ______________ $Å^3$

The volume of the unit cell is $V =$ ______________ $Å^3$

The packing efficiency of the cell based on these numbers is PE = ______________ %

The mass of all atoms in the unit cell is $m =$ ______________ g

The volume of the unit cell in cm^3 is V = ______________ cm^3

The density of Rh derived from these data is d = ______________ g/cm^3

8.6 Band Theory of Simple Metals

Introduction

The ***metallic bond*** is the interaction that holds metal atoms in the solid. The strength of the metallic bond varies considerably depending upon the metal. Consequently, metals vary from very high-melting substances such as iron (mp = 1535 °C) to low-melting substances such as mercury (mp = −39 °C).

Metals have low ionization energies and readily lose their valence electrons to become positively charged ions. In a metallic bond, valence electrons from all of the metal atoms in the solid are *delocalized* over the entire metal. The metal cations are immersed in the sea of valence electrons, and the electrostatic force exerted between the cations and the surrounding electrons holds the positively charged metal ions in place.

Bonding and electrical conduction in metals is best understood in terms of ***band theory***, which is the extension of molecular orbital theory (Section 6.5) to the very large number of atoms found in a metal.

Objectives

- Describe a metallic bond.
- Explain what is meant by an *energy band.*
- Define the *Fermi level* and identify it in a band diagram.
- Explain how a metal can be a conductor even when all of its valence orbitals are full.
- Define the *band gap.*
- Distinguish between a *valence band* and a *conduction band.*
- Distinguish between a metallic conductor, a semiconductor, and an insulator based on their band structures.

8.6-1. Introduction to Band Theory

The molecular orbital description of the delocalized electrons in metallic bonds provides a more complete picture of metallic bonding as well as an explanation for the electrical conductivity of metals. The explanation, which is called band theory, applies the concepts presented in the molecular orbital discussion in Chapter 6 to a very large number of orbitals. The orbitals in the solid are constructed in the same way as those in a molecule, but they apply to a crystal rather than a molecule, so they are called crystal orbitals rather than molecular orbitals. As the number of orbitals increases, the adjacent orbitals become more similar, and the resulting energy levels get closer together. In a piece of metal, the number of atoms and atomic orbitals in each crystal orbital is enormous (on the order of Avogadro's number), so the energy levels are so close that they can no longer be distinguished and the system is described in terms of energy bands rather than energy levels. The formation and properties of bands is the topic of this section.

8.6-2. Properties of Multi-Orbital Systems

Increasing the number of orbitals in a molecular orbital increases the energy spread of the molecular orbitals while decreasing the energy separation between adjacent orbitals.

Orbital X in Figure 8.9 has nine bonding interactions, while orbital A has only one. Each bonding interaction lowers the energy of the orbital, so X is at lower energy. Orbital Z has nine antibonding interactions, while orbital B has only one. Thus, Z is at a higher energy than B. We conclude that increasing the number of orbitals increases the energy difference between the highest and lowest energy orbitals; i.e., increases their energy spread ($\Delta E_2 > \Delta E_1$).

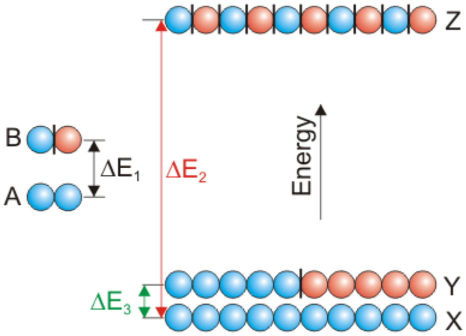


Figure 8.9: Energy Levels in Two- and Ten-Orbital Systems Only the two orbitals at lowest energy and the one at highest energy of the ten-orbital system are shown.

Orbital A is completely bonding, but orbital B is completely antibonding. They are very different types of orbitals, so their energies are very different. Orbital X has nine bonding interactions, while orbital Y has eight bonding interactions and one antibonding interaction. Orbitals X and Y are both strongly bonding, so they are close in energy.

8.6-3. The Definition of a Band

The energy levels in a metal are so close that they are represented by a band of energy.

As the number of orbitals increases, the energy spread of the molecular orbitals continues to increase, while the energy separation between adjacent levels continues to decrease. In a piece of metal, the number of atoms and orbitals is so large (on the order of Avogadro's number) that the energy levels are so close that they can no longer be distinguished. At this point, the energy levels are said to form an ***energy band***. Energy bands are represented by rectangles that show the spread in energy between the lowest and highest energy orbitals. Although the separation between levels is so small that discreet levels are not shown, they do exist and the electrons fill the levels in a band with the same rules as they do the levels in an atom (lowest energy, Pauli Exclusion Principle).

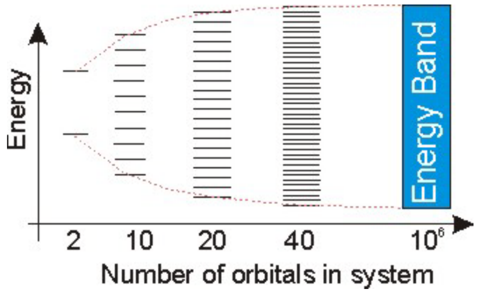


Figure 8.10: Band Formation The dotted lines represent the energy spread and show that the top and bottom energies begin to level off as the number of orbitals gets large.

8.6-4. Fermi Level

The highest-energy occupied level in a metal is called the Fermi level.

The electrons in a band occupy the lowest energy levels available, and their occupation is represented by shading the occupied portion of the band. The occupied level of greatest energy is called the ***Fermi level***. The band in Figure 8.11 is half-filled, so the Fermi level is the middle level of the band.

Metals conduct electricity when the electrons are free to move, but they are free only when there are empty orbitals into which they can move. A partially filled band like the one in the figure is formed when the atomic orbitals used to construct it are not full. Since the energy separation between adjacent levels in a band is so small, the separation between the highest energy filled orbitals and the lowest energy unfilled orbitals is nearly zero in a partially filled band. Thus, electrons near the Fermi level of a partially filled band can move easily into empty orbitals. Since these orbitals are delocalized over the entire metal, the electrons are free to move through the entire metal, and the metal conducts electricity. Metals with this band structure (partially filled bands) are called metallic **conductors**.

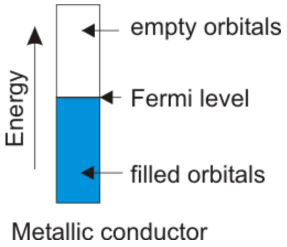


Figure 8.11: Band Structure for a Metallic Conductor Note: the shaded portion of the rectangle indicates the portion of the band that contains filled orbitals.

8.6-5. Valence Band, Conduction Band, and the Band Gap

The band gap is the energy separation between the valence and conduction bands.

Both occupied and unoccupied orbitals of a metal can combine to form bands. Electrons can move in bands that are not full, but they cannot move through a band that is full. The filled band at highest energy is occupied by valence electrons, so it is called the ***valence band***. The unfilled band of lowest energy is called the ***conduction***

band because it is the band in which electrons are free to move. The energy separation between the valence and conduction band is called the ***band gap***. As we show in the next section, the conductivity properties of the metal are determined by the magnitude of the band gap.

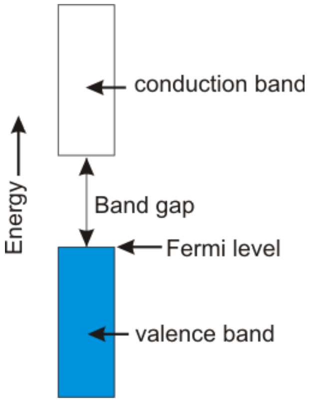


Figure 8.12: The Band Gap

8.6-6. Conductivity

Conductors have no band gap, semiconductors have moderate band gaps, and insulators have large band gaps.

The electrical conductivity properties of a metal depend upon its band gap.

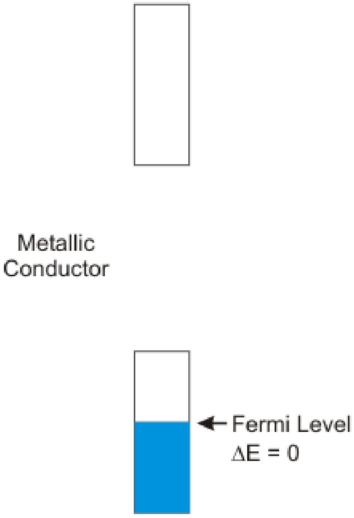


Figure 8.13

Metallic conductors have partially filled bands, so they have no band gap. Bands at higher energy are irrelevant to their conductivity.

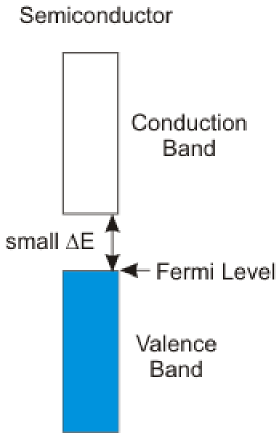


Figure 8.14

Semiconductors have band gaps that are not zero but are small enough that the conduction band can be populated at reasonable temperatures. The conductivity of semiconductors increases as the temperature is increased because the number of electrons in the conduction band increases as their thermal energy increases.

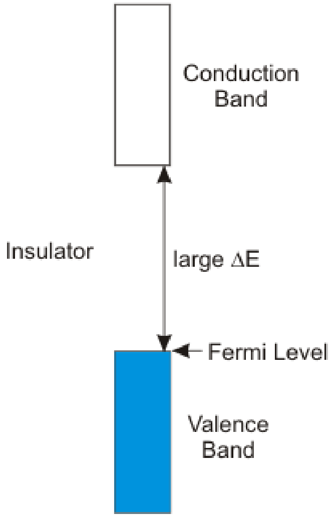


Figure 8.15

Insulators have band gaps that are so large that no electrons can occupy the conduction band at reasonable temperatures.

8.6-7. Band Overlap

A metal with filled orbitals can be a conductor if the bottom of a band formed from empty orbitals overlaps the top of the band formed from filled orbitals.

Metals with no unfilled orbitals can contain partially filled bands if the band formed from the filled atomic orbitals overlaps with a band formed from empty orbitals. This is the reason that metallic elements, such as zinc, that have no partially filled orbitals in their atoms can still be conductors. For example, Figure 8.16 shows the band structure of zinc. The filled 4s band and the unoccupied 4p band overlap, so the highest energy electrons in the 4s band move to lower energy in the 4p band to produce two partially filled bands. The partially filled bands make zinc a conductor.

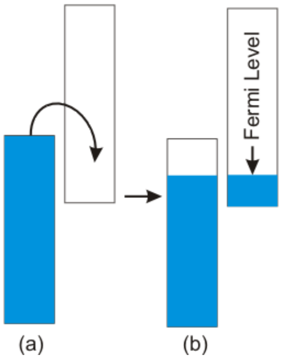


Figure 8.16: A Metallic Conductor Produced from Overlapping Bands

Partially filled bands can be formed in atoms with no partially filled sublevels if the band formed with filled atomic orbitals overlaps with one formed from empty atomic orbitals.

8.7 Ionic Solids and Ionic Radii

Introduction

The ionic bond (Chapter 4) is the interaction that holds the ions of an ionic substance in the solid state. In order to melt or break an ionic crystal, ionic bonds must be broken, and ionic bonds are usually quite strong. Consequently, ionic substances are typically hard and have high melting points, which means that they are typically solids at room conditions. However, the strength of an ionic bond depends upon the charge of the ions and their separation (Coulomb's Law). Thus, ionic compounds with small ions (small separation) that are highly charged have higher melting points than ionic compounds with large ions that carry lower charges. For example, the melting point of MgO (small ions with +2 and −2 charges) is 2852 °C, while that of CsI (large ions with +1 and −1 charges) is 626 °C. In this section, we examine the structure of some simple ionic compounds.

Objectives

- Describe the sodium chloride structure.
- Distinguish between the NaCl and CsCl structures.
- Determine the radius of an ion given the ionic radius of the other ion and the distance between the ions in a compound.

8.7-1. Ionic Radii

The distance between two adjacent ions in a crystal is equal to the sum of their ionic radii. For example, the distance between Li^{1+} and I^{1-} ions in a crystal of LiI is 2.96 Å, so we can write $r_{Li} + r_{I} = 2.96$Å. Ionic radii have been determined by examining many such distances. The ionic radii of the alkali metal ions (Group 1A) and the halide ions (Group 7A) are given in Table 8.4.

Cation	Radius (Å)
Li^{1+}	0.90
Na^{1+}	1.16
K^{1+}	1.52
Rb^{1+}	1.66
Cs^{1+}	1.81

Anion	Radius (Å)
F^{1-}	1.19
Cl^{1-}	1.67
Br^{1-}	1.82
I^{1-}	2.06

Table 8.4: Ionic Radii of Group 1A and 7A Ions

8.7-2. Ionic Radii Exercise

EXERCISE 8.5:

What is the ionic radius of Mg^{2+}, if the Mg–Cl distance in $MgCl_2$ is 2.53 Å?

the ionic radius of Cl^{1-} from Table 8.4 = ______________ Å

r_{Mg} = ______________ Å

8.7-3. LiI

Not all of the particles in an ionic solid are identical, but the same structural descriptions that are applied to metallic solids can be used to understand the crystal structure of many ionic compounds. For example, most of the alkali halides have a preference for a structure in which the anions pack in a face-centered cubic unit cell, as shown in Figure 8.17a, with the cations filling the void space as in Figure 8.17b.

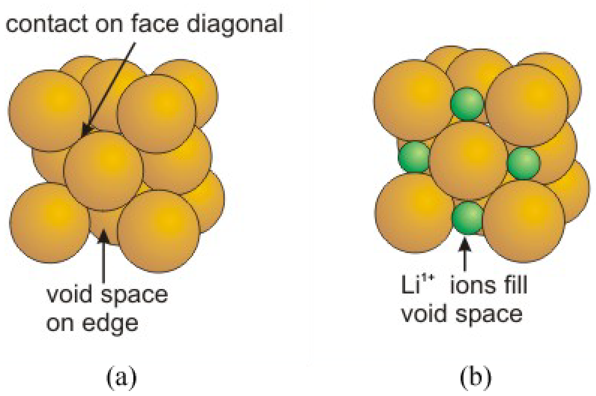


Figure 8.17

The three anions along a diagonal of a face touch in a fcc unit cell, but there is void space along each of the cell edges and in the body center and much smaller cations fill the space. Using geometry, we can calculate that to fill the void space perfectly, the radius of the cation should be a little less than half the radius of the anion ($r_{\mathrm{cation}} = 0.414 r_{\mathrm{anion}}$).

LiI nearly adopts the ideal structure ($r_{\mathrm{Li}}/r_{\mathrm{I}} = 0.44$) and has a very high packing efficiency. However, the Li^{1+} ions are slightly too large to fit into the holes, so the I^{1-} ions are pushed apart slightly, so they no longer make contact.

8.7-4. LiCl

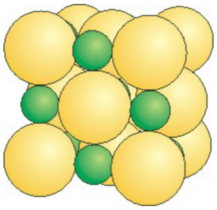


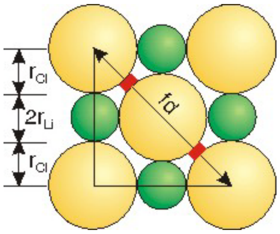
Figure 8.18: LiCl Unit Cell

Chloride ions are smaller than iodide ions, so their fcc arrangement has even smaller holes along the edge. Consequently, they must be pushed apart even farther to accommodate the Li^{1+} ions (Figure 8.18). The distance by which the chloride ions are separated is determined in the following exercise.

8.7-5. Packing Exercise

EXERCISE 8.6:

Use ionic radii ($r_{\mathrm{Li}} = 0.90$ Å; $r_{\mathrm{Cl}} = 1.67$ Å) and the figure to determine the void space (highlighted in red) between chloride ions in LiCl.



the unit cell edge is $a =$ ______________ Å

the face diagonal is $fd =$ ______________ Å

four chloride ionic radii = ______________ Å

the void space = ______________ Å

8.7-6. NaCl

Sodium chloride adopts the same structure type as lithium chloride. In fact, this structure type is called the sodium chloride structure, and LiCl is said to crystallize in the sodium chloride structure. In sodium chloride, the sodium cation is considerably larger than the ideal hole created by closest packed chloride anions. As shown in Figure 8.19, the chloride anions are moved even farther apart to accommodate the larger sodium ions. While this expansion of the packing in the unit cell lowers the packing efficiency, there is little energetic cost because each ion is still in direct contact with six ions of opposite charge. The major change in this expanded structure is that the like charges (anion-anion and cation-cation) are further separated, which is energetically favorable.

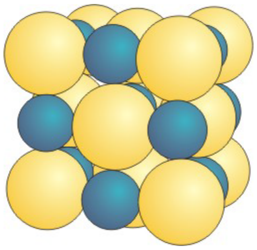


Figure 8.19: NaCl Structure

8.7-7. CsCl

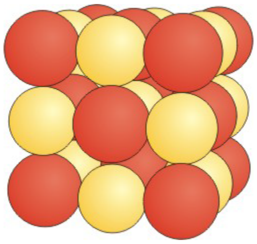


Figure 8.20a: CsCl Unit Cell CsCl in NaCl structure

In CsCl, the radius of the cesium ion is slightly larger than the radius of the chloride anions of the fcc lattice. Because the cations and anions are now nearly the same size, the fcc lattice is pushed apart. The packing efficiency drops down to that of a simple cube in which four of the corners are occupied by cations and four are occupied by anions. CsCl can be made to crystallize with the sodium chloride only under certain conditions.

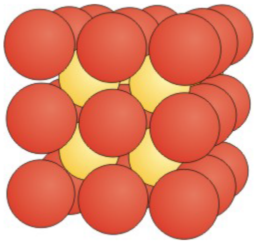


Figure 8.20b: CsCl Unit Cell The CsCl structure

Under normal conditions, the packing efficiency of these nearly equally sized ions is optimized in the arrangement, as shown in the figure. This structure, known as the cesium chloride structure, can be described as having chloride anions forming a simple cube with a cesium cation in the body center. Alternatively, it can be described as a simple cube of cesium cations with a chloride anion in the body center.

8.8 Network Covalent Solids

Introduction

Covalent solids are like ionic solids in that they are very large networks of particles rather than discrete molecules. They differ from ionic solids in that the particles are atoms, not ions, and they are held in their lattice sites by covalent bonds rather than ionic bonds. Because the atoms in the lattice are attached by strong covalent bonds, the materials have very high melting points and are very hard. In this section, we examine the structures of several common network covalent solids.

Objectives

- Describe the structure of graphite and explain why graphite is a lubricant.
- Describe the structures of diamond and the semiconductors Si and Ge.
- Describe the similarity between the structure of diamond and the semiconductors ZnS, GaAs, and IP.

8.8-1. Graphite

The carbon atoms in graphite are sp^2 hybridized and covalently bound together into a two-dimensional array in which the C–C distances are 1.4 Å (see Figure 8.21a). Layers of the two-dimensional arrays are held together loosely (3.4 Å between layers as shown in Figure 8.21b) by intermolecular interactions.

The covalent bonding within the layer gives graphite a high melting temperature. The large number of covalent bonds also produces band structures that make it a good conductor. However, the interaction between the layers is weak, so the layers can slip over each other, which makes graphite an excellent lubricant.

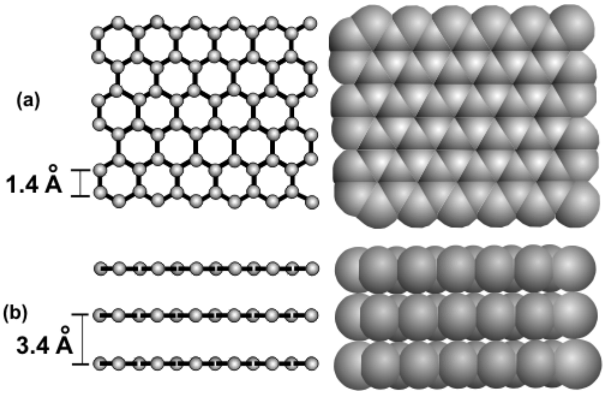


Figure 8.21: Graphite Ball-and-stick and space filling models of graphite that show a small portion of three layers.

8.8-2. Buckyball

Fullerenes are carbon compounds with structures based on the graphite structure. The most common fullerene is C_{60}, which is called buckminster-fullerene (or buckyball) after the architect of the geodesic dome. Buckyball was discovered in the early 1980's. It contains 20 hexagons and 12 pentagons and is the shape of a soccer ball. The hexagons are the same units that form the basis of graphite, but the pentagons are required for closure. A great deal of research was done on fullerenes to develop new technologies. For example, efforts were made to use it as a molecular ball-bearing lubricant, and to encapsulate drugs in its cavity, so they could be released slowly in the body. Buckyball is also a superconductor, so efforts were made to take advantage of this property as well. However, no practical uses of buckyball have yet been developed.

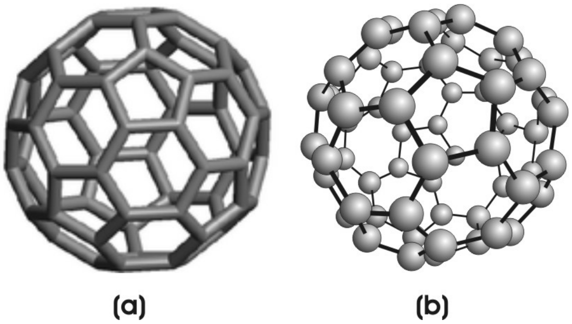


Figure 8.22: Buckyball Figure (a) shows the stick model of Buckyball that includes only the bonds to emphasize the hexagons and pentagons. Figure (b) is the ball-and-stick model that includes the carbon atoms.

8.8-3. Nanotubes

Nanotubes are based on the graphite structure. They are basic building blocks in molecular electronics.

A carbon nanotube is a rolled-up sheet of graphite that is only nanometers wide but up to a centimeter long. Nanotubes are very strong, and, depending on how the graphite sheets are rolled (straight across or at a diagonal), they are conductors or semiconductors. Single nanotubes have been used to make molecular wires, diodes, and transistors, and groups of nanotubes have been integrated into logic circuits, fundamental computer components. These devices are a hundred times smaller than those on present-day computer chips. Nanotubes are a basic building block in the new field of molecular electronics. Indeed, a new technology, one based on devices that measure less than 1000 nanometers, is currently being developed. This new technology is referred to as nanotechnology.

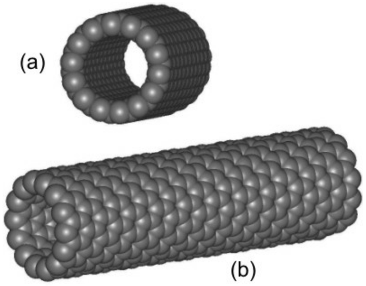


Figure 8.23: Nanotube The tube is viewed down its axis in a and along its side in b.

8.8-4. Diamond

Its strong bonds and structure make diamond the strongest substance known.

Directional sp^3 hybridized orbitals are used to create the three-dimensional framework of diamond. The directional bonds result in a much lower packing efficiency than in metals or ionic compounds where the spherical nature of the atoms and ions allows for much tighter packing. The figure shows one unit cell.

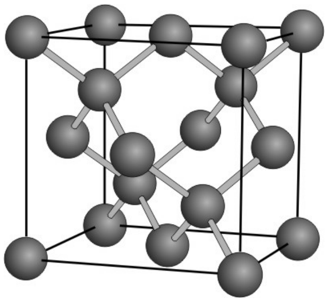


Figure 8.24: Diamond Structure

The electrons of the covalent bonds are delocalized over the entire structure, diamond has valence and conduction bands. Consequently, the diamond structure type is found for several common semiconductors (Si and Ge). Diamond, however, is an insulator because its band gap is very large.

8.8-5. Zinc Blende

The zinc blende structure is common amongst semiconductors.

The zinc blende structure differs from the diamond structure in that there are two sets of atoms (Zn and S) instead of one (C). However, the two sets occupy the same positions as do the carbon atoms in diamond: the corners and face-centers are occupied by one type of atom, but the four sites within the cell are occupied by another. The zinc blende structure type is the structure adopted by the most common semiconductors (ZnS, GaAs, InP).

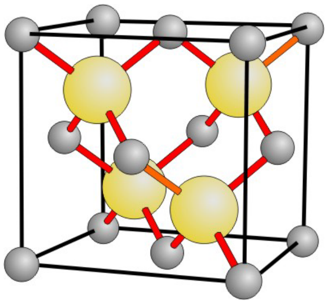


Figure 8.25: Zinc Blende Structure

8.8-6. Silica

Silica, silicon dioxide, is encountered most commonly as sand, which is used to make glass, cement, and ceramics. The crystalline form of silica that is found at room conditions is known as quartz. Quartz is based on a three-dimensional covalent network of SiO_4 tetrahedra. A high temperature form of SiO_2 (known as high cristobalite) is shown in the Figure 8.26. The silicon atoms (the gray spheres) also adopt the diamond-type structure but, in this structure, there is an oxygen atom (red sphere) located between each pair of silicon atoms.

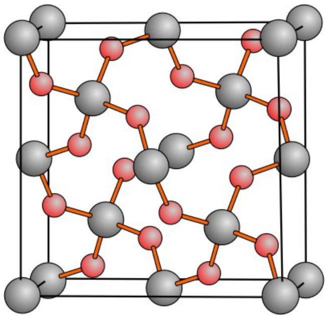


Figure 8.26: Structure of High Cristobalite, a Form of Quartz

8.8-7. Zeolite Structure

Zeolites are characterized by molecular scale channels.

Natural zeolites are aluminosilicates, extended networks that are built from tetrahedral AlO_4 and SiO_4 units that are bridged by oxygen atoms (each oxygen atom is part of two units). The structure of zeolites is filled with cavities (pores) and channels that are only a few angstroms wide (1 angstrom = 10 nm). The aluminosilicate framework is anionic, so natural zeolites are commonly found as their sodium salts. The cations sit inside the cavities. Small molecules can also get into the channels and interact with the oxygen atoms in the aluminosilicate framework, which leads to many uses for zeolites.

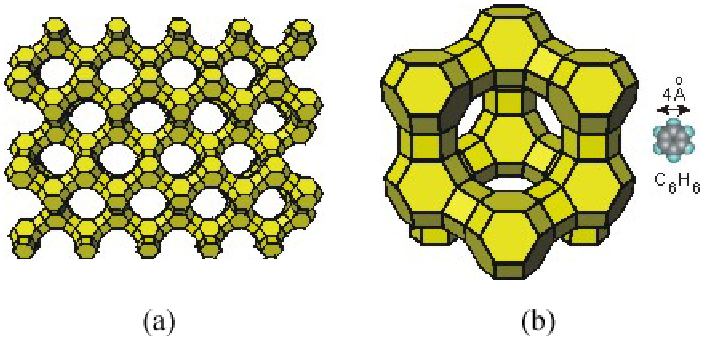


Figure 8.27: Zeolite (a) A section of a zeolite showing a series of channels. Al or Si atoms sit at the end of each line with O atoms bridging them. The openings in the structure that are too small for other molecules to enter are shown as closed surfaces. (b) The pore of this zeolite is formed by a ring that contains 12 atoms (Si and Al) and is 7 Å in diameter. A benzene molecule, which is about 4 Å across, is shown for comparison.

8.8-8. Zeolite Function

Molecular sieves

- The interaction between small molecules in the cavities and the oxygen atoms in the framework keeps the small molecules from leaving, so zeolites are used as molecular sieves. One common use is as a drying agent because water is small and interacts very strongly with the walls via hydrogen bonding. Consequently, when zeolite is added to a wet liquid, the water molecules enter the cavities but do not exit. The molecular sieves are then filtered out of the liquid to leave a dry liquid behind. The sieves can be restored by placing them in a hot oven where the thermal energy is sufficient for the water molecules to break their interactions with the framework.

Ion exchange

- The sodium ions are only loosely bound in the cavities, so they are easily displaced by other ions. Thus, zeolites can also be used for ion-exchange. Perhaps the most common ion-exchanger is the water softener. Water hardness is due to Ca^{2+} and Mg^{2+}. When "hard water" is passed through a zeolite column, the Ca^{2+} and Mg^{2+} displace Na^{1+} because the more highly charged ions interact more strongly. Thus, the water that leaves the column contains Na^{1+} rather than Ca^{2+} and Mg^{2+}, so it is "soft water."

Catalysts

- Chemistry can take place inside the pores. Indeed, some reactions that occur with difficulty on their own occur with relative ease within the cavities of a zeolite. The enhanced reactivity results because interactions with the aluminosilicate framework can make substances more reactive, i.e., zeolites can function as catalysts. The pore size dictates the size of both the reactants and the products, so chemists can select to react only certain molecules in a mixture by selecting a zeolite with the appropriate pore size to exclude larger molecules. Chemists also create zeolites with chemical groups attached to them that enhance certain reactions; i.e., they functionalize zeolites.

Molecular confinement

- Confinement and transportation of large amounts of gases presently requires a combination of very large volumes, very high pressures, and/or very low temperatures. However, storing the gases in the cavities of zeolites is presently being pursued by chemists and engineers. The process would involve synthesizing a zeolite with the cavity size appropriate for the gas and mixing the gas with the zeolite to get the gas molecules into the pores. Once the zeolite is saturated with the gas, the conditions (temperature, pressure, cation, or other method) would be changed to cause a structural change in the zeolite that would trap the gas. Restoring the original conditions would restore the original zeolite structure, so the gas would be released.

8.8-9. Clays

Clays are the most abundant minerals found in soils, rocks, and waters. Like zeolites, they are usually aluminosilicates. However, Mg is substituted for Al in many clays, and Fe fills certain of the Al sites in some clays to give them a red color. All clays exhibit a two-dimensional layered lattice structure rather than the porous network structure of zeolites. As shown in the following figures, the two major types of clays, kaolinite and smectite clays, differ in the organization of tetrahedral (SiO_4) and octahedral (AlO_6 or MgO_6) building blocks. The differences in their structure in turn result in dramatically different properties for these two types of clays.

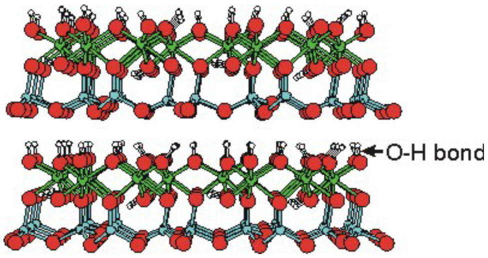


Figure 8.28a: Kaolinite Clay

Kaolinite clays consist of aluminosilicate sheets composed of a silicate layer (SiO_4 tetrahedra shown in blue) and an aluminate layer (AlO_6 octahedra shown in green). In their sedimentary formation, kaolinite clays may have water between the aluminosilicate layers. However, upon heating (firing) the water is driven out from between the layers, leaving only OH bonds on the surface formed by the aluminate layers. These terminal OH groups from strong hydrogen bonds to the oxygen atoms of the silicate portion of the neighboring layer providing a rigid material, which is why kaolinite clay is the main component of china clay.

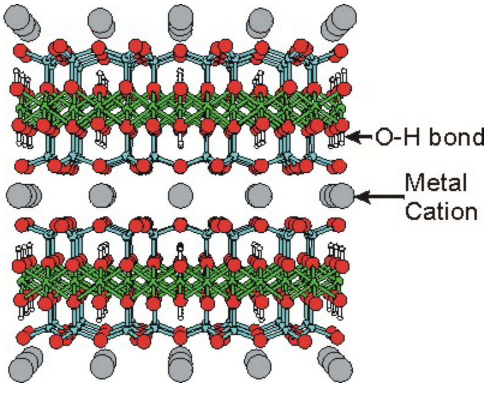


Figure 8.28b: Smectite Clay

Smectite (or swelling) clays consist of sheets composed of a layer of aluminate octahedra sandwiched between two layers of silicate tetrahedra. Other cations surrounded by water (hydrated metal ions), represented by the larger gray spheres in Figure 8.28b, often fill the space between these layers. There are fewer OH groups in this type of structure, and those that are present are "buried" on the aluminate layer between the two silicate layers, which effectively shields them from forming inter-layer hydrogen bonds. As a result, the layers in a smectite clay are not tightly held together, and other ions and molecules can penetrate in between these layers and force the sheets apart.

This property makes them chemically important for the same reasons as zeolites. The major difference being that the 3-D network of zeolites provides greater size and shape selectivity than the 2-D structure of clays. Interestingly, when a smectite clay is fired, the water can also be driven out of the crystal lattice. However without strong hydrogen bonding between the layers, the fired materials result in the flaky material mica, rather than the more robust china or porcelain.

8.9 Molecular Solids and Atomic Radii

Introduction

Molecular compounds form molecular solids. The molecules are held in the condensed states by relatively weak intermolecular forces (Table 7.2: Relative Strengths of Interaction). Because these forces are usually much weaker than those responsible for ionic or covalent solids, molecular solids tend to have lower melting points and are usually softer than the other solids. However, their properties can be quite diverse, as evidenced by the fact that hydrogen, water, table sugar ($C_{12}H_{22}O_{11}$), dry ice, and iodine form molecular solids that have melting points that range from -259 °C for H_2 to 186 °C for sugar, a range of over 400 °C. In addition, the intermolecular forces are typically tens of kilojoules, while covalent bond strengths are hundreds of kilojoules. Thus, covalent bonds are not broken when a substance melts, so molecules retain their identity in the liquid state.

8.9-1. Van der Waals Distance and Bond Length

Atoms that are closer than the sum of their van der Waals radii are interacting.

Unlike ionic or network covalent solids, individual molecules are easily identified in a molecular solid (Figure 8.29). Adjacent molecules interact through intermolecular forces (dotted lines in figure), while atoms within a molecule interact through much stronger covalent bonds (red rods in figure). Molecules are easily identified because the distance between atoms on adjacent molecules, which is called the van der Waals distance (d_{vdw}), is much greater than the distance between atoms within a molecule, which is called the bond length (L). In a network covalent solid such as SiO_2 (Figure 8.26), all Si–O distances between adjacent atoms are the same, so there are no identifiable SiO_2 molecules.

There are two X–X distances shown in crytalline X_2, and each defines a different atomic radius. The covalent radius of X is defined as one-half of the X–X bond length ($L = 2r_{\text{cov}}$), and the ***van der Waals radius*** of X is defined as one-half of the X–X van der Waals distance. The van der Waals radius of an atom is viewed as its "interaction distance." Two atoms closer than the sum of their van der Waals radii are assumed to be interacting.

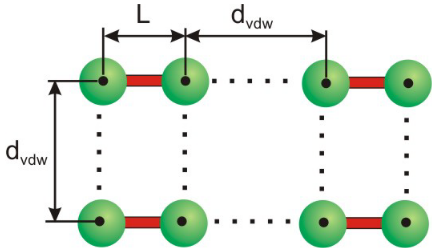


Figure 8.29: Four Molecules in Crystalline X_2

8.9-2. Representing Molecules with van der Waals Radii

The radii of the atomic spheres used in space-filling models are proportional to their van der Waals radii. The definition of the van der Waals radius is clarified in Figure 8.30, which is identical to Figure 8.29 except that space-filling representations are used rather than ball-and-stick. Note that the atomic spheres of X penetrate one another in an X_2 molecule, which means that the two atoms are much closer than the sum of their van der Waals radii. Two atoms much closer than the sum of their van der Waals radii are interacting strongly, so there is a bond between the two X atoms. The spheres on adjacent molecules are touching but not penetrating, so the X atoms of different X_2 molecules interact, but only weakly.

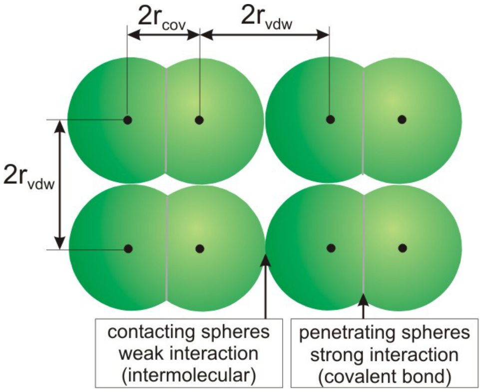


Figure 8.30: van der Waals Radii

8.9-3. Comparing Molecular Representations

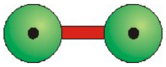


Figure 8.31a: Molecular Representations In the ball-and-stick representation, spheres are used to indicate the positions but not the sizes of the atoms.

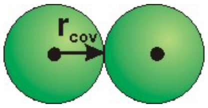


Figure 8.31b: Molecular Representations When atomic size is represented by the covalent radii, bonds are shown as the contact of spheres

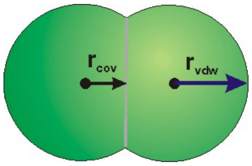


Figure 8.31c: Molecular Representations When atomic size is given with van der Waals radii (space-filling), bonds are indicated by the penetration of spheres.

8.9-4. Table of Radii

	H
r_{cov}	0.32
r_{vdw}	1.2

	C	**N**	**O**	**F**
r_{cov}	0.77	0.75	0.73	0.72
r_{vdw}	1.70	1.5	1.40	1.35

	Si	**P**	**S**	**Cl**
r_{cov}	1.11	1.06	1.02	0.99
r_{vdw}	2.10	1.9	1.85	1.80

	Ge	**As**	**Se**	**Br**
r_{cov}	1.22	1.20	1.17	1.14
r_{vdw}		2.0	2.00	1.95

Table 8.5: Covalent and van der Waals Radii in Å (1 Å = 100 pm) of Selected Nonmetals

8.9-5. Radii Exercise

EXERCISE 8.7:

What is the van der Waals distance in graphite as shown in Figure 8.21?

$d_{\text{vdw}} =$ ______________ Å

What is the van der Waals radius of carbon as determined from this distance?

$r_{\text{vdw}} =$ ______________ Å

8.9-6. Bond Length Exercise

EXERCISE 8.8:

Use the covalent radii in Table 8.5 to determine the Ge–Cl bond length.

$r =$ ______________ Å

8.10 Comparison of Solid Types

Introduction

Objectives

- Determine the relative melting points of two substances based on the type of solid they form.

8.10-1. Comparison of Solid Types

Type of Solid	Particles	Force of Interaction	Strength of Interaction*	Examples
Metallic	Atoms	Metallic Bonds	Variable	Na, Cu, Ag
Ionic	Ions	Ionic Bonds	Strong	NaCl, NH_4Br
Covalent	Atoms	Covalent Bonds	Strong	ZnS, C, SiO_2
Molecular	Molecules	Intermolecular	Weak to Moderate	CO, H_2O, CCl_4

*The strength of interaction dictates the melting and boiling points and the hardness of the substance.

Table 8.6: Summary of Solid Types

8.10-2. Questions

EXERCISE 8.9:

Choose the substance in each pair that has the higher melting point.

NaF	NaCl	SiO_2
MgO	Cl_2	SO_2

8.11 Exercises and Solutions

Links to view either the end-of-chapter exercises or the solutions to the odd exercises are available in the HTML version of the chapter.

Chapter 9 – Reaction Energetics

Introduction

We use the term ***energetics*** to combine two very important fields of study: thermodynamics and kinetics. Thermodynamics is the study of energy and its transformations. Kinetics is the study of the rates and mechanisms of reactions. A thermodynamic study of a reaction examines energy differences between the reactants and products. These studies allow us to predict how much product can be obtained. Thermodynamics is not concerned with how long the reaction takes or how it occurs. These latter concerns are the domain of kinetics. In this chapter, we examine the energetics of some reactions to better understand how reactions occur, to learn how to predict the feasibility of a reaction, and to determine the effect of temperature on both the amount of product and the rate of reaction.

9.1 First Law of Thermodynamics

Introduction

Thermodynamics is the study of energy and its transformations. In chemistry, thermodynamics studies consider the energy difference between the reactants and products. These studies allow us to predict the amount of product that we can expect. We start our study of thermodynamics with the first law of thermodynamics—energy cannot be created or destroyed.

Objectives

- Predict the sign of ΔE for common processes.
- Indicate the direction of energy flow from the sign of ΔE.
- Distinguish between system, surroundings, and universe.
- State the first law of thermodynamics.
- Define the terms q and w and explain what their signs indicate.
- Distinguish between *endothermic* and *exothermic*.
- Determine the energy change of a system given the amount of heat that it absorbs or gives off and the amount of work it does or has done on it.

9.1-1. Energy Change

The sign of ΔE indicates the direction of energy flow.

The energy change of a system is defined as the system's final energy minus its initial energy; that is, $\Delta E = E_{\text{final}} - E_{\text{initial}}$.

- $\Delta E > 0$ means that the energy of the final state of the system is greater than that of the initial state, so this **energy flows into the system**.
- $\Delta E < 0$ means that the energy of the final state of the system is less than that of the initial state, so this **energy flow out of the system**.
- $\Delta E = 0$ means that the energy of the final and initial states of the system are the same, so **there is no energy flow**.

9.1-2. Sign of ΔE Exercise

EXERCISE 9.1:

Indicate whether $\Delta E < 0$, $\Delta E > 0$, or $\Delta E = 0$ for each of the following. Assume that the system is the object mentioned in the problem.

heating water 25 °C to 50 °C
- $\Delta E < 0$
- $\Delta E > 0$
- $\Delta E = 0$

evaporating 1 g of water at 25 °C
- $\Delta E < 0$
- $\Delta E > 0$
- $\Delta E = 0$

heating a piece of zinc from 25 °C to 75 °C and then cooling it back to 25 °C
- $\Delta E < 0$
- $\Delta \mathrm{E} > 0$
- $\Delta E = 0$

moving positive charge closer to negative charge
- $\Delta E < 0$
- $\Delta E > 0$
- $\Delta E = 0$

moving a ball from a table top to the floor
- $\Delta E < 0$
- $\Delta E > 0$
- $\Delta E = 0$

9.1-3. First Law

Energy can be moved from one place to another, but it cannot be created or destroyed.

The **system** in a thermodynamic problem is simply that portion of the universe that is being studied. It exchanges energy with its **surroundings**. The system and its surroundings constitute the thermodynamic **universe**.

$$\Delta E_{\text{univ}} = \Delta E + \Delta E_{\text{sur}}$$

Note that both the universe and surroundings quantities are subscripted, but the system quantity is not.

The ***first law of thermodynamics***, states that energy is neither created nor destroyed.

$$\Delta E_{\text{univ}} = 0 \text{ for all processes} \qquad \text{First Law of Thermodynamics} \tag{9.1}$$

$\Delta E_{\text{univ}} = 0$ implies the following.

$$\Delta E = -\Delta E_{\text{sur}} \qquad \text{Energy Exchange} \tag{9.2}$$

We conclude that the first law of thermodynamics implies that **the energy of a system can be changed only by exchanging energy with its surroundings**.

9.1-4. Determining ΔE Exericse

EXERCISE 9.2:

75 J of energy is transferred when a hot rod is cooled in water. Determine the value of ΔE for the process when each of the following are considered to be the system.

rod ______________ J

water ______________ J

water and rod ______________ J

A reaction releases 175 kJ of energy. Answer the following if the reaction is the system.

$\Delta E =$ ______________ kJ

$\Delta E_{\text{sur}} =$ ______________ kJ

$\Delta E_{\text{univ}} =$ ______________ kJ

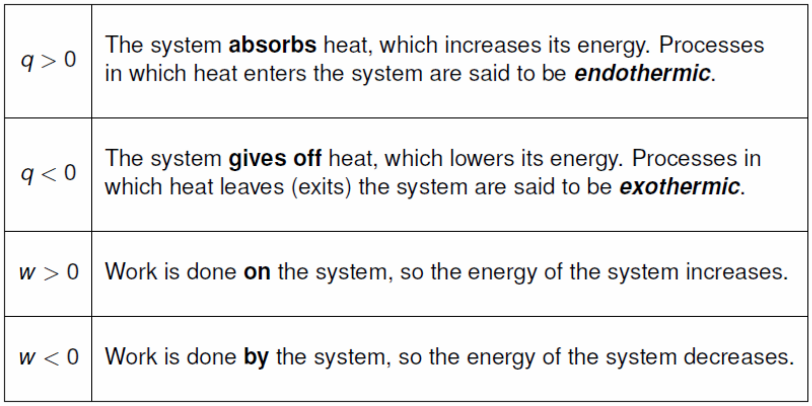
9.1-5. Heat and Work

When q and w are positive, energy flows into the system.

Heat (q) and work (w) are the two most common ways to move energy between a system and its surroundings. The energy of a system increases when it absorbs heat or when work is done on it, and its energy decreases when it gives off heat or does work. Thus, the following is another expression for the first law of thermodynamics.

$$\Delta E = q + w \qquad \text{Heat and Work in Energy Flow} \tag{9.3}$$

q is the heat absorbed by the system and **w is the work done on the system**.



$q > 0$	The system **absorbs** heat, which increases its energy. Processes in which heat enters the system are said to be ***endothermic***.
$q < 0$	The system **gives off** heat, which lowers its energy. Processes in which heat leaves (exits) the system are said to be ***exothermic***.
$w > 0$	Work is done **on** the system, so the energy of the system increases.
$w < 0$	Work is done **by** the system, so the energy of the system decreases.

Table 9.1: The Signs of Heat and Work and the Direction of Energy Flow

9.1-6. Heat and Work Exercise

EXERCISE 9.3:

A system absorbs 500 J of heat and does 300 J of work.

What is the value of q?

$q =$ ______________ J

What is the value of w?

$w =$ ______________ J

What is the energy change for the process?

$\Delta E =$ ______________ J

9.2 Enthalpy

Introduction

Typically, reactions are carried out at constant pressure and the initial and final temperatures are the same. Gases that are produced by a reaction that is open to the atmosphere can carry away some of the energy of the reaction (they do work when they escape), and that energy is lost. Thus, the thermodynamic property of a reaction that is carried out at constant pressure that is most important is the heat that is exchanged with the surroundings. In this section, we define that thermodynamic property.

Objectives

- Define the *enthalpy (heat) of reaction.*
- Determine the relative energies of the reactants and products given the enthalpy of reaction.
- Define the standard state.
- Explain the meaning of a superscript zero on a thermodynamic quantity.
- Explain what the *s*, *l*, or *g* after each substance in a thermochemical equation specifies.
- Determine the enthalpy change for the reaction of a given number of moles of a reactant given the thermochemical equation for the reaction.
- Determine the enthalpy change of a reaction given the enthalpy change for the reaction in which the coefficients have been multiplied by some number and/or the reaction is written in the reverse direction.

9.2-1. Enthalpy of Reaction

The enthalpy of reaction is the heat absorbed at constant T and P. It is positive for endothermic reactions and negative for exothermic reactions.

The ***enthalpy of reaction***, ΔH, is the heat absorbed by a reaction when it is carried out at constant temperature and pressure. Its sign indicates the direction of heat flow. ΔH is defined as the heat absorbed, so it is positive if the reaction absorbs heat from the surroundings and negative if the reaction gives off heat to the surroundings. **The sign of the heat flow is often designated by indicating that the heat was absorbed (positive) or released (negative)**. Thus,
+10 J is read 'ten joules are absorbed,' while −10 J is read 'ten joules are released.'

The reactants are at higher energy than the products in exothermic reactions.

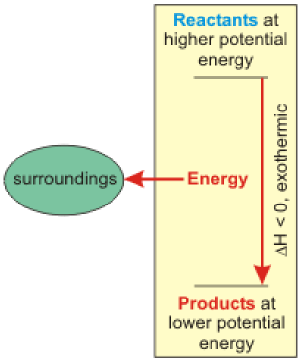


Figure 9.1a: Exothermic Processes

The reactants are higher in enthalpy than the products, so energy must be given off to the surroundings when the reactants are converted to products. Thus, $\Delta H < 0$ for the reaction. The reaction is exothermic because it gives off heat to the surroundings causing the surroundings to warm.

The reactants are at lower energy than the products in endothermic reactions.

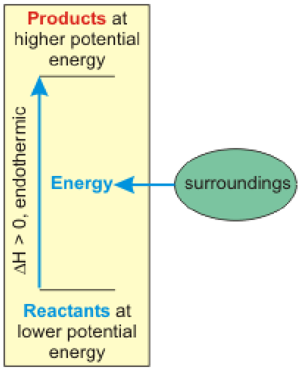


Figure 9.1b: Endothermic Processes

The reactants are lower in enthalpy than the products, so energy must be absorbed from the surroundings to convert the reactants to products. Thus, $\Delta H > 0$ for the reaction. The reaction is endothermic because it absorbs heat from the surroundings causing the surroundings to cool.

9.2-2. Standard States

Standard states are defined at 1 atm pressure, but there is no standard temperature.

Thermodynamic properties, such as ΔE and ΔH, depend upon the states of the substances. Consequently, tabulated values of thermodynamic properties are given for reactions in which the reactants and products are all in their ***standard states***.

- The standard state of a pure substance at a given temperature is its most stable form at that temperature and 1 atm pressure. Unless indicated differently, assume that solids and liquids are pure.
- Gases are considered pure substances even when there is a mixture of gases because the molecules are far apart and do not interact. Thus, the standard state of a gas is a partial pressure of 1 atm.
- The standard state of a dissolved substance is a concentration of 1 mole of substance per liter of solution at a pressure of 1 atm.

The standard state of a substance also depends upon the temperature, but **there is no standard temperature**. Tabulated values of thermodynamic properties are most often given at a temperature of 298 K (25 °C), and 298 K should be assumed if no temperature is given.

EXERCISE 9.4:

Indicate the standard state of each of the following.

oxygen at −20 °C
solid
liquid
1 atm gas
1 M concentration

water at +20 °C
solid
liquid
1 atm gas
1 M concentration

table sugar dissolved in water at 20 °C
solid
liquid
1 atm gas
1 M concentration

water at −20 °C
solid
liquid
1 atm gas
1 M concentration

table sugar ($C_{12}H_{22}O_{11}$) at 20 °C
solid
liquid
1 atm gas
1 M concentration

9.2-3. Standard Enthalpy of Reaction

The enthalpy change for a reaction in which all reactants and products are in their standard states is called the ***standard enthalpy of reaction*** and given the symbol $\Delta H°$ (the superscript '°' implies standard state conditions). Most enthalpies of reaction used in this course are standard enthalpies.

A ***thermochemical equation*** is a balanced chemical equation that includes a thermodynamic property such as $\Delta H°$. Enthalpy changes depend upon the states of the substances, so the state is indicated by the following in parentheses.

- s = solid
- l = liquid
- g = gas
- aq = aqueous (water) solution

The amount of heat released during reaction depends upon the amount of material that is consumed or produced. The enthalpy given for a thermochemical equation is the amount of heat given off or absorbed when the specified number of moles of each substance reacts or is produced. As an example, consider the following thermochemical equation.

$$2\ \mathrm{Na}(s) + 2\ \mathrm{H_2O}(l) \rightarrow 2\ \mathrm{NaOH}(aq) + \mathrm{H_2}(g) \quad \Delta H° = -368\ \mathrm{kJ}$$

The above thermochemical equation tells us that 368 kJ of heat are liberated when

- two moles of solid sodium react,
- two moles of liquid water react,
- two moles of NaOH are produced in an aqueous solution, and
- one mole of H_2 gas is produced.

9.2-4. Stoichiometry and Thermodynamics

The thermochemical equation,

$$\mathrm{P_4}(s) + 6\ \mathrm{Cl_2}(g) \rightarrow 4\ \mathrm{PCl_3}(g) \quad \Delta H° = -1152\ \mathrm{kJ}$$

indicates that 1152 kJ of heat is liberated (negative sign) when one mole of solid phosphorus reacts with six moles of chlorine gas to produce four moles phosphorus trichloride gas. Consequently, the heat of reaction can also be expressed as any of the following.

$$\frac{-1152\ \mathrm{kJ}}{1\ \mathrm{mol\ P_4}} \quad \text{or} \quad \frac{-1152\ \mathrm{kJ}}{6\ \mathrm{mol\ Cl_2}} \quad \text{or} \quad \frac{-1152\ \mathrm{kJ}}{4\ \mathrm{mol\ PCl_3}}$$

Multiplication of any of the expressions above by the appropriate number of moles of product or reactant results in the $\Delta H°$ for the reaction in which that number of moles is formed or consumed. For example, the following determines the enthalpy change that would accompany the reaction of four moles of chlorine gas.

$$4\ \mathrm{mol\ Cl_2} \times \frac{-1152\ \mathrm{kJ}}{6\ \mathrm{mol\ Cl_2}} = -768\ \mathrm{kJ}$$

9.2-5. Stoichiometry Exercise

EXERCISE 9.5:

Consider the thermochemical equation.

$$N_2(g) + 3\ H_2(g) \rightarrow 2\ NH_3(g) \quad \Delta H^\circ = -92\ \text{kJ}$$

What would be the value of ΔH° under the following circumstances.

one mole of ammonia is formed ________________ kJ

two moles of H_2 react ________________ kJ

7.0 g of N_2 react ________________ kJ

9.2-6. Properties of Enthalpy

We have seen that ΔH is proportional to the number of moles of substance that react. This means the following.

If the coefficients of a chemical equation are multiplied by some number, then the enthalpy of the resulting reaction equals the enthalpy of the original reaction multiplied by the same number.

For example consider the following two processes.

$$H_2O(s) \rightarrow H_2O(l) \qquad \Delta H^\circ = +6\ \text{kJ}$$

$$2\ H_2O(s) \rightarrow 2\ H_2O(l) \qquad \Delta H^\circ = +12\ \text{kJ}$$

The second equation is obtained by multiplying the first by two, so the enthalpy change of the second reaction is twice the enthalpy change of the first.

A second important property of enthalpy is the following.

The sign of ΔH is changed when the direction of the reaction is reversed.

For example consider the following two processes.

$$H_2O(s) \rightarrow H_2O(l) \qquad \Delta H^\circ = +6\ \text{kJ}$$

$$H_2O(l) \rightarrow H_2O(s) \qquad \Delta H^\circ = -6\ \text{kJ}$$

The first thermochemical equation indicates that 6 kJ are absorbed when 1 mole of ice melts. In the second equation, the direction of the process is reversed, so the sign of ΔH must be changed. We conclude that freezing 1 mole of liquid water releases 6 kJ of heat.

EXERCISE 9.6:

The following thermochemical equation for burning butane is given.

$$C_4H_{10}(l) + 6.5\ O_2(g) \rightarrow 4\ CO_2(g) + 5\ H_2O(l) \quad \Delta H° = -2855\ \text{kJ}$$

Determine the enthalpy of reaction for each of the following.

$2\ C_4H_{10}(l) + 13\ O_2(g) \rightarrow 8\ CO_2(g) + 10\ H_2O(l)$

______________ kJ

$4\ CO_2(g) + 5\ H_2O(l) \rightarrow C_4H_{10}(l) + 6.5\ O_2(g)$

______________ kJ

$8\ CO_2(g) + 10\ H_2O(l) \rightarrow 2\ C_4H_{10}(l) + 13\ O_2(g)$

______________ kJ

9.3 Enthalpies of Combustion

Introduction

Most of the energy utilized by humans comes from combustion reactions (reactions with O_2). The internal combustion engine that runs our cars gets its energy from the combustion of gasoline. Many homes are heated by the combustion of coal, oil, or natural gas. Many power plants generate electricity by burning (combusting) coal, and humans obtain the energy needed to sustain life by the combustion of carbohydrates. The carbon in the fuel is converted to CO_2 and the hydrogen is converted to H_2O by the reaction with O_2. In this section, we examine enthalpies (heats) of combustion.

Objectives

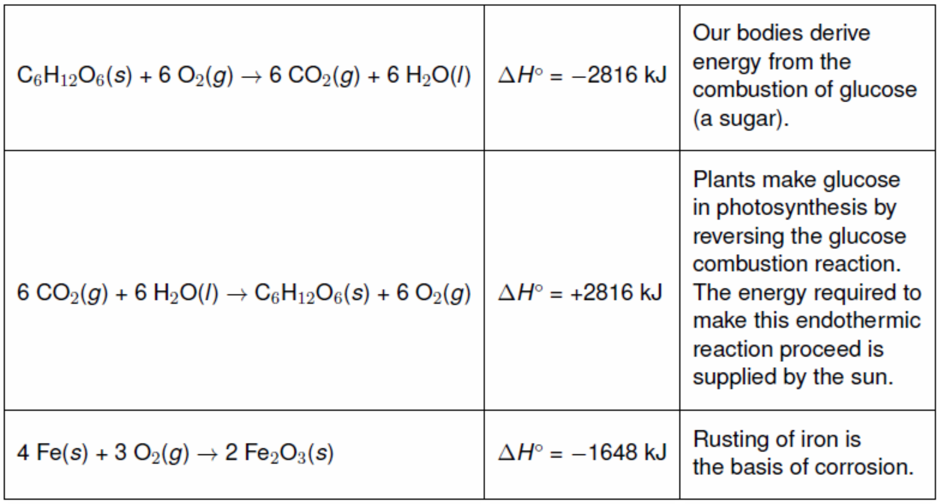
- Define enthalpy of combustion and write the chemical equation to which the enthalpy of combustion of a substance applies.

9.3-1. Enthalpies of Combustion

Combustion is the reaction of a substance with oxygen, and it is the major source of harnessed energy. Combustion reactions are always exothermic, and it is the energy released in combustion reactions that fuels our vehicles, heats our homes, and powers our bodies. The products of combustion are usually, but not always, the oxides of the elements comprising the molecule being combusted.

The standard molar ***enthalpy of combustion*** of a substance is the heat absorbed when one mole of the substance reacts with O_2 at standard conditions.

Consider the following thermochemical equations that deal with some common combustion reactions.



$C_6H_{12}O_6(s) + 6\ O_2(g) \rightarrow 6\ CO_2(g) + 6\ H_2O(l)$	$\Delta H^\circ = -2816$ kJ	Our bodies derive energy from the combustion of glucose (a sugar).
$6\ CO_2(g) + 6\ H_2O(l) \rightarrow C_6H_{12}O_6(s) + 6\ O_2(g)$	$\Delta H^\circ = +2816$ kJ	Plants make glucose in photosynthesis by reversing the glucose combustion reaction. The energy required to make this endothermic reaction proceed is supplied by the sun.
$4\ Fe(s) + 3\ O_2(g) \rightarrow 2\ Fe_2O_3(s)$	$\Delta H^\circ = -1648$ kJ	Rusting of iron is the basis of corrosion.

Table 9.2: Thermochemical Equations for Some Common Combustion Reactions

9.3-2. Combustion Exercise

<u>EXERCISE 9.7</u>:

The calorie content of carbohydrates, fats, and proteins are all derived from their heats of combustion because they are all burned in the body. In this example, we use the heat of combustion of sugar to determine the number of calories in a teaspoon of sugar. The thermochemical equation for the combustion of sucrose (table sugar) is the following.

$$C_{12}H_{22}O_{11}(s) + 12\ O_2(g) \rightarrow 12\ CO_2(g) + 11\ H_2O(l) \quad \Delta H^\circ = -5650\ \text{kJ/mol}$$

How many calories are in a heaping teaspoon of sugar (4.8 g)?

What is the number of moles of sugar present ($M_\text{m} = 342$ g/mol)?

______________ mol

What is the amount of heat liberated during the combustion?

______________ kJ

If there are 4.18 kJ in a dietary calorie, what is the number of dietary calories present in the sugar?

______________ Cal

9.4 Bond Energies

Introduction

Recall from Chapter 5 that bond formation involves a lowering of the energy of the system, i.e., bond formation is an exothermic process. Reversing the direction of the reaction, changes the sign of ΔH, so bond breaking is an endothermic process. The energy released or absorbed during a chemical reaction comes from or is stored in chemical bonds, and the enthalpy change of a reaction can be estimated from tabulated values of bond energies.

Prerequisites

- 5.1 The Covalent Bond

Objectives

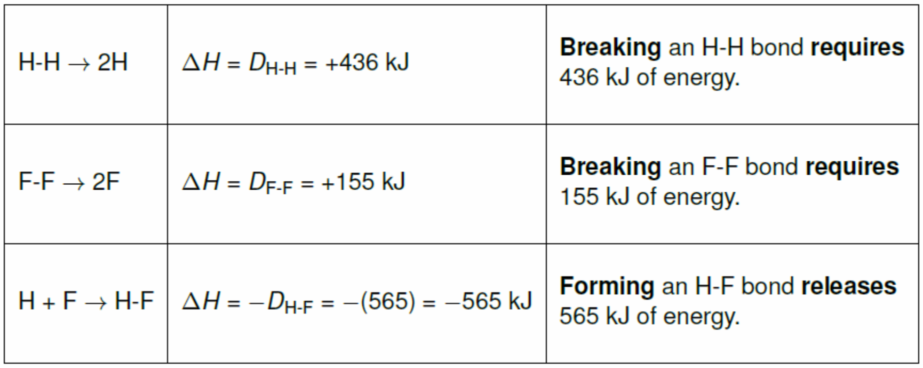
- Define the bond or dissociation energy.
- Estimate the enthalpy of reaction from bond energies.

9.4-1. Bond Energies

The ***bond energy*** or ***dissociation energy*** (D) of a bond is the energy required to break one mole of bonds in the *gas phase.*

A table of bond energies can be found in the resource named Bond Energies.

Bond energies are always positive because bonds require energy to be broken.



H-H → 2H	$\Delta H = D_{\text{H-H}} = +436$ kJ	**Breaking** an H-H bond **requires** 436 kJ of energy.
F-F → 2F	$\Delta H = D_{\text{F-F}} = +155$ kJ	**Breaking** an F-F bond **requires** 155 kJ of energy.
H + F → H-F	$\Delta H = -D_{\text{H-F}} = -(565) = -565$ kJ	**Forming** an H-F bond **releases** 565 kJ of energy.

Table 9.3: Examples of Some Thermochemical Equations involving Bond Energies

9.4-2. Estimating Enthalpy

Reactions involve breaking and forming bonds, and the heat generated or absorbed during a reaction is the net result. If we knew the energies of all of the interactions involved, we could determine the enthalpy of reaction by determining how much energy must be supplied to break all of the interactions that had to be broken and subtracting the energy that is released when all of the new interactions form. Bond energies give us estimates of these energies, but tabulated bond energies are averages. For example, a C-Cl bond in CCl_4 is different from a C-Cl bond in $COCl_2$, but only one C-Cl bond energy is tabulated. In addition, bond energies are defined only for gas phase molecules, so other interactions can be ignored, but many reactions occur in solution where solvation and other interactions complicate the problem. However, bond energies can be used to obtain approximate enthalpies from the following.

The enthalpy of a reaction can be *approximated* by the sum of the bond energies of the bonds that must be broken less the sum of the bond energies of those that must be formed.

$$\Delta H \sim \Sigma D_{\text{broken}} - \Sigma D_{\text{formed}} \qquad \text{Enthalpy of Reaction from Bond Energies} \qquad (9.4)$$

EXAMPLE:

For example, let us approximate the enthalpy of reaction for the following.

$$H_2(g) + F_2(g) \rightarrow 2\ HF(g)$$

One H-H bond and one F-F bond must be broken and two H-F bonds must be formed. The needed bond energies are given in Table 9.3.

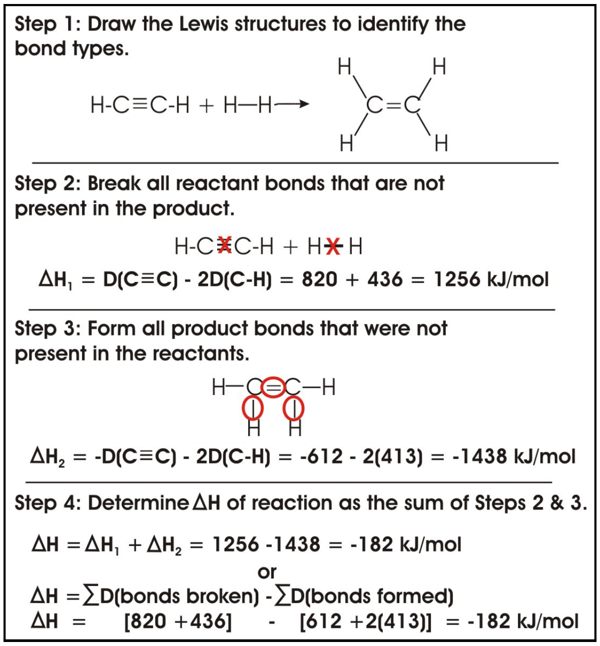
$$\begin{aligned}\Delta H &\sim \Sigma D_{\text{broken}} - \Sigma D_{\text{formed}} \\ &\sim D_{\text{H-H}} + D_{\text{F-F}} - 2D_{\text{H-F}} \\ &= 436 + 155 - 2(565) \\ &= -539\ \text{kJ}\end{aligned}$$

The above calculation works well for the HF example because there is only one kind of H-H, F-F, and H-F bonds and the reaction is a gas phase reaction.

EXAMPLE:

Use tabulated bond energies to estimate the enthalpy of the following reaction.

$$C_2H_2 + H_2 \rightarrow C_2H_4$$



Step 1: Draw the Lewis structures to identify the bond types.

Step 2: Break all reactant bonds that are not present in the product.

ΔH_1 = D(C≡C) - 2D(C-H) = 820 + 436 = 1256 kJ/mol

Step 3: Form all product bonds that were not present in the reactants.

ΔH_2 = -D(C≡C) - 2D(C-H) = -612 - 2(413) = -1438 kJ/mol

Step 4: Determine ΔH of reaction as the sum of Steps 2 & 3.

$\Delta H = \Delta H_1 + \Delta H_2$ = 1256 -1438 = -182 kJ/mol

or

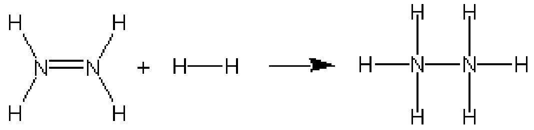
$\Delta H = \sum$D(bonds broken) - $\sum$D(bonds formed)

ΔH = [820 +436] - [612 +2(413)] = -182 kJ/mol

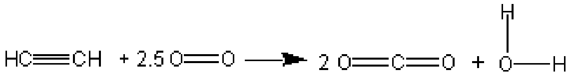
9.4-3. Bond Energy Exercise

EXERCISE 9.8:

Use the Bond Energies resource to estimate the enthalpy changes for the following reactions.



$\Delta H =$ ______________ kJ/mol



$\Delta H =$ ______________ kJ/mol

9.4-4. Bond Energy and Lewis Structure Exercise

EXERCISE 9.9:

Determine ΔH for the following reaction.

$$H_2CO(g) + NH_3(g) \rightarrow H_2CNH(g) + H_2O(g)$$

First determine the Lewis structures to get the bond orders of all bonds. Review Section 5.6 Determining Lewis Structures if you have forgotten how to determine Lewis structures.

Bond Orders: All bonds to hydrogen are single bonds, but the other bond orders need to be determined.

C-O bond order in H_2CO ______________

C-N bond order in H_2CNH ______________

Enthalpies: Use the Bond Energies resource to determine the following enthalpies. Break and form only those bonds that do not appear in both the reactant and product side.

energy required to break the reactant bonds ______________ kJ

energy released when product bonds are formed ______________ kJ

Finally, determine the enthalpy of reaction.

$\Delta H =$ ______________ kJ

9.5 Entropy

Introduction

A ***spontaneous process*** is one that takes place without intervention. A ball rolls down a hill spontaneously, but it does not roll uphill spontaneously. It can be made to roll uphill but only with intervention. We have used the concept that systems in nature strive to lower energy, so our first hypothesis might be that exothermic processes are spontaneous, while endothermic processes are not. However, there are spontaneous endothermic processes, such as evaporation. We saw in Chapter 8 that the energy of the molecules in the gas phase is much greater than those in the liquid phase, yet liquids do evaporate spontaneously, i.e., molecules go spontaneously from the lower energy liquid state into the higher energy gas phase. Clearly, there is another factor, and, in this section, we consider that factor.

Objectives

- Distinguish between translational, rotational, and vibrational motion.
- Explain how the entropy of a system depends upon how freely its molecules move.
- Define entropy.
- Determine whether the entropy of reaction is positive, negative, or very small.
- State the relationship between the entropy of a system and the order of a system.
- Indicate the effects on the entropy of a system caused by adding heat and how the effect is dependent upon the temperature at which the heat is added .

9.5-1. Probability and Constraints

Unconstrained systems are statistically favored over constrained ones.

There are $10! = 3,628,800$ ways to arrange ten books on a shelf, but the books are aphabetized in only one. Thus, there are 3,628,799 ways to disburse the books in a random or disordered manner, but only one in which the books are **constrained** to be in alphabetical order. If the books were alphabetized originally but then removed and returned to the shelf without the intervention of a librarian, they would spontaneously move to a disordered state for strictly statistical reasons. If we assume that there are only two systems in our set of books, constrained or ordered and unconstrained or disordered, then the process constrained → unconstrained is spontaneous because there are more ways in which the books can be disbursed in the unconstrained, disordered system. The process unconstrained → constrained is not spontaneous and occurs only with intervention (a librarian in this example).

9.5-2. Types of Motion

The kinetic energy of a molecule is a combination of translational, rotational, and vibrational contributions.

We saw above that systems that can be disbursed in a less constrained manner are favored over those whose disbursement is highly constrained, and it is the disbursement of energy that drives chemical processes. We now show how molecular systems disburse their energy.

Recall from Section 7.1 Gases that thermal energy (RT) is a measure of the average kinetic energy of the molecules in a system. Kinetic energy is energy of motion, and the motion of a molecule is a combination of three types of motion called ***degrees of freedom***.

- **translation**: straight line motion of the entire molecule through space
- **rotation**: circular motion of the atoms in a molecule about an axis fixed to the molecule
- **vibration**: atoms within a molecule moving relative to one another by causing small changes in bond lengths and bond angles

All atoms have three degrees of freedom because the motion of an atom can be described as a combination of its motion in the x-, y-, and z-directions. A molecule that contains n atoms has $3n$ degrees of freedom that are combinations of the three motions of its n atoms. The six degrees of freedom of a diatomic molecule are shown in Figure 9.2.

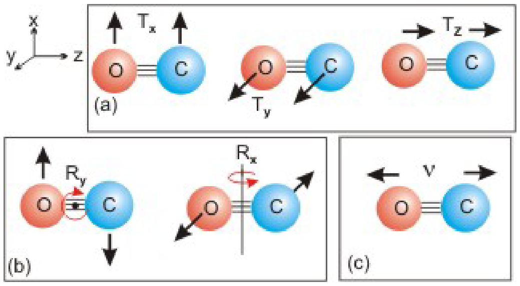


Figure 9.2: Degrees of Freedom of a Diatomic Molecule

Each atom of a diatomic molecule like CO has three degrees of freedom as they can each move in the x-, y-, or z-direction. Thus, the molecule has six degrees of freedom, which take the following forms.

- **a** Motion of both atoms in the same direction translates the molecule in that direction.
- **b** Motion in opposite directions along the x- or y-axis rotates the molecule about the y- or x-axis, respectively.
- **c** Movement in opposite directions along a bonding axis results in a vibration as the bond elongates and contracts. A vibration is referred to with the greek symbol nu (ν).

9.5-3. Entropy

Entropy is a measure of the number of ways that a system can distribute its energy.

For purely statistical reasons, a system that has more ways in which it can distribute its energy is favored over one that has fewer ways. Indeed, the number of ways in which the energy of a system can be distributed is such an important property of the system that a thermodynamic property is used to measure it. The thermodynamic property is called the ***entropy*** (S) of the system, which has units of joules per kelvin (J/K).

- Systems with higher entropies can distribute energy in more different ways than those with lower entropies.

The entropy of a system increases as the freedom of motion of its molecules increases. Gas phase molecules have much more freedom of motion than do molecules in the liquid or solid states, so the entropy of a system of gas phase molecules is much greater than that of the same molecules in a condensed state. Molecules in the liquid state have slightly more freedom of motion than those in the solid, so the entropy of a system of molecules in the liquid state is slightly greater than in the solid state. We will use the following conclusion frequently.

$S_{\text{gas}} >> S_{\text{liquid}} > S_{\text{solid}}$

9.5-4. Systems Strive to Increase Their Entropy

The two driving forces behind a process are the tendencies for systems to minimize their potential energy ($\Delta H < 0$) and to maximize the number of ways in which they can distribute their energy ($\Delta S > 0$). However, unless the entropy change is large, the tendency to minimize enthalpy is the dominant driving force. We have seen how to estimate enthalpy changes from bond energies, and we now examine how to predict whether the entropy change is large and positive, large and negative, or negligible.

The entropy change of a reaction is given as $\Delta S = S_{\text{products}} - S_{\text{reactants}}$, so $\Delta S > 0$ when the entropy of the products is greater than that of the reactants. At this point, we need only predict whether ΔS is large, and, if so, what is its sign. To do this, we recall that $S_{\text{gas}} >> S_{\text{liquid}} > S_{\text{solid}}$. Indeed, we will assume that $S_{\text{liquid}} \sim S_{\text{solid}} \sim 0$ to conclude the following.

Entropy changes are large only in reactions in which the number of moles of gas changes.

Thus, the sign and magnitude of the entropy change during a reaction can be estimated from the following.

- $\Delta S > 0$ for reactions that produce gas.
- $\Delta S < 0$ for reactions that consume gas

- $\Delta S \sim 0$ (is usually negligibly small) for reactions that do not involve a change in the number of moles of gas.

ΔS can be calculated, but the procedure is beyond the scope of this course. It is covered in Chapter 4 of *Chemistry - A Quantitative Science.*

9.5-5. Constraints and Disorder as Predictors of Entropy

Constrained systems are more ordered and have lower entropies than systems that are less constrained.

We have seen that adding constraints to the motion of particles reduces their freedom of motion, which decreases their entropy. In other words, constrained systems have lower entropies than do unconstrained systems. In addition, putting constraints on a system usually results in some ordering of the system. For example, motion is unconstrained in the gas phase, so the entropy of a gas is high. However, when intermolecular forces constrain the molecules, they align to increase their interactions. The effect of such alignments is to produce the short range order found in the liquid state. Increasing the constraints on a liquid forces the molecules to align so as to maximize their interactions and produce the long range order found in the solid state. Thus, the degree to which a system is ordered is a good indicator of its freedom of motion and, therefore, of its entropy. We conclude the following.

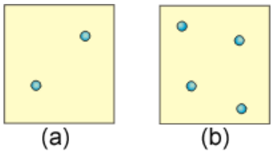
- The more disordered a system is, the greater is its entropy.

Indeed, entropy is commonly defined as a measure of the order in a system. However, entropy is a measure of the number of ways in which energy can be distributed in a system; the order of a system is simply a good predictive tool because ordered systems cannot distribute energy in as many ways as disordered ones.

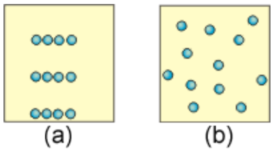
9.5-6. Entropy Exercise

EXERCISE 9.10:

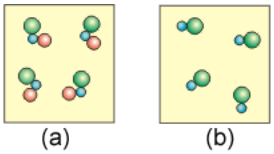
Predict which system in each pair has the greater entropy.



(a)
(b)



(a)
(b)



(a)
(b)

9.5-7. Effects of Heat and Temperature on Entropy

The number of ways a system can distribute its energy increases with the amount of energy it has to distribute, so the entropy of a system always increases with temperature. Similarly, adding heat to a system always increases the entropy of a system. However, 1 J of heat has much more impact when it is added to a system that has less energy (lower T) than it does when added to a system that has more energy (higher T). This relationship is expressed in the following equation, which defines entropy change.

$$\Delta S = \frac{\text{heat added reversibly}}{\text{temperature at which the heat is added}} = \frac{q_{\text{rev}}}{T}\ \text{J/K} \tag{9.5}$$

q_{rev} is used to indicate that the heat must be added reversibly, which means that it must be added so slowly that the slightest change could reverse the direction of heat flow. Equation 9.5 can be rearranged to $T\Delta S = q_{\text{rev}}$, so $T\Delta S$ is an energy term.

Using order as a predictor of entropy, we can understand the above with a simple analogy: the effect on the order of a room resulting when a book is casually dropped in it. The probability is very high that the book will NOT drop into its allotted location, so the dropped book will increase the disorder (entropy) of the system. In a neat room (representing a more ordered, lower temperature system), the effect of the out-of-place book is dramatic. However, its effect on a messy room (representing a higher temperature, less ordered system) is negligible as the out-of-place book is hardly noticeable. Similarly, adding 1 J of heat to a solid at 5 K (very ordered, low entropy) has a much more dramatic effect on the entropy than adding 1 J to the vapor at 500 K (disordered, high entropy).

9.5-8. Predicting Entropy Change Example

EXERCISE 9.11:

Predict the sign of $\Delta S°$ for each of the following reactions.

$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$
$\Delta S < 0$
$\Delta S > 0$
$\Delta S \sim 0$

$3\ H_2(g) + N_2(g) \rightarrow 2\ NH_3(g)$
$\Delta S < 0$
$\Delta S > 0$
$\Delta S \sim 0$

$Ag(s) + NaCl(s) \rightarrow AgCl(s) + Na(s)$
$\Delta S < 0$
$\Delta S > 0$
$\Delta S \sim 0$

$H_2O(l) \rightarrow H_2O(g)$
$\Delta S < 0$
$\Delta S > 0$
$\Delta S \sim 0$

$H_2O(l)$ at 25 °C $\rightarrow$ $H_2O(l)$ at 5 °C
$\Delta S < 0$
$\Delta S > 0$
$\Delta S \sim 0$

9.5-9. Entropy Change Example

EXERCISE 9.12:

Indicate which process in each of the following pairs increases the entropy of the system more.

adding 10 J of heat to neon at 300 K
adding 50 J of heat to neon at 300 K

adding 10 J of heat to neon at 300 K
adding 10 J of heat to neon at 800 K

adding 50 J of heat to neon at 800 K
adding 10 J of heat to neon at 300 K

melting 1 g of neon at its melting point
evaporating 1 g of neon at its boiling point

9.6 Second Law of Thermodynamics

Introduction

The fact that systems seek to increase their entropy is the basis of the Second Law of Thermodynamics, the topic of this chapter.

Objectives

- State the Second Law of Thermodynamics.

9.6-1. The Second Law of Thermodynamics

Spontaneous processes must increase the entropy of the universe.

We have seen that systems with higher entropies are statistically favored over those with lower entropies, but processes impact the entropy of both the system and its surroundings. In order to determine the spontaneity of a process, we must consider the entropy change that it causes in the universe, not just the system. Indeed, the second law of thermodynamics defines spontaneity in terms of this change.

- ***Second Law of Thermodynamics***: The entropy of the universe increases in all spontaneous processes; that is $\Delta S_{\text{univ}} > 0$ for all spontaneous processes.

In other words, ***spontaneous processes are those that increase the entropy of the universe***. Processes that reduce the entropy of the system can be accomplished, but only if the entropy of the surroundings is increased more than the entropy of the system is decreased.

9.6-2. Entropy and Heat Flow

Heat flows spontaneously from hot to cold, never cold to hot. (It is forced to flow cold to hot in a heat pump, but energy is required, so it is not spontaneous.) We now show that this is a consequence of the second law. Consider to thermal resevoirs at T_1 and T_2 that are in thermal contact as shown below.

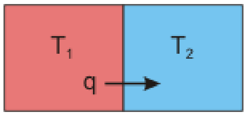


Figure 9.3

To determine the spontaneous direction of heat flow, we examine the entropy change associated with the flow of heat from T_1 to T_2. Applying the second law to the problem, we can write the following.

$$\Delta S_{\text{univ}} = \Delta S_1 + \Delta S_2 > 0$$

ΔS_1 and ΔS_2 are the entropy changes that the heat flow causes in the two reservoirs, which can be obtained by using Equation 9.5.

$$\Delta S_1 = \frac{-q}{T_1} \quad \Delta S_2 = \frac{+q}{T_2}$$

The negative sign indicates that heat is leaving the reservoir at temperature T_1, and the positive sign indicates that heat is entering the reservoir at temperature T_2. Substitution of these ΔS values into the ΔS_{univ} expression yields the following.

$$\Delta S_{\text{univ}} = \frac{-q}{T_1} + \frac{+q}{T_2}$$

Thus, $\Delta S_{\text{univ}} > 0$ and the process is spontaneous only if $T_1 > T_2$. In other words, only if the heat flows from the hotter sources to a cooler one.

9.7 Free Energy

Introduction

We now show that ΔS_{univ} can be written as a sum of system quantities, and, in doing so, derive a new thermodynamic property that includes the effects of both ΔH and ΔS on the spontaneity of any process carried out at constant temperature and pressure. The new property is called the free energy because it is the energy that is free to do work.

Objectives

- Define *Gibbs free energy*, and explain why it is important.
- Describe the two driving forces behind the free energy change, and write the expression that shows how they are related to the free energy.

9.7-1. Free Energy

A spontaneous process at constant T and P is one in which $\Delta G < 0$.

Entropy changes in the universe can be broken down into the changes in the system and its surroundings.

$$\Delta S_{\text{univ}} = \Delta S + \Delta S_{\text{sur}}$$

During the process, heat can be exchanged between the system and the surroundings, which changes the entropy of the surroundings. For a reaction carried out at constant T and P, the amount of heat that is transferred from the system to the surroundings is $q_{\text{sur}} = -\Delta H$, so $\Delta S_{\text{sur}} = -\Delta H/T$. An exothermic reaction releases heat into the surroundings, which increases the entropy of the surroundings. The entropy change in the universe resulting from a reaction carried out at constant temperature and pressure is the following.

$$\Delta S_{\text{univ}} = \Delta S - \Delta H/T$$

Multiplying both sides by $-T$, we obtain the following.

$$-T\Delta S_{\text{univ}} = \Delta H - T\Delta S$$

The above expression for ΔS_{univ} is a function of system quantities only, so it too is a system quantity. This new thermodynamic function of the system is called the **Gibbs free energy, ΔG** or simply the ***free energy***.

Thus, the driving forces behind a process carried out at constant T and P are combined into the Gibbs free energy expression.

$$\Delta G = \Delta H - T\Delta S \qquad \text{Gibbs Free Energy} \qquad (9.6)$$

- ΔG is the change in free energy. It is the energy that is free to do work, i.e., **$-\Delta G$ = maximum work that can be done by the process at constant T and P**. It dictates the spontaneous direction of the reaction. Reactions proceed spontaneously and do work in the direction in which $\Delta G < 0$.
- ΔH is the change in potential energy that results from breaking and forming interactions. Reactions that lower the potential energy of the system ($\Delta H < 0$) reduce the free energy, which is favorable.
- $T\Delta S$ is the change in free energy caused by changing the number of ways energy can be dispersed in the system. Processes that increase the entropy of a system ($\Delta S > 0$) are favored because they lower the free energy of the system by $T\Delta S$ joules.

9.7-2. Enthalpy and Free Energy

Equation 9.6 indicates that processes tend to minimize their potential energy ($\Delta H < 0$).

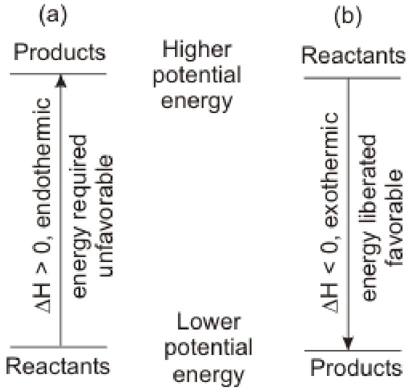


Figure 9.4: Enthalpy and Free Energy

- Endothermic reactions (Figure 9.4a) require energy, so they cannot occur spontaneously unless they can be driven by $T\Delta S$ energy. Thus, $T\Delta S > \Delta H$ for a spontaneous endothermic reaction.
- Exothermic reactions (Figure 9.4b) release energy, so they can occur spontaneously unless $T\Delta S$ is so negative that the released energy is not sufficient overcome the entropy term.

9.7-3. Entropy and Free Energy

Equation 9.6 indicates that processes tend maximize their entropy ($\Delta S > 0$).

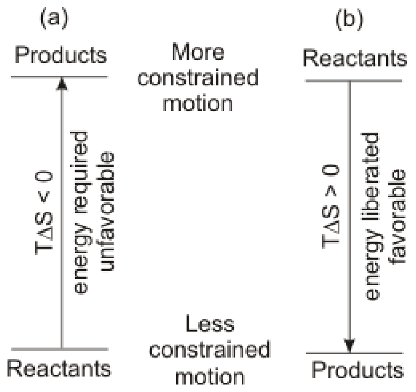


Figure 9.5: Entropy and Free Energy

- Processes for which $\Delta S > 0$ release energy that can be used to drive reactions uphill in enthalpy, but any $T\Delta S$ energy that is not used in this manner is free to do work.
- Processes for which $\Delta S < 0$ require energy, which must be supplied from ΔH if the process is to be spontaneous.

9.7-4. Free Energy and Reaction Spontaneity

There are driving forces in both the forward and reverse directions of most reactions, so double arrows are often used in chemical equations. A $\rightleftharpoons$ B shows that there are driving forces for both A $\rightarrow$ B and A $\leftarrow$ B. ΔG is the difference between these forces. If $\Delta G < 0$, the forward driving force is greater, so there is a net force in the forward direction and the reaction consumes A to produce B. When $\Delta G > 0$, the reverse driving force is greater, so there is a net force in the reverse direction, and the reaction produces A by consuming B. If $\Delta G = 0$, the two forces are equal, and there is no net driving force. At this point there is no longer a change in concentrations as the reaction has reached equilibrium. Indeed, $\Delta G = 0$ is the thermodynamic definition of equilibrium at constant temperature and pressure. As summarized in the Table 9.5, the following is true.

The sign of ΔG indicates the spontaneous direction of reaction.

The value of ΔG varies with the concentrations of the reactants and products, so it changes as the process continues. Consider the evaporation of water: $H_2O(l) \rightleftharpoons H_2O(g)$. Initially, only liquid is present, so there is no driving force in the reverse direction (no condensation). Consequently, $\Delta G < 0$ and the liquid begins to evaporate. However, as the pressure of the vapor increases, so does the driving force in the reverse direction, so ΔG gets less negative. Eventually, the pressure of the vapor is such that the driving force in the reverse direction equals that in the forward direction, $\Delta G = 0$, and the process has reached equilibrium.

$\Delta G < 0$	Reaction spontaneous as written ($\rightarrow$).
$\Delta G = 0$	Reaction is at equilibrium ($\rightleftharpoons$).
$\Delta G > 0$	Spontaneous direction is the opposite of what is written ($\leftarrow$).

Table 9.4: The Sign of the Free Energy and the Direction of Reaction

9.8 Standard Free Energy and the Extent of Reaction

Introduction

The difference between the free energy of a reaction (ΔG) and the standard free energy of reaction ($\Delta G°$) is an important one and one that is often confused by students. In this section, we examine the meaning of these two important thermodynamic properties.

Objectives

- Use the standard enthalpy and entropy of a reaction to predict the conditions of temperature at which the standard free energy is most likely negative.

9.8-1. Standard Free Energy

As is the case with enthalpies, entropies and free energies of reaction are usually given for the reaction carried out under standard conditions. The standard free energy is defined in terms of the standard enthalpy and entropy of reaction as the following.

$$\Delta G° = \Delta H° - T\Delta S°$$

Recall that the superscript zero means that all reactants and products are in their standard states at a specified temperature, so $\Delta G°$ is a constant for a reaction at that temperature.

EXERCISE 9.13:

Predict the signs of $\Delta H°$ and $\Delta S°$. Then use $\Delta G° = \Delta H° - T\Delta S°$ to predict the temperature conditions under which $\Delta G°$ is likely to be negative.

(a) $H_2(g) + Cl_2(g) \rightarrow 2\ HCl(g) \quad \Delta H° = -180$ kJ/mol

What is the sign of $\Delta H°$?	What is the sign of $\Delta S°$?
+	+
−	−
	~ 0

$\Delta G°$ is most probably negative at which of the following?
- all temperatures
- no temperatures
- low temperatures only
- high temperatures only

(b) $CCl_4(l) \rightarrow CCl_4(g)$

What is the sign of $\Delta H°$?	What is the sign of $\Delta S°$?
+	+
−	−
	~ 0

$\Delta G°$ is most probably negative at which of the following?
- all temperatures
- no temperatures
- low temperatures only
- high temperatures only

(c) $P_4(s) + 6\ Cl_2(g) \rightarrow 4\ PCl_3(g)$ $\Delta H < 0$

What is the sign of $\Delta H°$?

+

−

What is the sign of $\Delta S°$?

+

−

~ 0

$\Delta G°$ is most probably negative at which of the following?

all temperatures

no temperatures

low temperatures only

high temperatures only

9.8-2. Extent of Reaction

$\Delta G°$ is the value of ΔG when all reactants and products are in their standard states. Consider the process: $A(g) \rightleftharpoons B(g)$. If $\Delta G° < 0$, the reaction is spontaneous in the forward direction when both pressures are 1 atm, so equilibrium is attained by consuming A, which reduces P_A to less than 1 atm, and producing B, which increases P_B to more than 1 atm. If $P_B > P_A$ at equilibrium, the reaction is said to be extensive because the amount of product at equilibrium is much greater than the amount of reactant. If $\Delta G° > 0$, the process is spontaneous in the reverse direction at standard conditions. Equilibrium in this case is attained when $P_A > P_B$, so there is more reactant than product at equilibrium and the reaction A equilibrium B is not extensive. We conclude the following.

$\Delta G°$ indicates the extent of reaction.

9.8-3. Extent Exercise

EXERCISE 9.14:

One mole each of NH_3 and N_2H_2 are allowed to react in identical 1-L containers at 298 K. Which flask would contain the greater number of moles of H_2 when the reactions are complete?

You should read the replies to both answers to better understand the role of $\Delta G°$.

$2\ NH_3 \rightarrow N_2 + 3\ H_2$ $\Delta G° = +34$ kJ
$N_2H_2 \rightarrow N_2 + 2\ H_2$ $\Delta G° = -160$ kJ

9.8-4. Extent of Reaction Versus Temperature

$\Delta G° = \Delta H° - T\Delta S°$ can be re-arranged to give the common form of a straight line ($y = mx + b$) as follows.

y	$=$	m	x	$+$	b
$\Delta G°$	$=$	$-\Delta S°$	T	$+$	$\Delta H°$

Thus, a plot of $\Delta G°$ versus T is a straight line with a slope of $-\Delta S°$ and an intercept of $\Delta H°$. The intercept is $\Delta H°$, so $\Delta G° = \Delta > H°$ at $T = 0$. Indeed, we will assume that the sign of $\Delta G°$ is the same as the sign of $\Delta H°$ at low temperatures. However, the slope of the line is $-\Delta S°$, so $\Delta S°$ can dictate the sign of $\Delta G°$ at very high temperatures.

For example, consider the temperature dependence of $\Delta G°$ of reactions A - E as described in Table 9.5 and Figure 9.6.

Rxn	ΔH°	ΔS°	ΔG°
A	> 0	> 0	At low T, ΔH° dominates, so $\Delta G^\circ > 0$ and the reaction is not extensive. However, ΔS° is positive, so the slope is negative, which causes ΔG° to go negative at high T. Thus, the reaction is extensive at high T.
B	> 0	< 0	Both terms are unfavorable, so the reaction is not extensive at any temperature.
C	< 0	< 0	At low T, the favorable ΔH° dominates and the reaction is extensive. At high T, the unfavorable ΔS° dominates to make ΔG° positive and the reaction not extensive.
D	< 0	> 0	Both terms are favorable, so the reaction is extensive at all T.
E	< 0	~ 0	Reactions in which ΔS° is very small are dominated by ΔH° at all T.

Table 9.5: Standard Free Energy Versus Temperature

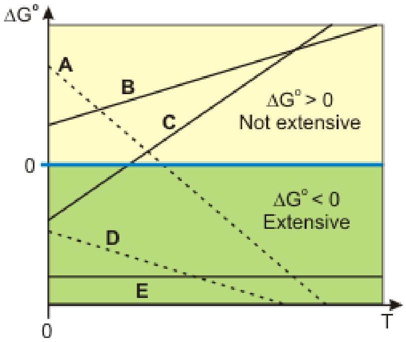


Figure 9.6: Standard Free Energy Versus Temperature

9.8-5. Summary

At very low temperatures, the $T\Delta S^\circ$ term is negligible, and ΔG° has the sign of ΔH°. At very high temperatures, the $T\Delta S^\circ$ term dominates (unless $\Delta S^\circ \sim 0$), and ΔG° has the sign of $-\Delta S^\circ$.

ΔH°	ΔS°	Extent
negative	positive	Exothermic reactions that increase entropy are always extensive because both terms are favorable.
negative	negative	Exothermic reactions that reduce entropy are more likely to be extensive at lower temperatures, where the unfavorable $T\Delta S$ term is negligible.
positive	positive	Endothermic reactions that increase entropy are more likely to be extensive at higher temperatures, where the favorable $T\Delta S$ term can dominate the unfavorable enthalpy change.
positive	negative	Both terms are unfavorable, so endothermic reactions that reduce entropy are never extensive.

Table 9.6: Predicting the Extent of Reaction

9.9 Activation Energy

Introduction

Thermodynamics compares the initial and final states only. It does not consider how the transition from one state to another is accomplished; that is the domain of kinetics. Energy considerations are also an important part of kinetics, and we use the one-step displacement of iodide by hydroxide to examine reaction energetics in this section.

Objectives

- Define *reaction coordinate*, *transition state*, and *activation energy*.
- Explain how the enthalpy of reaction is related to the activation energies of the forward and reverse reactions.

9.9-1. The Reaction

In this section we examine both the thermodynamics and kinetics of the following one-step reaction in which iodide is displaced by a hydroxide ion.Thermodynamics is concerned only with differences between the initial and final states of the reaction, while kinetics is concerned with how the reaction proceeds.

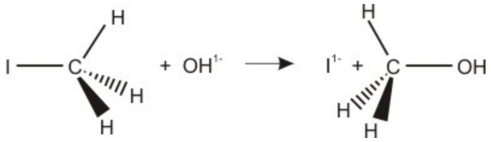
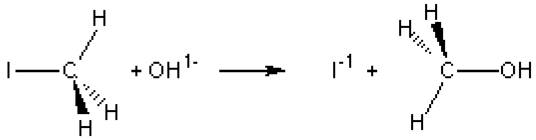


Figure 9.7

9.9-2. Thermodynamic View

Thermodynamics is concerned only with the difference between the initial and final states.

Consider the following reaction.



The properties of interest are $\Delta H°$, $\Delta S°$, and $\Delta G°$. Although all of these properties can be determined from tables, our goal is to estimate their sign and whether they are large or small.

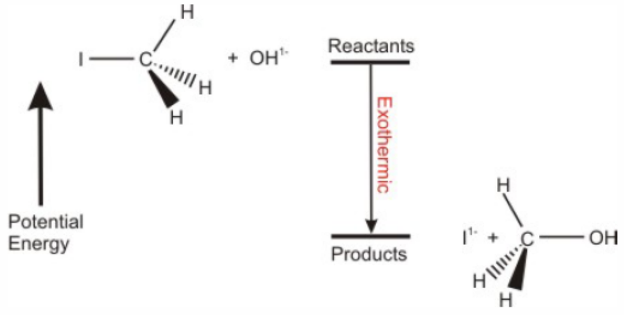
Enthalpy	The reaction involves breaking one C-I bond and forming one C-O bond. Refer to the Bond Energies resource for the C-O bond energy (358 kJ/mol) and the C-I bond energy (234 kJ/mol). $\Delta H^\circ \sim D_{\text{C-I}} - D_{\text{C-O}}$ $\Delta H^\circ \sim 234 - 358 \sim -120$ kJ/mol This is only a very rough approximation because this reaction is carried out in solution not in the gas phase. However, the formed bond is clearly stronger than the broken bond, so we can conclude that the **reaction is exothermic**.
Entropy	There are no gasses, so we assume that **$\Delta S^\circ \sim 0$ (is small)**.
Free Energy	Since $\Delta S^\circ \sim 0$ and $\Delta H^\circ < 0$, we conclude that $\Delta G^\circ \sim \Delta H^\circ < 0$. The reaction should be extensive, i.e., it is a reaction that should produce a lot of product.
Summary	$\Delta H^\circ < 0$, so the potential energy of the reactants is above that of the products because the C-O bond energy is stronger than the C-I bond. 

Table 9.7

9.9-3. Kinetic View

A video or simulation is available online.

Kinetics deals with the transition from reactants to products.

Kinetics is the study of the rates and mechanisms of reactions. In other words, kinetics looks at the transition from the initial to the final state. To do this, we define a reaction coordinate, which is normally a complicated combination of intermolecular distances and molecular structural changes. In order to form the C-O bond, the OH^{1-} ion must attack the carbon atom along the line through the center of the plane formed by the three H atoms. As the C-O distance decreases, the three H-C-H angles all increase from their original 109° as the H atoms separate, and the C-I bond elongates. Thus, the reaction coordinate involves changes in all of these parameters. As the C-O distance decreases, the H-C-H bond angles continue to increase, and the C-I bond continues to lengthen. The system reaches an energy maximum when the H-C-H bond angles are 120° and the CH_3 group is planar. The species that is formed at this point is called the transition state, which is the species that the reactants must pass through in their transition to the products. It is at the energy maximum, so it immediately changes into one of the species at lower energy. If the C-O bond shortens and the C-I bond breaks, the transition state leads to the products, but if the C-O bond breaks and the C-I bond shortens, the transition state leads to the reactants. Either action is possible.

Reactants must go through a transition state to reach the products, and the energy required to reach the transition state is called the activation energy.

The energy required to reach the transition state is called the activation energy (E_a). Once the products form, they can also collide to form the same transition state. The reaction between the substances on the right side of the chemical equation is called the *reverse reaction*, while reaction of the substances on the left side is called the *forward reaction*. Both reactions have activation energies. $E_\text{a}(\text{f})$ is the activation energy for the forward reaction, while E_a(r) is the activation energy for the reverse reaction. Activation energies are always positive. Note that $\Delta H = E_a(\mathrm{f}) - E_a(\mathrm{r})$, so $E_a(\mathrm{f}) < E_a(\mathrm{r})$ for exothermic reactions, but $E_a(\mathrm{f}) > E_a(\mathrm{r})$ for endothermic reactions.

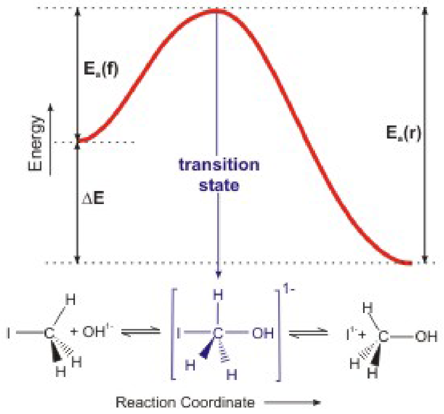


Figure 9.8: Reaction Diagram for $CH_3I + OH = CH_3OH + I^{1-}$

9.10 Rates of Reaction and The Rate Law

Introduction

In this section, we examine the factors that dictate the rate of a reaction, and then pull all of the factors together into a rate law for the reaction.

Prerequisites

- 7.1-11. Molarity (Determine the molarity of a substance in a mixture.)
- 7.1 Gases

Objectives

- Express the collision frequency between several particles in terms of their molar concentrations.
- State the two factors that dictate the fraction of collisions that lead to the transition state.
- Write the rate law that governs a reaction that occurs in one step given the balanced chemical equation for the reaction.
- Define the term *catalyst* and explain how a catalyst functions.

9.10-1. Collision Frequency

The frequency of collisions between two particles is proportional to the product of their concentrations.

We now turn our attention to the **rate of reaction**, i.e., how fast the concentrations change with time. In order for two molecules to react, they must collide. Thus, the rate of reaction is proportional to the frequency at which the *reactants* collide. The ***collision frequency*** is the number of collisions per unit volume per unit time, which normally has units of (moles of collisions) $\cdot$ liter^{-1} $\cdot$ s^{-1}.

The frequency of collisions between particles is proportional to the product of the molar concentrations of the colliding particles. Recall that the molar concentration of particle A is the number of moles of A in a liter and given the symbol [A]. [A] = 1 M is read “the concentration of A is 1 molar or 1 mole per liter.”

In the following examples, C is a proportionality constant that differs for each reaction and increases with temperature.

Particles	Collision Frequency	Comments
A + B	C[A][B]	The collision frequency between two particles is proportional to the product of their molar concentrations. Increasing either concentration increases the frequency of collisions between the particles. If both concentrations are doubled, the collision frequency increases by a factor of four.
P + P = 2P	$C[P][P] = C[P]^2$	For collisions between two identical particles, the collision frequency is proportional to the square of the concentration of the particle. Note that the concentration is raised to an exponent equal to the number of times the particle appears in the collision.
X + Y + Z	C[X][Y][Z]	Simultaneous collisions between three particles are very rare, so C would be very small.

Table 9.8

9.10-2. Orientation Effects

Only a fraction of colliding particles are oriented properly for reaction.

Only a fraction of the collisions between reactants results in the transition state. In fact, the reaction rate can be very small or even zero when the collision frequency between reactants is high if the fraction of collisions, X, that lead to the transition state is very small. The fraction depends upon both the energy and the orientation of the colliding molecules. We consider orientation effects here and energy in the following section.

Consider the relative orientations of reactants shown in Figure 9.8. The orientations shown in (a) and (b) do not lead to the transition state, while orientation (c) does. There are many more ways in which the molecules can collide with an orientation that does not lead to the transitions, so the fraction that does lead to the transition state is fairly low in this reaction.

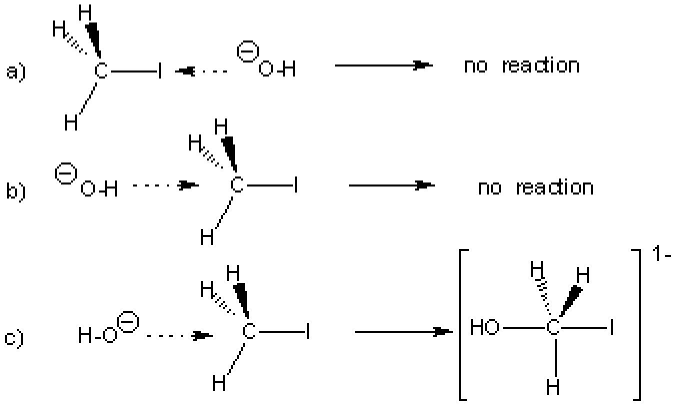


Figure 9.8: Orientation Effect (a) OH^{1-} ion attacks the iodine atom not the carbon, so transition state cannot form; (b) OH^{1-} ion attacks the correct position, but it is turned so that a C-O bond cannot form; (c) the only orientation that can lead to the transition state.

9.10-3. Energy Effect

Only a fraction of colliding particles have sufficient energy to react.

A collision must have enough energy to overcome the activation energy of the reaction. A collision between $OH^{1-}$and CH_3I must have enough energy to push the H atoms back and lengthen the C-I bond. The average energy of a collision depends upon the thermal energy ($\sim RT$). Consequently, the fraction of collisions leading to the transition state always increases with temperature.

9.10-4. Rate Law

Many reactions involve several steps to convert the reactants to the products. For example, the reaction between hydrogen and oxygen is a complicated reaction that involves many steps. However, some reactions, such as the displacement reaction between CH_3I and OH^{1-}, occur in a single collision (step).

Consider the rate of the reaction A + B → products.

The rate of a reaction equals the fraction of collisions (X) that lead to the transition state times the collision frequency (F), so we may write the following.

$$\text{rate} = \text{XF}$$

The collision frequency is proportional to the concentrations of the reactants, or the following.

$$\text{F} = \text{C[A][B]}$$

Combining these two equations, we note that the rate of the reaction equals the product of two constants, which is also a constant k = XC, times the products of the reactant concentrations.

$$\text{rate} = \text{XC[A][B]} = k\text{[A][B]}$$

This expression is the **rate law** of the reaction, and k is the ***rate constant*** of the reaction. X and C are each temperature dependent, so k is also temperature dependent.

The ***rate law*** for a simple, one-step reaction is equal to the rate constant for the reaction times the product of the concentrations of the **reactants** each raised to an exponent equal to their coefficient in the balanced chemical equation.

9.10-5. Rate Law Exercise

EXERCISE 9.15:

What are the rate laws for the following reactions, which all occur in a single step?

$O_3 + O \rightarrow 2\ O_2$	$2\ NOCl \rightarrow 2\ NO + Cl_2$
rate = ______________	rate = ______________
$2\ CO + O_2 \rightarrow 2\ CO_2$	$H_2 \rightarrow 2\ H$
rate = ______________	rate = ______________

9.10-6. Catalysts

A catalyst increases the speed of a reaction by lowering its activation energy.

The rate law for the simple reaction A + B → C is rate = k[A][B]. Consequently, the rate of reaction can be changed by changing the concentrations: increasing the reactant concentrations increases the rate of reaction. Indeed, as a reaction proceeds, the rate of reaction slows because the reactants are consumed. The rate of reaction can also be changed by changing the rate constant. The rate constant can be increased in three ways.

- **Increasing the temperature**. Increasing the temperature increases the rate constant by increasing the thermal energy and the average energy of the collisions. Consequently, the fraction of collisions that reach the transition state increases.
- **Decreasing the activation energy**. Lowering the activation energy increases the rate constant by reducing the energy required to reach the transition state. Consequently, a larger fraction of collisions reaches the transition state.
- **Assuring the correct orientation of reactant**. Forcing the reactants to align correctly when they interact, increases the rate constant because a larger fraction of the interactions result in the transition state.

The last two methods of increasing the rate constant are accomplished with the use of catalysts. ***Catalysts*** speed reactions by assuring that the reacting molecules align correctly for reaction and/or by providing a pathway with a lower activation energy. ***Enzymes*** are proteins that bind to reacting molecules (substrates). The binding weakens the reactant bonds, which lowers the activation energy, and they can force close alignment of two reactants, which assures the correct orientation.

9.10-7. Ozone Depletion

As an example of catalytic behavior, we consider the problem of ozone depletion in the upper atmosphere. O_3 in the upper atmosphere protects us from ultraviolet radiation from the sun. It is removed by reaction by atomic oxygen.

$$\mathrm{O} + \mathrm{O}_3 \rightarrow 2\ \mathrm{O}_2 \quad E_a = 17\ \mathrm{kJ/mol}$$

Fortunately, the activation energy is so high that the reaction is very slow at the temperature of the upper atmosphere. However, chlorine atoms can catalyze the reaction. The chlorine atoms are produced when high energy light from the sun is absorbed by chlorofluorocarbons (CFC's), which were common in refrigeration and spray cans.

$$\mathrm{CF_2Cl_2} + hv \rightarrow \mathrm{CF_2Cl} + \mathrm{Cl}$$

The chlorine atoms catalyze the depletion of ozone in two steps. Their chemical equations and activation energies follow.

1 $\mathrm{Cl} + \mathrm{O}_3 \rightarrow \mathrm{O}_2 + \mathrm{ClO} \quad E_a' = 2\ \mathrm{kJ/mol}$

2 $\mathrm{ClO} + \mathrm{O} \rightarrow \mathrm{Cl} + \mathrm{O}_2 \quad E_a'' = 0.4\ \mathrm{kJ/mol}$

Summing the two steps yields the same ozone depletion reaction that occurs in the absence of chlorine atoms ($\mathrm{O} + \mathrm{O}_3 \rightarrow 2\ \mathrm{O}_2$). The chlorine atoms speed the reaction but are unchanged by it, so they are a catalyst for the reaction. They provide a different path with a lower activation energy (the activation energies for the two steps are 2 and 0.4 kJ/mol, respectively), so the reaction is much faster in the presence of chlorine.

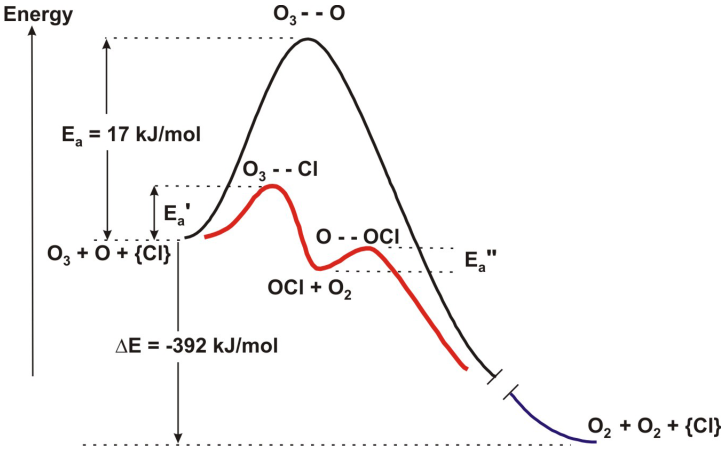


Figure 9.9: Reaction Diagram for Ozone Depletion Shown is the reaction diagram for the ozone depletion reaction in the absence (black curve) and presence (red curve) of chlorine atoms.

9.11 Equilibrium and the Equilibrium Constant

Introduction

Although it is common to say that a reaction has stopped, reactions don't really stop. Instead, they reach a dynamic equilibrium in which the molecules on the right side of the chemical equation continue to produce those on the left and vice versa. At equilibrium, however, the amounts of products and reactants are no longer changing because they are being consumed and produced at the same rate. In this section, we discuss the equilibrium process from the viewpoints of both kinetics and thermodynamics and introduce the equilibrium constant.

Objectives

- Explain what is meant by a 'dynamic equilibrium.'
- Write the equilibrium constant expression for a reaction from the balanced chemical equation.
- Determine the value of an equilibrium constant from the equilibrium concentrations (or pressures) of all reactants and products.
- Determine the equilibrium concentration (or pressure) of one substance from the equilibrium concentrations (or pressures) of all other substances in the equilibrium mixture and the value of the equilibrium constant.
- Explain what is meant by an *extensive reaction* and predict whether a reaction is extensive from the value of its equilibrium constant.
- Relate the equilibrium constant to the standard free energy of reaction.
- Use standard enthalpy and entropy changes to predict the extent of reaction.
- Predict the effect that a temperature change has on the equilibrium constant of a reaction.

9.11-1. Equilibrium and the Equilibrium Constant

A reaction reaches equilibrium when the rates of the forward and reverse reactions are equal.

As a reaction proceeds, the concentrations of the reactant molecules decrease while those of the product molecules increase. Consequently, the rate of the forward reaction decreases, while that of the reverse reaction increases. When the two rates are equal, reactants and products are formed at the same rate that they are consumed and the reaction reaches **equilibrium**. Chemical equilibria are *dynamic* because reaction continues, even though the concentrations of the reactants and products no longer change. Double or equilibrium arrows ($\rightleftharpoons$) are used in reactions at equilibrium to emphasize that the reaction takes place in both the forward and reverse directions. Consider the reaction: $CH_3OH^{1-} \rightleftharpoons I^{1-}CH_3OH$.

	Reaction	Rate
Forward Reaction	$CH_3I + OH^{1-} \rightarrow I^{1-} + CH_3OH$	$R_f = k_f[CH_3I][OH^{1-}]$
Reverse Reaction	$I^{1-} + CH_3OH \rightarrow CH_3I + OH^{1-}$	$R_f = k_f[CH_3OH][I^{1-}]$

At equilibrium, $R_f = R_r$, so we can write the following.

$$k_f[CH_3I][OH^{1-}] = k_r[CH_3OH][I^{1-}]$$

Rearranging the above to get the rate constants on one side and the concentrations on the other, we obtain the following.

$$\frac{k_f}{k_r} = \frac{[CH_3OH][I^{1-}]}{[CH_3I][OH^{1-}]}$$

The ratio of concentrations equals the ratio of rate constants, which is a constant at a given temperature. Thus, the above expression is a constant, which is called the ***equilibrium constant*** for the reaction and given the symbol K.

$$K = \frac{[CH_3OH][I^{1-}]}{[CH_3I][OH^{1-}]}$$

The equilibrium constant expression equals the equilibrium concentrations of the substances on the right side of the chemical equation (the products) divided by the equilibrium concentrations of the substances on the left side of the chemical equation (the reactants). The concentration of each substance is raised to an exponent equal to the coefficient of the substance in the balanced chemical equation.

9.11-2. Some Examples of Equilibrium Constant Expressions

The concentration of a gas in an equilibrium constant expression equals its partial pressure in atmospheres, while the concentration of a solute is given by its molar concentration. Solids and liquids enter as unity (1).

The form of the 'concentration' of a substance in the equilibrium constant expression depends upon the state of the substance.

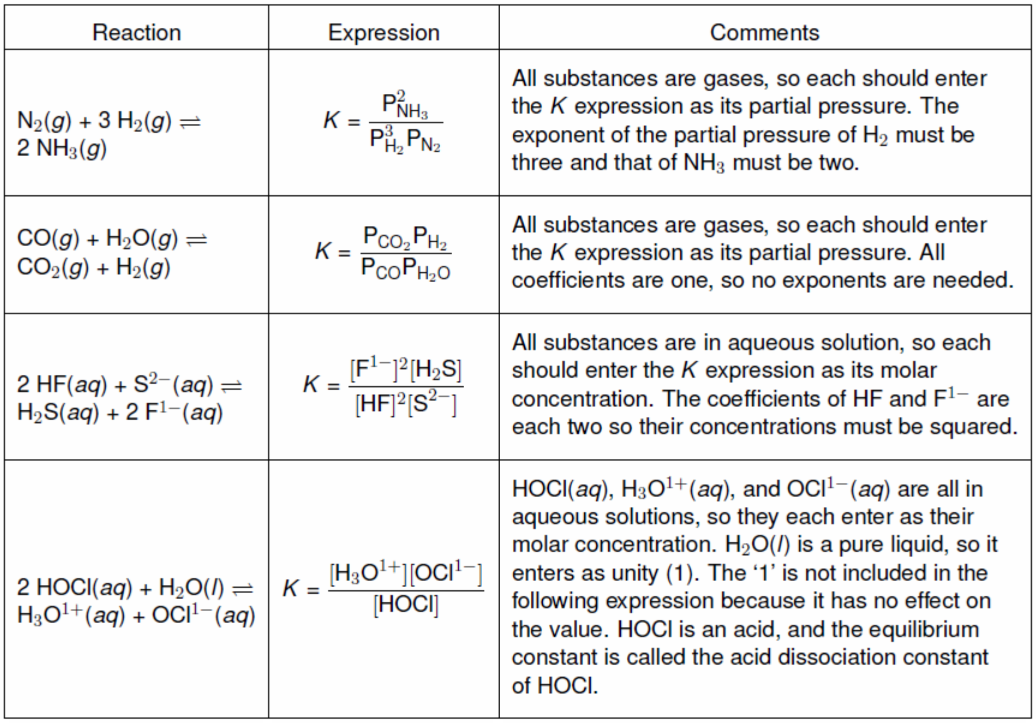
- Pure *solids* and *liquids* enter the equilibrium constant expression as one (1) because their concentrations do not change during a reaction.
- *Gases* enter K as their partial pressures in atmospheres. Thus, substance X would enter the expression as P_X if X was a gas.
- *Substances that are dissolved in solution* enter K as their molar concentrations. Substance X enters the expression as [X] if X is dissolved in solution.

For example, consider the following equilibrium.

$$aA(g) + bB(aq) \rightleftharpoons xX(s) + yY(aq)$$
$$K = \frac{1^x[Y]^y}{P_A^a[B]^b} = \frac{[Y]^y}{P_A^a[B]^b}$$

The 'concentration' of X appears as 1 because X is a solid; the 'concentration' of A is its partial pressure because A is a gas; and the 'concentrations' of B and Y are their molar concentrations because they are solutes in an aqueous solution.

The following examples should help.



Reaction	Expression	Comments
$N_2(g) + 3\ H_2(g) \rightleftharpoons 2\ NH_3(g)$	$K = \frac{P_{NH_3}^2}{P_{H_2}^3 P_{N_2}}$	All substances are gases, so each should enter the K expression as its partial pressure. The exponent of the partial pressure of H_2 must be three and that of NH_3 must be two.
$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$	$K = \frac{P_{CO_2} P_{H_2}}{P_{CO} P_{H_2O}}$	All substances are gases, so each should enter the K expression as its partial pressure. All coefficients are one, so no exponents are needed.
$2\ HF(aq) + S^{2-}(aq) \rightleftharpoons H_2S(aq) + 2\ F^{1-}(aq)$	$K = \frac{[F^{1-}]^2[H_2S]}{[HF]^2[S^{2-}]}$	All substances are in aqueous solution, so each should enter the K expression as its molar concentration. The coefficients of HF and F^{1-} are each two so their concentrations must be squared.
$2\ HOCl(aq) + H_2O(l) \rightleftharpoons H_3O^{1+}(aq) + OCl^{1-}(aq)$	$K = \frac{[H_3O^{1+}][OCl^{1-}]}{[HOCl]}$	HOCl(*aq*), $H_3O^{1+}(aq)$, and $OCl^{1-}(aq)$ are all in aqueous solutions, so they each enter as their molar concentration. $H_2O(l)$ is a pure liquid, so it enters as unity (1). The '1' is not included in the following expression because it has no effect on the value. HOCl is an acid, and the equilibrium constant is called the acid dissociation constant of HOCl.

Table 9.9: Some Examples of Equilibrium Constant Expressions

As shown in the following exercise, the equilibrium constant for a reaction can be determined from known equilibrium concentrations or it can be used with other known equilibrium concentrations to determine an unknown concentration.

9.11-3. *K* Calculation Exercise

EXERCISE 9.16:

Use the following chemical equation to answer the questions: $N_2O_4 \rightleftharpoons 2\ NO_2$.

Calculate the value of K at a temperature where the following equilibrium concentrations are found: $P_{NO_2} = 0.12$ atm and $P_{N_2O_4} = 0.075$ atm.

$K =$ ______________

What is the equilibrium pressure of N_2O_4 if the equilibrium pressure of NO_2 is 0.36 atm and $K = 0.19$?

____

9.11-4. Extensive Reactions

An extensive reaction is one in which $K >> 1$; that is, one in which the equilibrium concentrations of the products exceed those of the reactants.

Determining how much reactant should be used in a reaction to produce a given amount of product is a common calculation in chemistry. In such calculations, it is often assumed that one of the reactants, called the limiting reactant, disappears completely, but this is the case only when K is very large. When the equilibrium constant is not very large, there will be a substantial amount of at least some reactants at equilibrium, so the amounts can be determined only if the value of the equilibrium constant is known.

A reaction with a very large equilibrium constant is said to be an ***extensive reaction***. The value of K is large when at least one of the concentrations in the denominator is very small. Thus, almost no limiting reactant remains at equilibrium in an extensive reaction, and the approximation that it disappears completely is valid.

EXERCISE 9.17:

Indicate whether the products, reactants, or neither would dominate the equilibrium mixture formed by adding equal amounts of all reactants in each of the following reactions.

$H_2(g) + I_2(g) \rightleftharpoons 2\ HI(g) \quad K = 600$
- products
- reactants
- neither

$HF(aq) + H_2O(l) \rightleftharpoons F^{1-}(aq) + H_3O^{1+}(aq) \quad K = 7 \times 10^{-4}$
- products
- reactants
- neither

$HCN(aq) + NH_3(aq) \rightleftharpoons CN^{1-}(aq) + NH_4^{1+}(aq) \quad K = 0.7$
- products
- reactants
- neither

9.11-5. Thermodynamic Definition of K

Thermodynamic Basis for Equilibrium

There is a driving force for the forward reaction that depends upon the concentrations of the substances on the left side of the chemical equation and one for the reverse direction that depends upon the concentrations of those on the right side. The difference between these two driving forces is ΔG. Thus, there are three possibilities.

- $\Delta G < 0$: the driving force in the forward direction is greater, so the reaction proceeds from left to right ($\rightarrow$).
- $\Delta G > 0$: the driving force in the reverse direction is greater, so the reaction proceeds from right to left ($\leftarrow$).
- $\Delta G = 0$: the driving forces are equal, so the reaction is at equilibrium ($\rightleftharpoons$).

Thus, $\Delta G = 0$ is the criterion for equilibrium, but it is the value of ΔG° that indicates where the equilibrium will be established. Indeed, the equilibrium constant for a reaction is related to the standard free energy of the following reaction.

$\Delta G^\circ = -RT \ln K.$

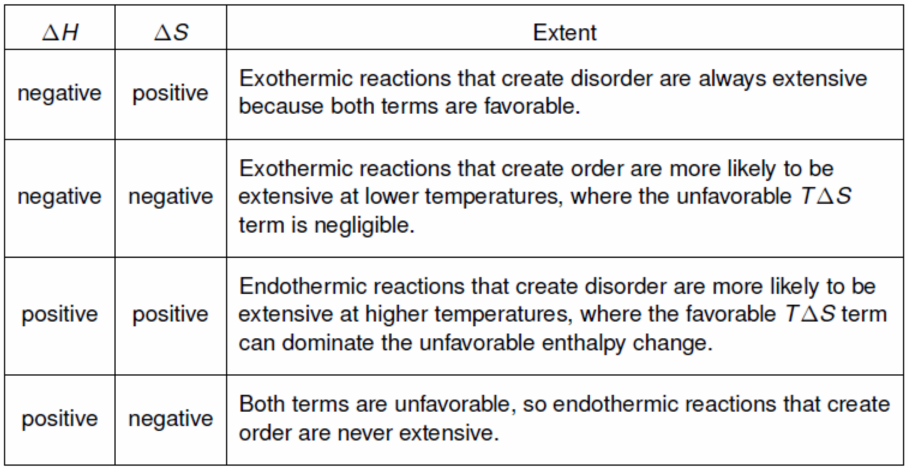
- $\Delta G \sim 0 \rightarrow K \sim 1 (\ln 1 = 0)$. When $K \sim 1$, the numerator and denominator of the equilibrium constant expression are nearly the same, so the equilibrium mixture is composed of comparable concentrations of both the reactants and products.
- $\Delta G^\circ << 0 \rightarrow K >> 1$. $K >> 1$ when the numerator (product concentrations) is much larger than the denominator (reactant concentrations), so the equilibrium mixture is dominated by the products, i.e., the reaction is extensive.
- $\Delta G^\circ >> 0 \rightarrow K << 1$. $K << 1$ when the numerator (product concentrations) is much smaller than the denominator (reactant concentrations), so the equilibrium mixture is dominated by the reactants, i.e., very little reaction takes place.

9.11-6. Predicting Extent of Reactions

The extent of reaction is determined by ΔG°, but ΔG° is related to the standard enthalpy and entropy changes by the following.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

By analogy to the discussion in Section 9.7, we can draw the following conclusions about the extent of a reaction.



ΔH	ΔS	Extent
negative	positive	Exothermic reactions that create disorder are always extensive because both terms are favorable.
negative	negative	Exothermic reactions that create order are more likely to be extensive at lower temperatures, where the unfavorable $T\Delta S$ term is negligible.
positive	positive	Endothermic reactions that create disorder are more likely to be extensive at higher temperatures, where the favorable $T\Delta S$ term can dominate the unfavorable enthalpy change.
positive	negative	Both terms are unfavorable, so endothermic reactions that create order are never extensive.

Table 9.10

9.11-7. Predicting Extent of Reactions Exercise

EXERCISE 9.18:

Use the chemical equation and the equilibrium composition to determine the sign of $\Delta G°$. Use the change in moles of gas to determine the sign of $\Delta S°$. Determine the sign of $\Delta H°$ from the other two.

$2\ HCl(g) \rightleftharpoons H_2(g) + Cl_2(g)$; Equilibrium: $[H_2] = [Cl_2] << [HCl]$

$\Delta G°$	$\Delta S°$	$\Delta H°$
$+$	$+$	$+$
$-$	$-$	$-$
~ 0	~ 0	~ 0

$HF(aq) + NO_2^{1-}(aq) \rightleftharpoons F^{1-}(aq) + HNO_2(aq)$; Equilibrium: $[F^{1-}] \sim [HNO_2] \sim [HF] \sim [NO_2^{1-}]$

$\Delta G°$	$\Delta S°$	$\Delta H°$
$+$	$+$	$+$
$-$	$-$	$-$
~ 0	~ 0	~ 0

$N_2(g) + 3\ H_2(g) \rightleftharpoons 2\ NH_3(g)$; Equilibrium: $[N_2] \sim [H_2] << [NH_3]$

$\Delta G°$	$\Delta S°$	$\Delta H°$
$+$	$+$	$+$
$-$	$-$	$-$
~ 0	~ 0	~ 0

9.11-8. Effect of T on K

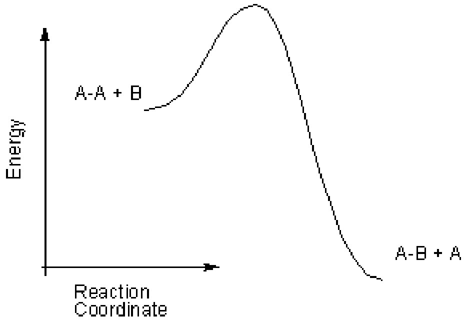
The value of an equilibrium constant varies with temperature. Changes in temperature change the thermal energy of the molecules, which changes the fraction of molecules at higher energy. *The fraction of molecules at higher energy increases when the temperature is increased.*

- **Exothermic reactions**: The reactants are on the higher energy side, so increasing the temperature increases the fraction of reactant molecules at equilibrium. Consequently, the equilibrium constants of exothermic reactions decrease when the temperature is increased.
- **Endothermic reactions**: The products are at higher energy, so increasing the temperature increases the fraction of product molecules at equilibrium. Consequently, the equilibrium constants of endothermic reactions increase when the temperature is increased.

9.11-9. Example

EXERCISE 9.19:

Assume that all reactants and products in the following are gases to answer the questions.



The equilibrium concentration of A-B is greater at which of the following?
high T
low T

Which is the stronger bond?
A-A
A-B

Is the reaction extensive?
Yes
No

Which reaction has the higher rate constant?
forward
reverse

9.12 Le Châtelier's Principle

Introduction

An open door that is not moving is at equilibrium. However, the equilibrium position of the door can be changed by applying pressure to either side. Reactions at equilibrium react in a similar fashion when they are exposed to a chemical stress.

Objectives

- Use Le Châtelier's Principle to determine the effect of changing the temperature or the concentration of one substance on the concentration of another substance in the equilibrium mixture.

9.12-1. Le Châtelier's Principle

Equilibrium mixtures respond to the addition or removal of material in a manner consistent with the following principle.

- **Le Châtelier's Principle: a system at equilibrium will respond to a stress in such a way as to minimize the effect of the stress**.

1 Increasing the concentration (or pressure) of one substance in an equilibrium mixture results in some reaction of that substance. The concentrations of the other substances on the same side of the equilibrium are reduced and the concentrations of those on the opposite side are increased by the reaction.

2 Decreasing the concentration (or pressure) of one substance in an equilibrium mixture results in some reaction of the other substances to replace some of what was removed. The concentrations of the other substances on the same side of the equilibrium as the removed substance all increase, while those of the substances on the opposite side decrease as a result of this reaction.

Adding or removing a pure liquid or solid does not affect the equilibrium mixture because the concentration of the pure substance is unchanged. However, the concentrations of all solutes are changed when solvent is removed.

EXERCISE 9.20:

Consider the following equilibrium.

$$AgCl(s) + 2\ NH_3(aq) \rightleftharpoons Ag(NH_3)_2^{1+}(aq) + Cl^{1-}(aq) \quad \Delta H < 0$$

Indicate whether each of the following actions would increase, decrease, or not affect the equilibrium concentration of Cl^{1-}

adding $Ag(NH_3)_2{}^{1+}$
- increase
- decrease
- not affect

removing $Ag(NH_3)_2{}^{1+}$
- increase
- decrease
- not affect

adding solid AgCl
- increase
- decrease
- not affect

adding NH_3
- increase
- decrease
- not affect

increasing temperature
- increase
- decrease
- not affect

9.13 Exercises and Solutions

Links to view either the end-of-chapter exercises or the solutions to the odd exercises are available in the HTML version of the chapter.

Chapter 10 – Solutions

Introduction

Solutions are homogeneous mixtures, i.e., mixtures whose properties are uniform throughout. Solutions are all around us. We live in a solution of gases called the atmosphere. A carbonated beverage is a solution of a gas in a liquid. Brass and solder are solutions of a solid in a solid. Solutions that are predominately water are called aqueous solutions. Drinks, blood, and the ocean are all aqueous solutions. All of the reactions we discuss at the end of this chapter and in the following two chapters take place in aqueous solutions, and an understanding of solutions is necessary to understanding these reactions. In this chapter, we examine the properties of solutions, predict whether one substance will dissolve in another, and discuss the nature of aqueous solutions of ionic substances.

10.1 Concentration

Introduction

The properties of a solution made from substances A and B depend upon the dominant type of interaction in the solution. The dominant interaction, A-A, B-B, or A-B, depends upon the relative number of each type of molecule, which is given by their concentrations. If the concentration of A is much greater than that of B, then A-A interactions dominate, and the solution properties are similar to those of A. Thus, the concentration of each substance in a solution is an important property of the solution. Although there are many ways to express concentration, we focus on the most common form used in the chemistry laboratory in this section.

Prerequisites

- 7.1 Partial Pressures

Objectives

- Define the terms *solution*, *solvent*, and *solute*.
- Distinguish between *homogeneous* and *heterogeneous* mixtures.
- Determine the molarity of a solution given the amount of solute a given volume of solution contains.
- Determine the volume required to deliver a given number of moles of solute or the number of moles of solute in a given volume of a solution of known molarity.

10.1-1. Definitions

Solutions involving liquids are comprised of a solvent and at least one solute.

homogeneous mixture	Homogeneous mixtures are mixtures that have constant composition throughout. A mixture made by mixing water and alcohol or by dissolving sugar in water is homogeneous because the alcohol, sugar, and water molecules are dispersed evenly throughout the mixture. Thus, the ratio of sugar or alcohol molecules to water molecules is the same no matter the location or size of the sample. Consequently, the properties of the mixture are also the same throughout.
heterogeneous mixture	Heterogeneous mixtures do not have uniform composition. Mixing table salt and sugar or water and oil produces a heterogeneous mixture because the properties of a sample of the mixture can vary from those of one substance to those of the other.
solution	A solution is a homogeneous mixture. A mixture of water and alcohol is a solution as is a mixture made by dissolving sugar in water.
solvent	The component of a solution that dictates the phase of a solution. If a liquid is present, it is the solvent. Water is the most common solvent. If more than one liquid is present, the liquid in greater amount is usually considered to be the solvent, but water is sometimes considered the solvent even if it is not present in the greatest amount.
solute	A solute is a component of a solution that is not the solvent. A solution is made by dissolving one or more solutes in a solvent.
concentration	The concentration of a solute is the ratio that relates the amount of the solute to the amount of either the solvent or the entire solution.

Table 10.1: Some Definitions

10.1-2. Molarity

The molarity of a solute is the number of moles of that solute per liter of solution.

The concentration of a solute gives the amount of solute present in a given amount of solution or solvent. There are many ways to give concentration, but the most common method in the chemistry laboratory is molarity. The **molarity** of a solute is defined as the number of moles of solute per liter of solution, which can be stated mathematically as follows.

$$M_{\mathrm{A}} = [\mathrm{A}] = \frac{\text{moles of solute}}{\text{liters of solution}}$$

The expression "[A] = 0.1 M" is read as "the concentration of A is 0.1 molar." It means that each liter of solution contains 0.1 mol A.

Molarity is useful in determining how much solute is needed to prepare a solution.

EXAMPLE:

For example, to determine the mass of NaCl required to make 2.0 L of a 0.20 M solution of NaCl:

$$2.0\text{ L solution} \times \frac{0.20\text{ mol NaCl}}{1\text{ L sol'n}} \times \frac{58.5\text{ g NaCl}}{1\text{ mol NaCl}} = 23.4\text{ g NaCl}$$

It is also useful in determining the amount of solute in a given amount of solution.

EXAMPLE:

For example, to determine the number of moles of NaCl present in 250 mL of 0.20 M NaCl:

$$250 \text{ mL sol'n} \times \frac{1 \text{ L sol'n}}{1000 \text{ mL sol'n}} \times \frac{0.20 \text{ mol NaCl}}{1 \text{ L sol'n}} = 0.050 \text{ mol NaCl}$$

10.1-3. Molarity Exercise

EXERCISE 10.1:

100 mL of solution contains 4.8 g sugar. What is the molar concentration of sugar (sucrose) in the solution [$C_{12}H_{22}O_{11}$]? How many mL of this solution would contain 0.0030 mol $C_{12}H_{22}O_{11}$?

1. First compute the molar mass of sugar.

______________ g/mol

2. Next, determine the number of moles of sugar.

______________ mol sugar

3. Determine the molarity of the sugar as the number of moles of sugar divided by the number of liters of solution in which it is dissolved.

______________ M

4. Use the molarity and the desired number of moles to determine the volume of solution required.

______________ mL sol'n

10.1-4. Solute to Solvent Ratio

Most of the solutions that we encounter are aqueous solutions, and their properties depend upon the ratio of solute to water particles. In this section, we examine the ratio of solute and solvent particles in a typical aqueous solution. We can determine the number of moles of solute present in a given volume of solution of known molarity, but, in order to determine the number of moles of solvent in a liter of solution, we must know the density of the solution, i.e., we must know the mass of a unit volume of the solution.

$$\text{density} = \frac{\text{mass of solution}}{\text{volume of solution}}$$

The density of water is 1.0 g/mL, or 1.0 g/cm^3. The density of a solution that is predominately water will be close to that of pure water.

10.1-5. Solution Exercise

EXERCISE 10.2:

How many water molecules are present for each sugar molecule ($C_{12}H_{22}O_{11}$, $M_m = 342$ g/mol) in a 0.1 M aqueous solution of sugar? Assume that the density of the solution is the same as pure water (1.0 g/mL).

Solution: We need to determine the ratio of moles of sugar to moles of water. We know there is 0.10 mol of sugar in a liter of solution, so we need to determine how many moles of water are in a liter of solution, which we can get from the mass of water in the solution since the mass of the solution = mass of water + mass of sugar.

1. First, we determine the mass of 1.0 L of solution.

______________ g soln

2. Next, compute the mass of sugar in 1.0 L of solution.

______________ g sugar

3. Next, determine the mass of water in 1.0 L of solution.

______________ g H_2O

4. Now, determine the number of moles of water in 1.0 L of solution.

______________ mol H_2O

5. Finally, determine the ratio of water molecules to sugar molecules in the 0.10 M solution.

______________ mol water/mol sugar

The properties of the solution are much more like those of water than those of sugar because there are so many more water molecules present. Indeed, this is why the density of the solution is nearly the same as that of pure water.

10.2 Solution Process

Introduction

In this section, we break the solution process into steps and examine the energy requirements of each step.

Prerequisites

- 9.2 Enthalpy (definition of enthalpy)
- 9.7 Free Energy (relationship between the standard free energy and the extent of a process)
- 9.11 Equilibrium and the Equilibrium Constant
- 9.5 Entropy (meaning of entropy)

Objectives

- Define the term solubility.
- Explain the three events involved in dissolving one substance in another and predict the sign of the enthalpy change for each.

10.2-1. Solubility

A substance is usually soluble when $\Delta H°$ of solution is negative or only slightly positive.

The maximum concentration that a solute can have in a given solvent at a given temperature is called its ***solubility*** in that solvent at that temperature. We will use the following terms to describe relative solubilities.

- **soluble**: A solute is soluble if its solubility is at least 0.1 M.
- **slightly soluble**: Substances with solubilities between 0.01 M and 0.1 M are slightly soluble.
- **insoluble**: Substances with solubilities less than 0.01 M are insoluble.
- **miscible**: Two liquids that are completely soluble in one another are said to be miscible. For example, alcohol and water are miscible, but water and gasoline are not.

Substance	Solubility in Water at 25 °C	Description		Substance	Solubility in Water at 25 °C	Description
NaCl	6 M	soluble		$CaSO_4$	0.02 M	slightly soluble
MgO	0.0003 M	insoluble		CuS	10^{-18} M	insoluble

Table 10.2: Some Solubilities

A solution in which the solute concentration is equal to its solubility is said to be **saturated**. When excess solid is added to a saturated solution, an equilibrium is established between the solid and the dissolved solute. For example, the following equilibrium is established when an excess of NaCl solid is added to water.

$$\mathrm{NaCl}(s) \rightleftharpoons \mathrm{NaCl}(aq)$$

The solubility of NaCl is given by the extent of the above reaction, which is given by the value of ΔG° for the reaction. $\Delta G^\circ = 0$ when [NaCl] = 1 M, which is above the minimum concentration established for a soluble substance (0.1 M). Thus, ***a substance is considered soluble when ΔG° is negative or only slightly positive***.

ΔS° is frequently positive for the solution process, so ***a substance is usually soluble if ΔH° of solution is negative or only slightly positive***. We consider the factors that determine ΔH° of solution in the next section.

10.2-2. Solution Process for Dissolving a Polar Solute in H_2O

To form a solution, the solute particles must be separated, cavities must be created in the solvent, and the solute particles must enter the cavities.

The following enthalpy changes must take place in order to create a solution. Note that all changes are at standard conditions, but the superscript zero has been omitted.

- ΔH_{solute} is the energy required to separate the solute particles.
- $\Delta H_{\text{solvent}}$ is the energy required to create the cavities in the solvent that will accommodate the solute particles.
- ΔH_{mixing} is the energy change produced when the solute particles enter the cavities in the solvent.

The processes and the energies involved when a polar solute dissolves in water are shown below.

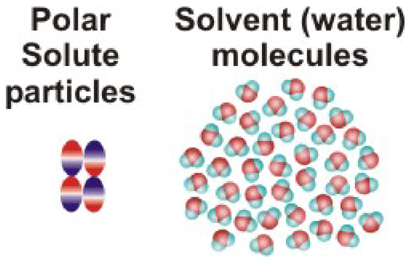


Figure 10.1a: Solution Process: Initial Conditions

Dipolar and dispersion forces between solute particles keep the solute in the solid state, while dispersion, dipolar, and hydrogen bonding forces keep the solvent in the liquid state. For ionic solutes, it is the ionic bonds that are holding the ions in the solid.

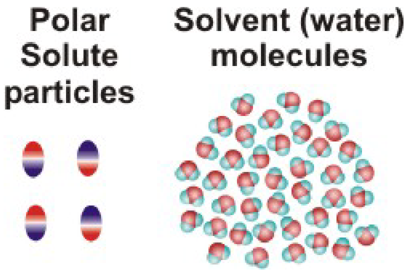


Figure 10.1b: Solution Process: ΔH_{solute}

ΔH_{solute} is the energy required to overcome the forces that hold the solute particles together. Dipolar and dispersion forces must be overcome for polar solutes, and ionic bonds must be broken for ionic solutes. ΔH_{solute} is always positive because separating the solute particles always requires energy.

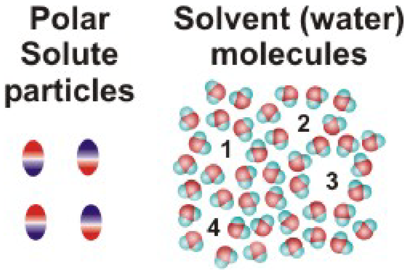


Figure 10.1c: Solution Process: $\Delta H_{\text{solvent}}$

$\Delta H_{\text{solvent}}$ is the energy required to separate solvent molecules to create cavities for the solute particles. $\Delta H_{\text{solvent}}$ is always positive because intermolecular forces must be overcome when the solvent particles are separated. When water is the solvent, the primary contribution to $\Delta H_{\text{solvent}}$ is the energy required to break hydrogen bonds.

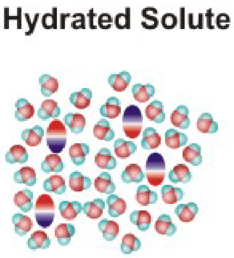


Figure 10.1d: Solution Process: ΔH_{mixing}

ΔH_{mixing} is the energy change that results when the solute enters the solvent cavities. ΔH_{mixing} is negative because interactions between the solvent and the solute always lower the energy of the system. The negative ends of the water dipoles interact with the positive ends of the solute dipoles (blue), while the positive ends of the water dipoles interact with the negative ends of the solute dipoles (red) to lower the energy. The solute is said to be solvated (hydrated when the solvent is water) as a result of these interactions.

10.2-3. Solvation

Solvation involves the creation of cavities in the solvent and solute particles entering those cavities.

The last two steps of the solution process (creating the cavities and placing the solute in the cavities) are combined into one term called ***solvation***.

$$\Delta H_{\text{solvation}} = \Delta H_{\text{solvent}} + \Delta H_{\text{mixing}}$$

The result is that the solute becomes ***solvated***. When the solvent is water, the process is called ***hydration*** and the solute becomes **hydrated**.

The energy change of the solution process can then be expressed as: $\Delta H_{\text{solution}} = \Delta H_{\text{solute}} + \Delta H_{\text{solvation}}$.

Recall that a substance is soluble in a solvent when $\Delta H_{\text{solution}}$ is negative or only slightly positive. Thus, a solute is most soluble in solvents in which the energy of solvation ($\Delta H_{\text{solvation}}$) is sufficiently exothermic to overcome the energy required to separate the solute particles (ΔH_{solute}). Consequently, ***a solute is most soluble in a solvent when the solute-solvent interactions are strong***, but interactions between different particles are strong when the same type of interactions are common to both types of particles. This is summarized by the general statement that ***like dissolves like***, which implies the following.

- Ionic and polar solutes are soluble in polar solvents.
- Nonpolar molecules are soluble in nonpolar solvents.

Thus, water is a good solvent for ionic compounds, such as NaCl and NH_4NO_3, and polar molecules, such as HCl and NH_3, but it is a poor solvent for nonpolar molecules, such as I_2 and CCl_4.

10.2-4. Like Dissolves Like Exercise

EXERCISE 10.3:

Use the rule that **like dissolves like** to answer the following.

Which of the following is more soluble in water?
HBr
Br_2

Which of the following is a better solvent for I_2?
CS_2
H_2O

In which of the following solvents would KCl be more soluble?
CCl_4
H_2O

10.3 Organic Compounds

Introduction

We concluded the last section with "like dissolves like." That is, polar solutes tend to be soluble in polar solvents such as water, while nonpolar molecules tend to be soluble in nonpolar solvents and insoluble in polar solvents such as water. However, large molecules can have both polar and nonpolar regions. In this section, we examine the solubility of such molecules in water.

Prerequisites

- 7.3 Intermolecular Interactions

Objectives

- Distinguish between hydrophobic and hydrophilic and explain the hydrophobic effect.
- Relate the solubility of a substance in water to the relative sizes of its hydrophilic and hydrophobic regions.

10.3-1. Organic Compounds

Regions of a molecule that interact well with water are hydrophilic, while regions that do not are hydrophobic.

Water is such an important solvent that we classify molecules by how well they interact with it. The term ***hydrophilic*** comes from the Greek for "water-loving" and is applied to molecules and regions of molecules that interact strongly with water. HCl and NH_3 are both polar molecules, so they are hydrophilic and water soluble molecules. The term ***hydrophobic*** comes from the Greek for "water-hating" and is applied to molecules that do not interact well with water and are not water soluble. I_2 and CCl_4 are nonpolar molecules that do not interact well with water, so they are both hydrophobic and water insoluble.

Organic compounds are based on carbon and usually contain a number of C–C and C–H bonds, both of which are nonpolar and hydrophobic, but organic molecules can also contain C–O and C–N bonds, both of which are polar and hydrophilic. Thus, organic compounds can contain both hydrophilic and hydrophobic regions.

Water molecules interact so much better with one another than with hydrophobic regions that water excludes or avoids hydrophobic regions whenever possible. In fact, water sets up an ice-like structure around hydrophobic regions. Indeed, it is the entropy decrease resulting from the formation of the ice-like structure that is most responsible for the low solubilities of hydrophobic substances. This effect is so strong and important that it is called the ***hydrophobic effect***. This effect is critical in the folding of proteins and formation of biological membranes.

10.3-2. Hydrophobic and Hydrophilic Examples

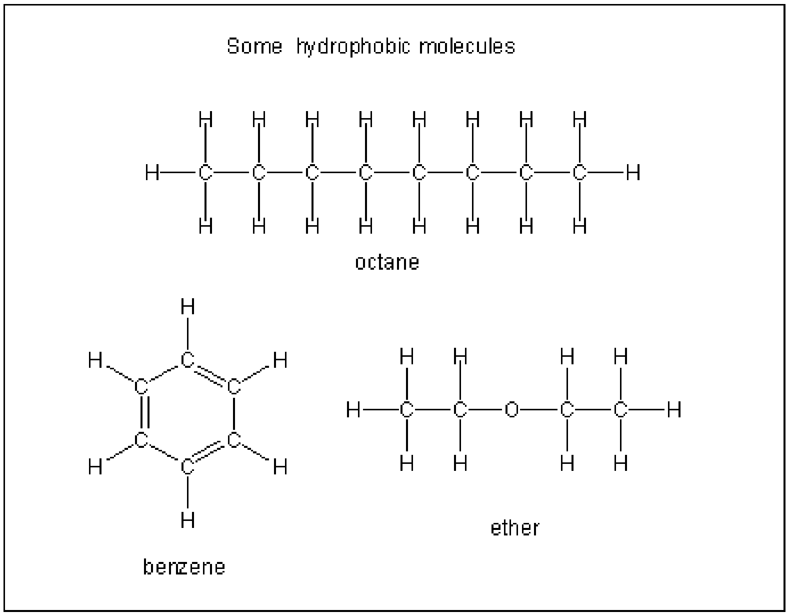


Figure 10.2a: Hydrophobic Molecules Hydrophobic molecules are not soluble in water because they contain many C–H bonds and are not very polar.

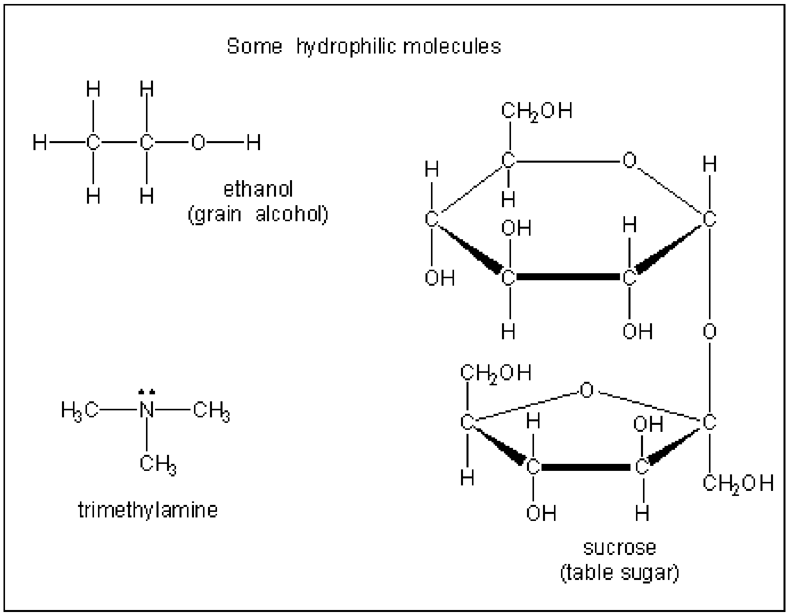


Figure 10.2b: Hydrophilic Molecules Hydrophilic compounds are water soluble because they contain O–H groups or a nitrogen lone pair that can interact strongly with water.

10.3-3. Acetone

Acetone, $(CH_3)_2C{=}O$, is a common laboratory solvent because many organic substances are soluble in it, and it is miscible with water. Acetone contains CH_3 groups that interact with other organic compounds through dispersion forces, so many organic substances dissolve in acetone. However, it also contains a polar C=O group, which makes the molecule hydrophilic. As with alcohols, the water solubility of compounds like this depends upon the lengths of the carbon chains; as the hydrophobic portion of the molecule increases, its solubility in water decreases. For example, $(CH_3CH_2CH_2CH_2)_2C{=}O$ is only slightly soluble in water.

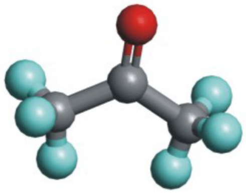


Figure 10.3: Ball-and-Stick Model of Acetone

10.3-4. Alcohols

The solubility of alcohols decreases as the hydrophobic region gets larger.

The water solubility of compounds that contain both hydrophobic and hydrophilic regions depends upon the relative sizes of the two regions. Consider the solubilities of alcohols in water and hexane (C_6H_{14}) shown in Table 10.3. The hydroxyl (O–H) group is hydrophilic, while the CH_2 groups are hydrophobic. Consequently, the solubility of an alcohol in water depends upon the relative number of O–H and CH_2 groups in the alcohol. As the relative number of CH_2 groups increases, the hydrophobic nature of the alcohol increases and its solubility in water decreases, while its solubility in nonpolar solvents, such as C_6H_{14}, increases. Increasing the relative number of hydroxyl groups makes the alcohol more hydrophilic and more soluble in water. Thus, hexanol ($CH_3(CH_2)_5OH$) is only slightly soluble in water (0.059 M), but hexanediol ($HO(CH_2)_6OH$), which has one hydroxyl group at each end, is miscible with water.

		Solvent
Alcohol	**H_2O**	**C_6H_{14}**
CH_3OH	∞	0.12 M
CH_3CH_2OH	∞	∞
$CH_3(CH_2)_2OH$	∞	∞
$CH_3(CH_2)_3OH$	0.91 M	∞
$CH_3(CH_2)_4OH$	0.31 M	∞
$CH_3(CH_2)_5OH$	0.059 M	∞
$CH_3(CH_2)_6OH$	0.015 M	∞

Table 10.3: Solubilities of Some Alcohols

10.3-5. Ether or Water Exercise

Ether is a common solvent that contains hydrophobic regions and is not very polar, but water is a very polar solvent with no hydrophobic regions.

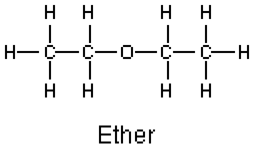


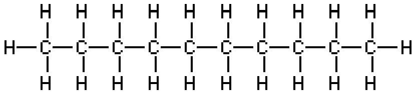
Figure 10.4

Consequently, polar substances are more soluble in water, and nonpolar substances are more soluble in ether (like dissolves like).

EXERCISE 10.4:

Are each of the following more soluble in water or in ether?

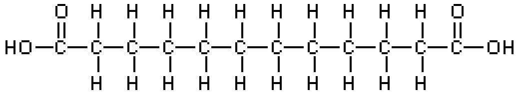
Decane



$CH_3(CH_2)_8CH_3$

water
ether

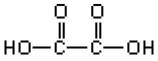
Dodecanedioic acid



$HOOC(CH_2)_{10}COOH$

water
ether

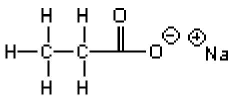
Ethanedioic (oxalic) acid



$HOOC-COOH$

water
ether

Sodium propanoate



$CH_3CH_2COO^{-}\ Na^{+}$

water
ether

10.4. Detergents and Micelles

Introduction

Grease and stains are hydrophobic, but we remove them by washing our dishes and clothing in water. We can do this because of the special properties of detergents, the topic of this section.

Prerequisites

- 7.3 Intermolecular Interactions

Objectives

- Describe a detergent and identify its head and tail.
- Describe *monolayers* and explain why they form.
- Describe micelles and explain how they function to dissolve hydrophobic materials in water.

10.4-1. Detergents and Soaps

Detergents and soaps each have a hydrophilic (polar) head and a long hydrophobic tail.

A ***detergent*** is a substance that has both a hydrophobic region, which interacts well with grease and stains, and a hydrophilic region, which interacts well with water. As an example, consider sodium dodecyl sulfate (SDS), which is a small detergent molecule. There are four different representations used for detergents.

1 space-filling

2 ball-and-stick

3 condensed structure that does not show C–H bonds explicitly

4 common abbreviation that is a skeletal drawing that indicates carbon atoms in the tail as the junction of two or more lines; the polar head is represented by a circle

Each drawing type is shown in Figures 10.5a, 10.5b, 10.5c, and 10.5d. The hydrophobic region of SDS consists of eleven CH_2 groups and one CH_3 group. The hydrophilic region consists of an anionic sulfate group. These regions are referred to as the hydrophobic **tail** and the hydrophilic or polar **head** of the detergent. The tails of most detergents contain 15 to 19 carbon atoms, so the 12-carbon chain of SDS is short for a detergent.

Soaps are derived from fatty acids and are similar to detergents except the polar head is a COO^{1-} (carboxylate) group. Their Ca^{2+} salts are water insoluble, and, since Ca^{2+} is a major source of water hardness, they do not function very well in hard water.

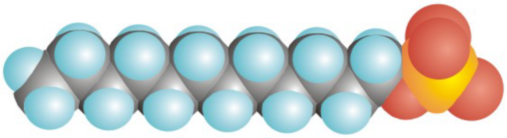


Figure 10.5a: Space-Filling Representation of SDS, a Detergent

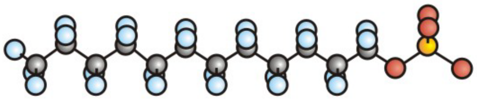


Figure 10.5b: Ball-and-Stick Representation of SDS, a Detergent

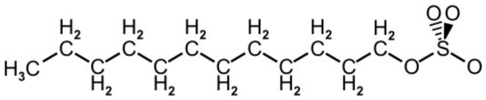


Figure 10.5c: Condensed Structure Representation of SDS, a Detergent

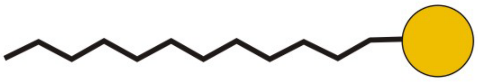


Figure 10.5d: Common Abbreviation Representation of SDS, a Detergent

10.4-2. Monolayers

At low concentrations, detergents form monolayers in which the tails extend out of solution.

The hydrophobic tails of a detergent interact well with one another, but the hydrophobic effect is so strong that they avoid water. Thus, when a small amount of a detergent is added to water, the polar heads enter the water but the hydrophobic tails do not. Consequently, a layer of detergent molecules that is only one molecule thick forms on the surface.

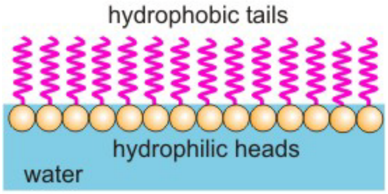


Figure 10.6: SDS Monolayer At small concentrations, SDS forms a monolayer (a layer that is one molecule thick) on the surface of the water. The hydrophobic tails stick up out of the water, while the hydrophilic heads enter the water.

10.4-3. Micelles

Micelles, which are composed of many detergent molecules, contain a hydrophobic center and a hydrophilic shell.

An increase in detergent concentration coupled with agitation forces the tails into the water, but the hydrophobic interaction is so strong that the tails attract one another (dispersion forces). The result is the formation of spheres, called ***micelles***, that are composed of 80–100 molecules. The surface of the micelle is composed of the polar heads, while the interior is an organic solvent (the strongly interacting tails). Thus, grease and stains are removed in water by the addition of a detergent, which forms micelles with agitation. The hydrophobic grease and stain molecules "dissolve" in the center of the micelle. The micelle, which dissolves in water because the surface is formed of the ionic heads, can then be washed away.

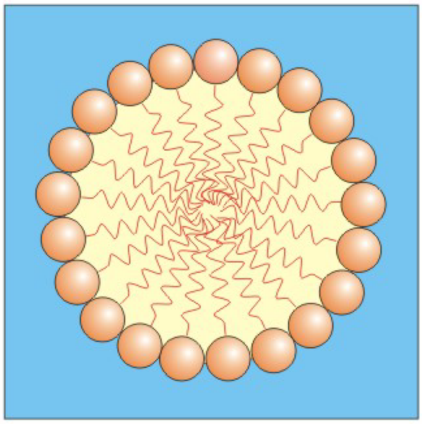


Figure 10.7: A Cross-Sectional View of a Micelle The polar heads are in direct contact with the aqueous environment and form a spherical shell around the hydrophobic interior.

10.5 Electrolytes

Introduction

Ionic compounds are not soluble in most solvents, but water is so polar that some ionic compounds do dissolve in it. Blood contains many ions, and the concentrations of those ions are critical to our well-being. Ions in water are responsible for water "hardness." In this section, we examine the nature of aqueous solutions of ionic compounds.

Prerequisites

- 1.8 Electromagnetism and Coulomb's Law
- 7.3 Intermolecular Interactions

Objectives

- Indicate whether a substance is an electrolyte or a nonelectrolyte.

10.5-1. Definitions

Aqueous solutions of electrolytes conduct electricity due to the presence of ions in solution. Ionic compounds, acids, and bases are electrolytes.

Consider the apparatus shown in Figures 10.8a and 10.8b. Two pieces of metal (**electrodes**) are immersed in a solution and connected to a power supply. The light bulb glows only if the solution conducts electricity, which completes the circuit. In order for solutions to conduct electricity, they must contain charged particles, i.e., ions. Thus, the light bulb glows only if the electrodes are dipped into a solution that contains ions.

Materials that dissolve in water as ions are called ***strong electrolytes***, and those that dissolve as molecules are called nonelectrolytes. However, some compounds dissolve as molecules that react with water to produce ions. If their reaction with water is extensive, they too are classified as strong electrolytes, but if the reaction produces some ions but is not extensive, the compound is classified as a ***weak electrolyte***. Solutions of strong electrolytes cause the light to burn brightly, those of nonelectrolytes do not cause the light to burn at all, and those of weak electrolytes cause the light to burn, but not as brightly because the concentrations of the ions are low.

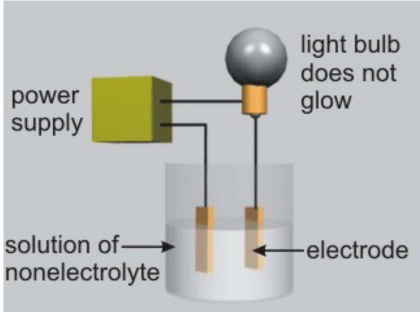


Figure 10.8a: Solutions of Nonelectrolytes Do Not Conduct Electricity

When no electrolytes (ions) are present, electricity is not conducted through the solution and the light bulb does not glow. Compounds whose aqueous solutions do not conduct electricty are called nonelectrolytes.

- Molecular compounds that are not acids or bases are nonelectrolytes. H_2O and most organic compounds are nonelectrolytes.

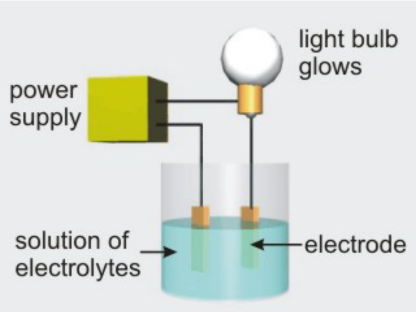


Figure 10.8b: Solutions of Electrolytes Do Conduct Electricity

Electrolytes (ions) conduct charge through the solution and complete the circuit, so the light bulb glows. Two types of compounds are electrolytes.

- **Ionic compounds** dissolve to produce metal cations and nonmetal anions. The ions can also be derived from polyatomic ions, such as ammonium or sulfate ions.
- **Acids** are compounds that produce H^{1+} when they dissolve in water. Production of the H^{1+} also produces a cation. For example, an aqueous solution of HCl is hydrochloric acid: $HCl \rightarrow H^{1+} + Cl^{1-}$. Since ions are produced when acids dissolve in water, acids are electrolytes. However, not all hydrogen-containing compounds are acids. Acids are those compounds whose formulas begin with an H. For example, HNO_3, $HClO_4$, and H_2SO_4 are some other common acids, while CH_4 is not an acid.

Solution	Glow	Solution Type	Solution Particles
water	none	nonelectrolyte	H_2O molecules
table salt	bright	strong electrolyte	Na^{1+} + Cl^{1-} ions
HCl	bright	strong electrolyte	$HCl \rightarrow H^{1+} + Cl^{1-}$ is extensive.
HF	dim	weak electrolyte	$HF \rightarrow H^{1+} + F^{1-}$ is NOT extensive.
table sugar	none	nonelectrolyte	$C_{12}H_{22}O_{11}$ molecules
$NaNO_3$	bright	strong electrolyte	Na^{1+} + $NO_3{}^{1-}$ ions
NaOH	bright	strong electrolyte	Na^{1+} + OH^{1-} ions
rubbing alcohol	none	nonelectrolyte	C_3H_5OH molecules
ammonia	dim	weak electrolyte	$NH_3 + H_2O \rightarrow NH_4{}^{1+} + OH^{1-}$ is NOT extensive.

Table 10.4: Conduction Properties of Some Aqueous Solutions

10.5-2. Ionic Compounds as Electrolytes

Ionic compounds are strong electrolytes, so when a solid ionic compound is dissolved in water, it goes into solution completely as ions. We will no longer use (aq) to indicate that an ion is in solution because isolated ions in chemcial equations are always in solution. Consider the following dissociations.

$$NaCl(s) \rightarrow Na^{1+} + Cl^{1-} \quad MgCl_2(s) \rightarrow Mg^{2+} + 2\ Cl^{1-} \quad K_2S(s) \rightarrow 2\ K^{1+} + S^{2-}$$

A solution of NaCl contains only Na^{+1} and Cl^{1-} ions; there are no NaCl molecules. Note that the chemical equation for the dissociation must have the same stoichiometry as the substance. Thus, the formula $MgCl_2$ indicates that there are two Cl^{1-} ions for every one Mg^{2+} ion, so the dissociation must express the same stoichiometry. Many ionic compounds contain polyatomic ions, but the bonds that hold the atoms in polyatomic ions are covalent and do not dissociate in water, so polyatomic ions enter solution intact.

$$NaNO_3(s) \rightarrow Na^{1+} + NO_3{}^{1-} \quad MgSO_4(s) \rightarrow Mg^{2+} + SO_4{}^{2-} \quad K_3PO_4 \rightarrow 3\ K^{1+} + PO_4{}^{3-}$$

10.5-3. Acids and Bases as Electrolytes

Ionic compounds are not the only class of compounds that are electrolytes; acids and bases are electrolytes as well. The first chemical definition of acids and bases was made by Svante Arrhenius.

An **Arrhenius acid** is a substance that produces H^{1+} ions when dissolved in water, and an **Arrhenius base** is a substance that produces OH^{1-} ions when dissolved in water.

Acids can be identified because the acidic protons are usually written first in their chemical formulas. For example, H_2S is an acid, so the protons appear first in its formula, but NH_3 is not, so the protons do not appear first in its formula. In Arrhenius theory, acids ionize in water in a manner similar to ionic substances, but only strong acids ionize completely. The common strong acids are HCl, HBr, HI, HNO_3, $HClO_4$, and H_2SO_4. For example, the following chemical equations represent the Arrhenius view of dissolving three strong acids in water.

$$HCl(g) \rightarrow H^{1+} + Cl^{1-} \quad HNO_3(l) \rightarrow H^{1+} + NO_3{}^{1-} \quad HClO_4(l) \rightarrow H^{1+} + ClO_4{}^{1-}$$

Most acids dissociate only partially in water, so they are weak acids. Weak acids are weak electrolytes because they produce only small amounts of H^{1+} and the anion in water. HF, HNO_2, and $HClO_2$ are examples of weak acids. The light bulb glows only dimly in a 0.1 M solution of a weak electrolyte because there are far fewer ions to conduct the electricity. Hydrofluoric acid is a weak acid as less than 10% of the HF molecules in a typical solution dissociate into their ions. To emphasize the fact that there are many more molecules than ions in a solution of a weak acid, the solution process is written with equilibrium arrows.

$$HF(aq) \rightleftharpoons H^{1+} + F^{1-} \quad HNO_2(aq) \rightleftharpoons H^{1+} + NO_2{}^{1-} \quad HClO_2(aq) \rightleftharpoons H^{1+} + ClO_2{}^{1-}$$

Metal hydroxides are the most common strong bases.

$$\mathrm{NaOH}(s) \rightarrow \mathrm{Na}^{1+} + \mathrm{OH}^{1-} \quad \mathrm{Ba(OH)_2}(s) \rightarrow \mathrm{Ba}^{2+} + 2\ \mathrm{OH}^{1-}$$

Most weak bases are also ionic and produce OH^{1-} ions as the result of the reaction of the anion with water. For example, F^{1-} and $\mathrm{NO_2}^{1-}$ ions are weak bases.

$$\mathrm{F}^{1-} + \mathrm{H_2O} \rightleftharpoons \mathrm{HF}(aq) + \mathrm{OH}^{1-} \quad \mathrm{NO_2}^{1-} + \mathrm{H_2O} \rightleftharpoons \mathrm{HNO_2}(aq) + \mathrm{OH}^{1-}$$

Ammonia is the most common example of a molecular substance that is a weak base.

$$\mathrm{NH_3}(aq) + \mathrm{H_2O} \rightleftharpoons \mathrm{NH_4}^{1+} + \mathrm{OH}^{1-}$$

10.5-4. Nonelectrolytes

Nonelectrolytes retain their molecular identity in solution.

Sucrose (table sugar) is a nonelectrolyte, so dissolving sucrose in water is represented as

$$\mathrm{C_{12}H_{22}O_{11}}(s) \rightarrow \mathrm{C_{12}H_{22}O_{11}}(aq)$$

10.5-5. Distinguishing Strong Electrolytes and Nonelectrolytes Exercise

EXERCISE 10.5:

Indicate whether each substance is an electrolyte or a nonelectrolyte.

- H_2O
  - electrolyte
  - nonelectrolyte
- $C_{12}H_{22}O_{11}$
  - electrolyte
  - nonelectrolyte
- NaCl
  - electrolyte
  - nonelectrolyte
- $NaNO_3$
  - electrolyte
  - nonelectrolyte
- HCl
  - electrolyte
  - nonelectrolyte
- NaOH
  - electrolyte
  - nonelectrolyte
- CH_3OH
  - electrolyte
  - nonelectrolyte

10.5-6. Distinguishing Strong and Weak Electrolytes Exercise

EXERCISE 10.6:

Indicate whether each substance is a strong electrolyte or a weak electrolyte.

- H_2SO_3
  - strong
  - weak
- HNO_3
  - strong
  - weak
- KF
  - strong
  - weak
- NH_3
  - strong
  - weak

10.5-7. Ion Concentrations in Solutions of Strong Electrolytes

Ionic compounds, such as NaCl, are strong electrolytes because all of the solid NaCl that dissolves dissociates into ions. Thus, a solution labeled 0.10 M NaCl contains Na^{1+} and Cl^{1-} ions, but no NaCl molecules. The ions react independently of one another; a chloride ion in a solution of NaCl is the same as one in a solution of KCl or $\mathrm{MgCl_2}$. Thus, it is the concentration of the ion, not the parent compound, that is important in solution chemistry. To convert from the concentration of the parent compound to that of any ion requires the stoichiometry of the chemical equation for the dissociation, which is given by the stoichiometry of the compound.

EXAMPLE:

For example, to determine the concentration of chloride ions in a 0.10 M $MgCl_2$ solution, we recognize that there are two moles of chloride ions for every one mole of $MgCl_2$ and write the following.

$$[Cl^{1-}] = \frac{0.10 \text{ mol } MgCl_2}{1 \text{ L solution}} \times \frac{2 \text{ mol } Cl^{1-}}{1 \text{ mol } MgCl_2} = \frac{0.20 \text{ mol } Cl^{1-}}{1 \text{ L solution}} = 0.20 \text{ M}$$

An aqueous solution that is labeled 0.10 M $MgCl_2$ is 0.10 M in Mg^{2+} ions and 0.20 M in Cl^{1-} ions, but it contains no $MgCl_2$!

10.5-8. Ion Concentration Exercise

EXERCISE 10.7:

What are the concentrations of the ions in the following solutions?

0.0364 M $BaCl_2$	0.108 M K_3PO_4
$[Ba^{2+}]$ = ______________ M	$[K^{1+}]$ = ______________ M
$[Cl^{1-}]$ = ______________ M	$[PO_4{}^{3-}]$ = ______________ M

10.6 Electrolyte Solutions

Introduction

Electrolytes are hydrated in aqueous solution. In this section, you can view an animation showing a crystal of NaCl dissolving in water.

Objectives

- Describe how a crystal of sodium chloride dissolves in water.

10.6-1. The Water Dipole

Ionic bonds must be broken when an ionic substance dissolves, but ionic bonds are strong interactions, so ΔH_{solute} is large and positive. Thus, $\Delta H_{\text{solvation}}$, the enthalpy of solvation (hydration in this case because the solvent is water), must be large and negative for an ionic substance to dissolve in water. In other words, the interaction between the water molecules and the ions must be very strong. This strong interaction arises because water has a strong dipole, which points from the center of the hydrogen atoms toward the electronegative oxygen atom. The large dipole of water also increases its dielectric constant (ϵ in Coulomb's Law), so water effectively shields each ion from the charge of surrounding ions.

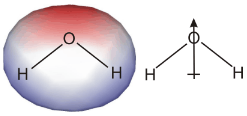


Figure 10.9: Water Dipole

10.6-2. The Solution Process

A video or simulation is available online.

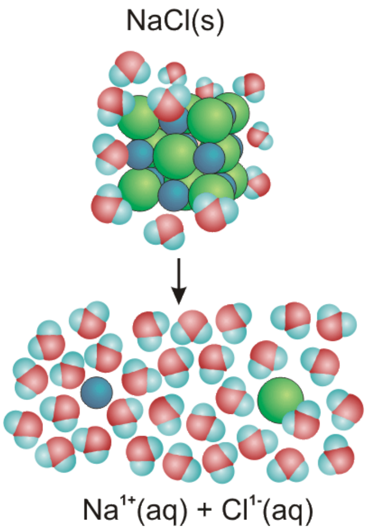


Figure 10.10: Dissolving Sodium Chloride in Water

- The sodium and chloride ions in a crystal adopt the sodium chloride structure with each sodium ion (represented by the blue spheres) surrounded by six chloride ions (represented by the green spheres) and each chloride ion surrounded by six sodium ions. Water is a very polar molecule with the center of positive charge residing between the two hydrogen atoms, and the negative charge centered on the oxygen atom. Only a small fraction of the water molecules are shown. There would be hundreds of water molecules for each ion in a typical solution, and the water molecules would be in contact with each other.
- The positive ends of the water dipoles interact with the chloride anions (green) on the surface of the crystal, while the negative ends interact with the sodium cations (blue) at the surface. The interactions are sufficiently strong to pull the ions on the surface of the crystal out into the solution.
- Six strongly interacting water molecules solvate (or hydrate in this case) each chloride ion in solution. There are many layers of water molecules around each ion. Note that the positive end of the dipole of each water molecule faces the chloride ion.
- The sodium ion is hydrated in the same manner as the chloride ion, except that it is the negative end of the water dipole that faces the cation. As in the case of the anion, the cation is surrounded by several layers of water molecules. The two oppositely charged ions do not recombine because the dipoles of the intervening water molecules arrange themselves in such a way as to insulate the two charges.

10.7 Dissolution of Ionic Substances

Introduction

Not all ionic substances are soluble in water. Indeed, most are not. In this section, we examine the factors that dictate the solubility of ionic substances in water and develop some simple rules to help us predict solubilities.

Prerequisites

- 1.8 Electromagnetism and Coulomb's Law (Describe the factors that dictate the force of attraction of two opposite charges suspended in some medium.)
- 4.5 Polyatomic Ions (Identify polyatomic ions.)

Objectives

- Relate solubility to the charge on the ions.

10.7-1. Dissolution and Coulomb's Law

The process whereby an ionic substance dissolves in water is called ***dissolution***. The chemical equation for the dissolution of calcium carbonate is $CaCO_3(s) \rightarrow Ca^{2+} + CO_3{}^{2-}$. As an approximation, we assume that an ionic substance is soluble when the force of attraction between its ions in solution is small enough that the ions can exist separately in solution, i.e., the force is not great enough that the separated ions attract one another to reverse the dissolution process. The force of attraction is described by Coulomb's Law.

$$F = \frac{kq_1q_2}{\epsilon r^2}$$

Although the solubility of ionic compounds is more complicated than a simple Coulombic attraction of the ions, we can still use Coulomb's Law to understand the process qualitatively by examining the factors that dictate the strength of the force of attraction. Thus, an ionic compound is likely soluble in water if the following are true.

- **r is very large**. r is a property of the solution because it is the distance between the ions in the solution. r depends only upon concentration; ions in concentrated solutions are closer than ions in dilute solutions. If a substance is soluble, then the force of attraction cannot be great even at moderate concentration, so r cannot be very large.
- **ϵ is large**. ϵ is the dielectric constant of the solvent and measures how well the solvent screens the charges in solution. The dielectric constant of water is about 40 times greater than that of a nonpolar solvent such as hexane (C_6H_{14}). This means that the force of attraction of two oppositely charged ions separated by the same distance is 40 times greater in C_6H_{14} than in water, so the ions are much less likely to recombine in water. The dielectric constants of several common solvents are given in Table 10.5.
- **q_1q_2 is small**. The product of the charges on the ions is the only factor that is a property of the ionic solute. Recall that the charges on ions typically fall in the range of -3 to $+3$; thus, q_1q_2 lies between 1 and 9. If the magnitude of the charge on either ion is 1, the magnitude of q_1q_2 cannot exceed 3, but if neither charge is 1, then the magnitude of q_1q_2 cannot be less than 4. Consequently, we expect that ionic compounds containing highly charged ions will not be as soluble in water as those containing $+1$ and -1 ions because the force of attraction between highly charged ions is too strong.

In general, ionic substances that contain a $+1$ and/or a -1 ion are more soluble than those that do not.

Solvent	Formula	ϵ		Solvent	Formula	ϵ
acetic acid	CH_3COOH	6.20		acetone	$(CH_3)_2C{=}O$	21.0
benzene	C_6H_6	2.28		carbon disulfide	CS_2	2.63
carbon tetrachloride	CCl_4	2.24		dimethyl sulfoxide	$(CH_3)_2S{=}O$	47.2
ether	$(C_2H_5)_2O$	4.27		ethanol	C_2H_5OH	25.3
hexane	C_6H_{14}	1.89		methanol	CH_3OH	33.0
water	H_2O	80.10				

Table 10.5: Dielectric Constants of Selected Solvents at 20 °C

10.7-2. Dissolution and Coulomb's Law Exercise

EXERCISE 10.8:

Use the rule that compounds with lower q_1q_2 products are more soluble than those with high q_1q_2 products to select the more soluble compound in each pair.

CsI	CaS	$CaCl_2$
$AlPO_4$	NH_4NO_3	Al_2O_3

10.7-3. Solubility Rules

The solubility rules offer only a rough guideline to the solubility of ionic compounds; there are many exceptions.

We have seen that the solubility of simple ionic compounds in water can be related in a simple way to the charge on the ions. The magnitude of q_1q_2 ranges from 1 (1×1) to 9 (3×3) if ions with charges greater than 3 are neglected. In addition, if the magnitude of either charge is 1, then the product ranges from 1 to 3. However, the magnitude of the charge product ranges from 4 to 9 if neither charge is 1. Thus, the attraction between charges is much smaller if the magnitude of one of the charges is only 1, and as a rough first approximation, ionic substances that contain a $+1$ or a -1 ion are soluble, while those that contain no $+1$ or -1 ions are not. This generalization is given by the solubility rules shown in Table 10.6.

Rule 1	Compounds of NH_4^{1+} and Group 1A ions are soluble.	Compounds containing a +1 and/or −1 ion are probably soluble. Hydroxides (OH^{1-}) are insoluble except by Rule 1, so they are a common exception.
Rule 2	Compounds of NO_3^{1-}, ClO_4^{1-}, ClO_3^{1-}, and $C_2H_3O_2^{1-}$ are soluble.	
Rule 3	Compounds of Cl^{1-}, Br^{1-}, and I^{1-} are soluble *except* those of Ag^{1+}, Cu^{1+}, Tl^{1+}, Hg_2^{2+}, and Pb^{2+}.	The insoluble halides appear to violate the +1/−1 rule for solubility, but these metals are late metals that are fairly electronegative, so their halides are not very ionic. For example, the Ag–Cl bond is only 30% ionic, and the Pb–Cl bond is only 15% ionic (see Chapter 5.2-5 Exceptions). Consequently, Coulomb's Law doesn't really apply here.
Rule 4	Compounds of SO_4^{2-} are soluble *except* those of Ca^{2+}, Sr^{2+}, Ba^{2+}, and Pb^{2+}.	Sulfates are the only soluble compounds that do not have to contain an +1 or −1 ion.
Rule 5	Most others are NOT soluble in water.	If an ionic substance is not soluble by Rules 1 through 4, then it is probably not soluble in water.

Table 10.6: Solubility Rules for Ionic Substances in Water

10.7-4. Solubility is a Matter of Degree

Solubilities vary from very soluble to very insoluble, but no ionic solid is completely soluble in water and none is completely insoluble. As is usually the case in chemistry, it is a matter of degree. Consider the following solubilities of some sulfates.

Compound	Molar Solubility
$BaSO_4$	0.000013
$PbSO_4$	0.00014
$SrSO_4$	0.00073
Hg_2SO_4	0.00010
$CaSO_4$	0.015
Ag_2SO_4	0.027
$Al_2(SO_4)_4$	1.1
$FeSO_4$	1.9
$MgSO_4$	3.0
$MnSO_4$	4.2

Table 10.7

In general, the solubilities in Table 10.7 are consistent with the solubility rules. However, our definition of soluble was that the solubility of the substance had to be at least 0.1 M, and a slightly soluble substance had to have a solubility between 0.01 and 0.1 M, so the following are inconsistencies in the solubility rules.

- $CaSO_4$ is slightly soluble, not insoluble.
- Ag_2SO_4 is slightly soluble, not soluble.
- Hg_2SO_4 is insoluble, not soluble.

Thus, Ag^{1+} and Hg_2^{2+} should be added to the list of ions that form insoluble sulfates if Ca^{2+} is included. We conclude that care must be taken when using the solubility rules too literally. They are only very rough guidelines.

10.7-5. Predicting Solubility Exercise

EXERCISE 10.9:

Which of the following compounds can be used to make a solution that is 0.1 M in Pb^{2+} ions?

$PbSO_4$
$Pb(NO_3)_2$
PbI_2
$Pb(OH)_2$

Which of the following compounds can be used to make a solution that is 0.1 M in ${CrO_4}^{2-}$ ions?

K_2CrO_4
$BaCrO_4$
$FeCrO_4$
Ag_2CrO_4

10.8 Precipitation of Ionic Substances

Introduction

Most reactions between ionic compounds take place in aqueous solutions, but not all of the species present in the solutions necessarily take part in the reactions. A ***net ionic equation***, or simply ***net equation***, is one that shows only those ions that are involved in the reaction. In this section, we learn how to predict which ions are involved in precipitation reactions and how to write net ionic equations for their reaction.

Prerequisites
- 1.8 Electromagnetism and Coulomb's Law

Objectives
- Write the net ionic equation for a simple precipitation reaction.
- Use the solubility rules to predict whether an ionic compound is expected to be soluble in water.
- Write a net ionic equation for the precipitation of an ionic compound from solution.
- Use the solubility rules to predict whether mixing two solutions will produce a precipitate.

10.8-1. Formation of AgCl

A net ionic equation shows only the ions involved in the precipitation. Spectator ions are not included.

It is often the case that when two clear solutions are mixed, a solid called a ***precipitate*** forms, or a precipitation reaction occurs. The ions that are present in solution but are not involved in the reaction are called ***spectator ions***. Spectator ions are present because they were paired with a reacting ion initially. For example, consider the net ionic equation to explain the fact that when solutions of NaCl and $AgNO_3$ are mixed, a white precipitate forms. First, we determine if the compound formed from each anion-cation combination is soluble (anion-anion and cation-cation interactions are repulsive and can be ignored). The following are possible combinations.

- $Na^{1+} + {NO_3}^{1-}$
- $Ag^{1+} + Cl^{1-}$

$NaNO_3$ is soluble from both Rules 1 and 2, so $Na^{1+} + {NO_3}^{1-}$ are spectator ions. AgCl is NOT soluble from Rule 3. Therefore, the white precipitate is AgCl. The net ionic equation is $Ag^{1+} + Cl^{1-} \rightarrow AgCl$.

$Ag^{1+} + Cl^{1-}$ → AgCl

→

The aqueous solution on the right contains Ag^{1+} and $NO_3{}^{1-}$ ions. The aqueous solution on the left contains Na^{1+} and Cl^{1-} ions.

→

$NaNO_3$ is soluble by Rules 1 and 2, and AgCl is insoluble by Rule 3. Thus, mixing the two solutions produces a solution of Na^{1+} and $NO_3{}^{1-}$ ions as well as a white precipitate of AgCl.

10.8-2. Video on the AgCl Precipitation Process

A video or simulation is available online.

The animation shows the addition of $AgNO_3$, which comes in from the top, to a solution of NaCl. Note the hydration of each of the ions. The ions are mobile in solution and do encounter each other. Only a very small fraction of the water molecules are shown for clarity. Recall that there are hundreds of water molecules for each ion.

- When the two cations or the two anions encounter one another, the force is repulsive.
- When Ag^{1+} and $NO_3{}^{1-}$ encounter one another, the force of attraction is weak enough that the shielding of the intervening water molecules (dielectric) prevents reaction.
- When Ag^{1+} encounters Cl^{1-}, the driving force to form a bond (mostly covalent in nature) is sufficient to overcome the shielding from water, and AgCl precipitates from solution.

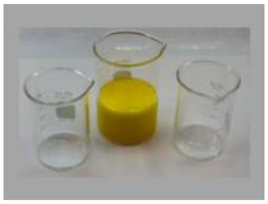
Note that the Na^{1+} and $NO_3{}^{1-}$ ions are surrounded only by water molecules at the beginning and end of the reaction, so they are unaffected by the reaction, i.e., they are spectator ions.

10.8-3. Predicting a Precipitate

EXERCISE 10.10:

Write the net ionic equation that describes the formation of a yellow precipitate when solutions of lead acetate and potassium iodide are mixed.

→



$K^{1+} + I^{1-}$ and $Pb^{2+} + C_2H_3O_2{}^{1-}$ → ?

First, determine which pair of ions reacts.

$Pb^{2+} + K^{1+}$
$Pb^{2+} + I^{1-}$
$C_2H_3O_2{}^{1-} + Cl^{1-}$
$C_2H_3O_2{}^{1-} + K^{1+}$

Write the balanced equation (Cation + Anion → Precipitate).

____________ + ____________ → ____________

10.8-4. Practice

EXERCISE 10.11:

Use the method developed previously and Table 10.6 to determine whether a reaction occurs when aqueous solutions containing the following are mixed. If a reaction does occur, write the balanced equation.

Sodium Phosphate and Silver Nitrate

Select the reacting ions or "no reaction."

Na^{1+} + Ag^{1+}
Na^{1+} + $NO_3{}^{1-}$
$PO_4{}^{3-}$ + Ag^{1+}
$PO_4{}^{3-}$ + $NO_3{}^{1-}$
no reaction

If there is a reaction, write the balanced equation (Cation + Anion → Precipitate).

____________ + ____________ → ____________

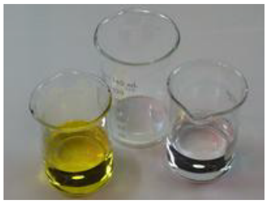
Ammonium Sulfate and Sodium Phosphate

Select the reacting ions or "no reaction."

$NH_4{}^{1+}$ + Na^{1+}
$NH_4{}^{1+}$ + $PO_4{}^{3-}$
$SO_4{}^{2-}$ + Na^{1+}
$SO_4{}^{2-}$ + $PO_4{}^{3-}$
no reaction

If there is a reaction, write the balanced equation (Cation + Anion → Precipitate).

____________ + ____________ → ____________



Potassium Chromate and Lead Nitrate

Select the reacting ions or “no reaction.”

- $Pb^{2+} + K^{1+}$
- $Pb^{2+} + CrO_4{}^{2-}$
- $NO_3{}^{1-} + K^{1+}$
- $NO_3{}^{1-} + CrO_4{}^{2-}$
- no reaction

If there is a reaction, write the balanced equation (Cation + Anion → Precipitate).

__________ + __________ → __________

Barium Acetate and Ammonium Sulfate

Select the reacting ions or “no reaction.”

- $Ba^{2+} + NH_4{}^{1+}$
- $Ba^{2+} + SO_4{}^{2-}$
- $C_2H_3O_2{}^{1-} + NH_4{}^{1+}$
- $C_2H_3O_2{}^{1-} + SO_4{}^{2-}$
- no reaction

If there is a reaction, write the balanced equation (Cation + Anion → Precipitate).

__________ + __________ → __________

Cobalt(II) Chloride and Sodium Phosphate

Select the reacting ions or “no reaction.”

- $Co^{2+} + Na^{1+}$
- $Co^{2+} + PO_4{}^{3-}$
- $Cl^{1-} + Na^{1+}$
- $Cl^{1-} + PO_4{}^{3-}$
- no reaction

If there is a reaction, write the balanced equation (Cation + Anion → Precipitate).

__________ + __________ → __________

Ammonium Sulfate and Silver Nitrate

Select the reacting ions or "no reaction."

$NH_4^{1+} + Ag^{1+}$

$NH_4^{1+} + NO_3^{1-}$

$SO_4^{2-} + Ag^{1+}$

$SO_4^{2-} + NO_3^{1-}$

no reaction

If there is a reaction, write the balanced equation (Cation + Anion → Precipitate).

____________ + ____________ → ____________

10.9 Solubility Equilibria

Introduction

A precipitate is in equilibrium with its ions in solution, and, in this section, we show how to treat that equilibrium quantitatively.

Prerequisites

- 9.11 Equilibrium and the Equilibrium Constant (Write the equilibrium constant expression for a reaction involving solids and solutes.)

Objectives

- Write the chemical equation to which the solubility product constant applies and write the solubility product constant expression for a compound.
- Determine the concentration of an ion in equilibrium with another ion of known concentration in a saturated solution of a compound composed of the ions.

10.9-1. Solubility Equilibria

When the amount of solid that is added to water exceeds the amount that is soluble in water at that temperature, the solid reaches equilibrium with the ions. For example, when solid AgCl is added to water, only a small amount of the solid dissolves as it reaches equilibrium with its ions.

$$\mathrm{AgCl}(s) \rightleftharpoons \mathrm{Ag}^{1+} + \mathrm{Cl}^{1-}$$

Recall that pure solids and liquids enter the equilibrium expression as 1 (unity), so the equilibrium constant for the above process would be written as $K = [\mathrm{Ag}^{1+}][\mathrm{Cl}^{1-}]/1$. Note that the equilibrium concentrations of the ions are determined by the solubility of AgCl and that the equilibrium constant is simply the product of the ion concentrations because the denominator is one. Consequently, the equilibrium constant is called the ***solubility product constant*** and given the symbol K_{sp}. The solubility product constant of AgCl is

$$K_{\mathrm{sp}} = [\mathrm{Ag}^{1+}][\mathrm{Cl}^{1-}] = 1.8 \times 10^{-10}$$

The fact that the value of K_{sp} is so small indicates how insoluble AgCl is. The expressions and values of several silver compounds are given in Table 10.8.

Compound	**K_{sp} expression**	**K_{sp} value**
AgCl	$[Ag^{1+}][Cl^{1-}]$	1.8×10^{-10}
Ag_2CrO_4	$[Ag^{1+}]^2[CrO_4{}^{2-}]$	1.1×10^{-12}
AgI	$[Ag^{1+}][I^{1-}]$	8.3×10^{-17}
Ag_2S	$[Ag^{1+}]^2[S^{2-}]$	6.3×10^{-50}
Ag_3PO_4	$[Ag^{1+}]^3[PO_4{}^{3-}]$	2.6×10^{-18}

Table 10.8: Solubility Product Constant Values and Expressions for Some Compounds of Silver

10.9-2. Exercise

EXERCISE 10.12:

The solubility product constant is given for a substance, but it applies to a process. Check your understanding by answering the following questions.

K_{sp} of zinc carbonate is 1.0 x 10^{-10}.

Write the process to which this number applies.

______ $\rightleftharpoons$ ______ + ______

Write the expression to which it applies. Specify the cation concentration first in the expression.

$K_{sp} =$ ______

K_{sp} of iron(III) hydroxide is 1.6×10^{-39}.

Write the process to which this number applies.

______ $\rightleftharpoons$ ______ + ______

Write the expression to which it applies. Specify the cation concentration first in the expression.

$K_{sp} =$ ______

10.9-3. Determining Equilibrium Concentrations

EXERCISE 10.13:

Solubility product constants can be used to determine the equilibrium concentrations of the ions present. The following example shows how this is done.

What is maximum [Fe^{3+}] that can exist in a solution in which [OH^{1-}] = 1.0×10^{-7} M?

The K_{sp} of iron(III) hydroxide is 1.6×10^{-39}.

First, write the process to which the solubility product constant applies.

__________ $\rightleftharpoons$ __________ + __________

Next, write the solubility product constant expression for the process with the cation concentration specified first.

$K_{sp} =$ __________

Substitute the known values for K_{sp} and [OH^{1-}] into the solubility product constant expression and solve for [Fe^{3+}].

__________ M

10.10 Exercises and Solutions

Links to view either the end-of-chapter exercises or the solutions to the odd exercises are available in the HTML version of the chapter.

Chapter 11 – Electron Transfer Reactions and Electrochemistry

Introduction

Redox, or electron transfer, reactions constitute one of the broadest and most important classes of reactions in chemistry. All reactions that involve molecular oxygen, such as combustion and corrosion, are electron transfer reactions. Biological processes, such as respiration, photosynthesis, and the breakdown of food molecules, consist of sequences of electron transfer reactions that serve to transport and utilize energy from the sun. Batteries are devices that allow us to utilize the free energy of electron transfer reactions.

11.1 Electron Transfer or Redox Reactions

Introduction

We begin our study of electron transfer reactions by introducing some terms and definitions and examining the electron transfer process.

Prerequisites

- 1.8 Electromagnetism and Coulomb's Law
- 4.2 Orbital Occupancies of Ions Exercise (Determine the electron occupancy of an ion from the occupancy of its atom and vice versa.)
- 4.4 Oxidation States (Determine the oxidation states of the atoms in a compound or ion.)
- 9.7 Free Energy (Describe the factors that dictate whether a chemical process is spontaneous.)
- 2.3 Bohr Model

Objectives

- Describe an electron transfer reaction.
- Define oxidation and reduction.
- Define oxidizing and reducing agent.
- Indicate whether a substance can act as an oxidizing agent or as a reducing agent or both.
- Identify the oxidizing and reducing agents in a redox reaction.
- Determine the number of electrons transferred in a balanced chemical equation for an electron transfer reaction.
- Identify the donor and acceptor orbitals in a simple redox reaction.
- Explain the effect of orbital energy on electron transfer.
- Identify the factor responsible for oxidizing and reducing strengths.
- Describe a redox couple and write the abbreviation for a given couple.

11.1-1. Electron Transfer Introduction Video

A video or simulation is available online.

11.1-2. Electron Transfer

Electrons move from one species to another in electron transfer reactions.

The reaction that occurs when iron (steel wool) is placed in a solution of $CuSO_4$ is shown in the table below.

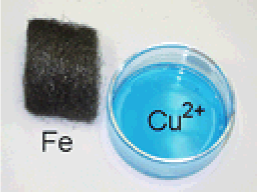
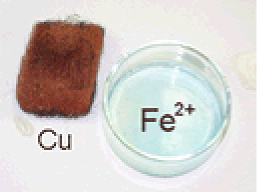
		→		
Steel wool consists primarily of Fe atoms.	Cu^{2+} ions gives a $CuSO_4$ solution its blue color.	→	The steel wool is coated with metallic Cu where it was immersed in the $CuSO_4$ solution.	The solution loses color because the Cu^{2+} have been displaced by colorless Fe^{2+} ions.

Table 11.1: An Electron Transfer Reaction

We can make the following observations:

1. The deep blue color of the $CuSO_4$ solution, which is due to the presence of Cu^{2+} ions, is lost.
2. A brown solid forms. Analysis shows that the solid is metallic copper.
3. The steel wool disintegrates as the Fe atoms disappear.
4. Analysis shows that Fe^{2+} ions are produced in the solution.

and draw the following conclusions:

1. Cu^{2+} has been converted to Cu.
2. Fe has been converted into Fe^{2+}.

In the reaction, the oxidation state of copper changes from +2 in the Cu^{2+} ions in solution to 0 in the atoms comprising metallic copper. Each Cu^{2+} ion must gain two electrons to become a Cu atom. Similarly, the oxidation state of iron changes from 0 in the atoms comprising the steel wool to +2 in the Fe^{2+} ions in solution. Each Fe atom must lose two electrons to be converted to an Fe^{2+} ion. Thus, each Fe atom gives up two electrons, while each Cu^{2+} gains two electrons, i.e., two electrons are transferred from iron atoms to Cu^{2+} ions in solution. This is an example of an **electron transfer reaction**. The reaction is written as

$$Cu^{2+} + Fe \rightarrow Cu + Fe^{2+}$$

11.1-3. Oxidation and Reduction

Reduction is a gain of electrons, oxidation is a loss of electrons, and electron transfer reactions are also called redox reactions.

Reduction is a gain of electrons. The added electrons "reduce" the oxidation state of the substance. Cu^{2+} ions gain two electrons, so they are reduced to Cu atoms. Note that the two-electron reduction lowers the oxidation state of copper from +2 in the ion to 0 in the atom.

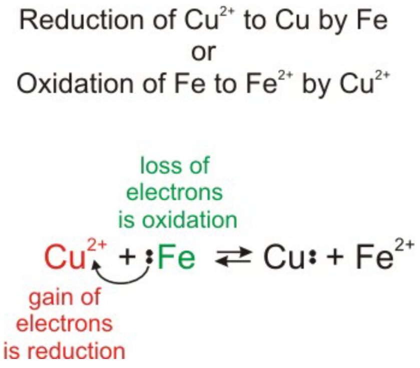


Figure 11.1

Oxidation is a loss of electrons. The loss of negative charge causes an increase in oxidation state of the substance. Fe atoms lose two electrons, so they are oxidized to Fe^{2+} ions. Note that the two-electron oxidation raises the oxidation state of iron from 0 in the atom to +2 in the ion.

Redox reactions are those that involve oxidation and reduction. Electron transfer reactions always involve both an oxidation and a reduction because electrons cannot be gained if none are lost.

11.1-4. Oxidizing and Reducing Agents

Oxidizing reagents (oxidants) are reduced when reducing agents are oxidized.

Electron transfer results from a combination of oxidation and reduction. A species cannot be oxidized unless another species accepts the electrons and is reduced. That is, oxidation causes reduction and *vice versa*. Consequently, the species that is oxidized by the reaction is referred to as the ***reducing agent*** or ***reductant***, and the species that is reduced by the reaction is called the ***oxidizing agent*** or ***oxidant***.

The reducing agent contains the electrons that are transferred during the reaction, so it is in its reduced form, which we will designate Red_1. Transferring the electrons converts it to its oxidized form, which we will call Ox_1. Similarly, the oxidizing agent has unfilled orbitals that can accept the transferred electrons, so it is in its oxidized form, Ox_2. Accepting the electrons converts it to its reduced form, Red_2. A typical redox reaction can be expressed as follows.

$$\mathrm{Red}_1 + \mathrm{Ox}_2 \;\rightarrow\; \mathrm{Ox}_1 + \mathrm{Red}_2$$

Thus, ***the reducing agent, Red$_1$, can be identified as the reduced form (form in lower oxidation state) of species 1, while the oxidizing agent, Ox$_2$ is the oxidized form (form in higher oxidation state) of species 2.***

11.1-5. Requirements for Reducing and Oxidizing Agents

The oxidation state of an atom should be high if it is to be an oxidizing agent and low if it is to be a reducing agent.

In order to function as a reducing agent, a substance must be able to give up electrons and attain a higher oxidation state, so reducing agents must contain atoms that can be oxidized. Similarly, oxidizing agents must be able to accept electrons to attain a lower oxidation state, so oxidizing agents must contain atoms that can be reduced. For example, the nitrogen atom in NH_3 has an oxidation state of −3, which is the lowest oxidation state that nitrogen can have. Therefore, NH_3 can be oxidized but not reduced, so it can be a reducing agent. The nitrogen atom in $NO_3{}^{1-}$ is in the +5 oxidation state, the highest it can have, so nitrate ion cannot be oxidized or serve as a reducing agent, but it can be reduced and function as an oxidizing agent.

EXERCISE 11.1:

Indicate whether each of the following could function only as a reducing agent, only as an oxidizing agent, or as both.

Na	Br_2	$MnO_4{}^{1-}$
reducing	reducing	reducing
oxidizing	oxidizing	oxidizing
both	both	both

11.1-6. Oxidizing and Reducing Agents in Reactions

To determine the oxidizing and reducing agents in a redox reaction, you must first identify the atoms whose oxidation states are changing. Oxidation state changes are usually assigned to a single atom of a molecule or polyatomic ion involved in a redox reaction, but the molecule or ion is the oxidizing or reducing agent. The following points should help you identify the oxidizing and reducing agents:

1 Any atom present as an **element** is being oxidized or reduced.

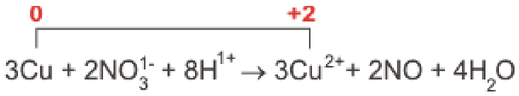
2 O and H are frequently found in redox reactions, but recall from Chapter 4 that the oxidation states of O and H in most of their compounds are −2 and +1, respectively, so they seldom change oxidation states. Thus, ***H_2O, H^{1+}, or OH^{1-} are seldom involved in the electron transfer***. Exceptions occur when either is elemental (O_2 and/or H_2).

3 Transition metals and polyatomic ions are frequently involved in redox reactions.

Identify the oxidizing agent, the reducing agent, and the number of electrons transferred in the following redox reaction.

$$3\ \mathrm{Cu} + 2\ \mathrm{NO_3}^{1-} + 8\ \mathrm{H}^{1+} \rightarrow 3\ \mathrm{Cu}^{2+} + 2\ \mathrm{NO} + 4\ \mathrm{H_2O}$$

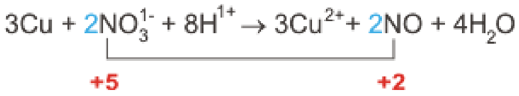
We identify elemental copper (Point 1) as a redox reactant. Point 2 can be used to ignore O and H. Copper is oxidized from 0 to +2, so ***Cu is the reducing agent***.



We identify nitrate ion (Point 3) as a redox reactant. Point 2 can be used to ignore O and H. The oxidation state of nitrogen in the nitrate ion is determined using the rules developed in Section 4.4 as

$$\begin{aligned} \text{charge on ion} &= \mathrm{OX_N} + 3\mathrm{OX_O} \\ -1 &= \mathrm{OX_N} + 3(-2) \\ \mathrm{OX_N} &= -1 + 6 \\ &= +5 \end{aligned}$$

Similarly, the oxidation state of nitrogen in NO is +2, so nitrogen is reduced from +5 to +2. However, the oxidizing agent is the molecule or ion, not the atom, so **nitrate ion is the oxidizing agent**. Actually, the oxidizing agent is nitric acid due to the presence of the H^{1+} ions. The simplest definition of an acid is a substance that produces H^{1+} ions in water. Acids are discussed in detail in Chapter 12.



11.1-7. Electrons Transferred

The number of electrons transferred in a reaction, i.e., the number gained by the oxidizing agent or lost by the reducing agent, is an important characteristic of a balanced redox equation. Consider the following redox equation:

$$\mathrm{Cr} + 3\ \mathrm{Ag}^{1+} \rightarrow \mathrm{Cr}^{3+} + 3\ \mathrm{Ag}$$

Each chromium atom loses three electrons as its oxidation state changes from 0 to +3. There is only one chromium atom in the equation, so the number of electrons lost by the chromium atoms in the above equation is

$$n = 1\ \text{Cr atom} \times \frac{3\ \text{electrons}}{1\ \text{Cr atom}} = 3\ \text{electrons}$$

Each silver ion gains one electron as its oxidation state changes from +1 to 0. However, there are three silver ions, so the number of electrons lost is

$$n = 3\ \mathrm{Ag}^{1+}\ \text{ions} \times \frac{1\ \text{electron}}{1\ \mathrm{Ag}^{1+}\ \text{ion}} = 3\ \text{electrons}$$

The balanced equation involves a three-electron transfer, i.e., $n = 3$.

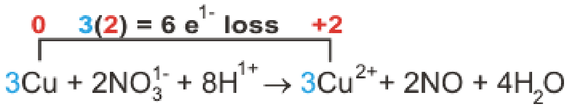
11.1-8. Electrons Transferred Example

The following demonstrates the method for determining the number of electrons transferred in both the oxidation and reduction processes.

Redox Reaction:

$$3\ \mathrm{Cu} + 2\ \mathrm{NO_3}^{1-} + 8\ \mathrm{H}^{1+} \ \rightarrow\ 3\ \mathrm{Cu}^{2+} + 2\ \mathrm{NO} + 4\ \mathrm{H_2O}$$

Oxidation:

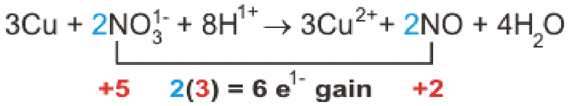


Copper's oxidation state changes from 0 to +2, which is a two-electron loss by each copper atom. There are three copper atoms in the equation, so

$$n = 3\ \text{Cu atoms}\ \times \frac{2\ \text{electrons}}{1\ \text{Cu atom}} = 6\ \text{electrons}$$

This is a six-electron oxidation.

Reduction:



The nitrogen atom in the nitrate ion is in a +5 oxidation state, but the N atom is +2 in NO. Thus, each nitrogen atoms gains three electrons. There are two nitrogen atoms on each side of the equation, so

$$n = 2\ \text{N atoms}\ \times \frac{3\ \text{electrons}}{1\ \text{N atom}} = 6\ \text{electrons}$$

This is a six-electron reduction.

As required, the number of electrons gained in the reduction equals the number lost in the oxidation. We conclude that the reaction is a six-electron transfer reaction.

11.1-9. Practice

EXERCISE 11.2:

Indicate the oxidizing agent (Ox), the reducing agent (Red), and the number of electrons transferred (n) in the following redox reactions.

$$2\ Ag^{1+} + Cu \rightarrow 2\ Ag + Cu^{2+}$$

Ox = ______________ Red = ______________ $n =$ ______________

$$2\ Cr + 6\ H^{1+} \rightarrow 2\ Cr^{3+} + 3\ H_2$$

Ox = ______________ Red = ______________ $n =$ ______________

$$Fe_2O_3 + 3\ CO \rightarrow 2\ Fe + 3\ CO_2$$

Ox = ______________ Red = ______________ $n =$ ______________

$$5\ Au + 3\ MnO_4{}^{1-} + 24\ H^{1+} \rightarrow 5\ Au^{3+} + 3\ Mn^{2+} + 12\ H_2O$$

Ox = ______________ Red = ______________ $n =$ ______________

11.1-10. Donor/Acceptor

A video or simulation is available online.

Reducing agents are also called electron donors, while oxidizing agents are also called electron acceptors.

In a redox reaction, electrons transfer from a set of orbitals on the electron donor called the ***donor orbitals*** into a set of orbitals on the acceptor called the ***acceptor orbitals***. The ***redox electrons*** are in the donor orbitals, so the donor must be in a reduced form of the substance, which is designated Red_1. The acceptor orbitals can accept the redox electrons, so the acceptor must be in an oxidized form, which is designated Ox_2.

Electron transfer removes electrons from the donor orbitals of the reducing agent, so they are converted into acceptor orbitals, and the substance into an oxidizing agent. Similarly, the transfer places electrons into the acceptor orbitals of the oxidizing agent, so they are converted into donor orbitals and the substance into a reducing agent.

The spontaneous process $Red_1 + Ox_2 \rightarrow Ox_1 + Red_2$ is considered below.

Reactants

Reactant 1 is in its reduced form (Red_1), so it is a donor. Reactant 2 is in the oxidized form (Ox_2), so it is an acceptor. As we shall see in the next section, the fact that the reaction is spontaneous usually implies that the donor orbitals are higher in energy than the acceptor orbitals.

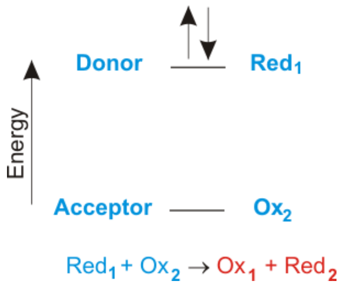


Figure 11.2: Reactant Energies

Products

Electron transfer empties the redox orbital of Reactant 1, so Product 1 is in its oxidized form (Ox_1). Electron transfer fills the redox orbital on Reactant 2, so it is in its reduced form (Red_2). Ox_1 has an empty orbital, so it is now an acceptor (oxidizing agent), and Red_2 has a filled orbital, so it is now a donor (reducing agent). Thus, ***electron transfer converts the oxidizing agent into a reducing agent and the reducing agent into an oxidizing agent.***

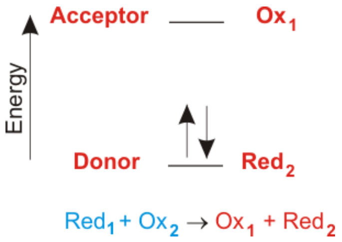


Figure 11.3: Product Energies

11.1-11. Lower Energy

Spontaneous electron transfer occurs between oxidizing and reducing agents if the products are weaker reducing and oxidizing agents.

Recall from Section 9.7 that a reaction proceeds spontaneously at constant temperature and pressure so as to minimize its free energy. Furthermore, a reaction is extensive if its standard free energy change is negative. Thus, electrons transfer spontaneously from a donor to an acceptor if the transfer reduces their free energy, and they transfer extensively if the transfer reduces the standard free energy. We shall soon see that there are several factors that contribute to the standard free energy change, but the most important is often the orbital energy difference. Thus, ***the driving force behind many redox reactions arises because the acceptor orbitals are much lower in energy than the donor orbitals***.

In an extensive electron transfer, the donor orbitals are at higher energy than the acceptor orbitals in the reactants, but the acceptor orbitals are at higher energy in the products. Consequently, the produced oxidizing agent is weaker than the reacting oxidizing agent (the acceptor orbital is lower in the reactants). In addition, the produced reducing agent is weaker than the reactant reducing agent (the donor orbital is higher in the reactants). We conclude that ***spontaneous electron transfer occurs between stronger oxidizing and reducing agents to produce weaker reducing and oxidizing agents.*** Weak reactants do not react to produce strong ones.

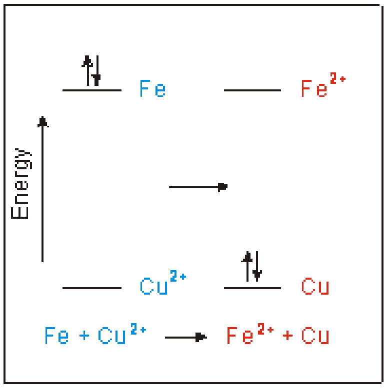


Figure 11.4

Electron transfer between Fe and Cu^{2+} is extensive because the occupied orbitals of Fe are much higher in energy than the unfilled orbitals of Cu^{2+}.

Electron transfer from Cu back to Fe^{2+} is not extensive (Cu does not reduce Fe^{2+}) because the electrons of Cu are much lower in energy than the unfilled orbitals of Fe^{2+}. Electrons do not transfer extensively to higher energy.

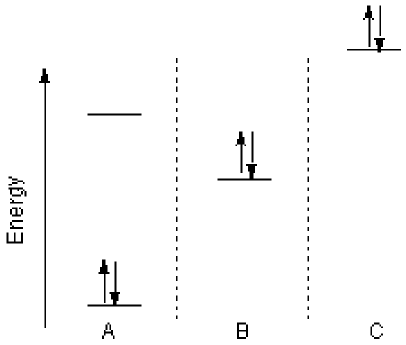
11.1-12. Oxidizing and Reducing Agent Strengths

Strong reducing agents have high-energy electrons, and strong oxidizing agents have unfilled orbitals at low energy.

Strong reducing agents have high-energy electrons, and strong oxidizing agents have unfilled orbitals at low energy. When a strong oxidizing agent comes into contact with a strong reducing agent, the high-energy electrons in the donor orbitals flow spontaneously into the unfilled orbitals at much lower energy on the acceptor. As we shall soon see, the free energy that is released can be used to do work in batteries. If the donor orbitals are much lower than the acceptor orbitals, the reducing and oxidizing agents are too weak, and the electrons are not transferred.

EXERCISE 11.3:

Use the following energy diagram of the valence orbitals of A, B, and C to answer the question. Add two electrons to the unfilled orbital on A to form A^{2-} and remove the electrons from the occupied orbitals on A, B, and C to form A^{2+}, B^{2+} and C^{2+}. Assume that orbital energy differences are the dominant term in the free energy to answer the following.



best oxidizing agent
- A^{2+}
- A
- A^{2-}
- B
- B^{2+}
- C
- C^{2+}

oxidizes A^{2-} but not A
- A
- A^{2-}
- B
- B^{2+}
- C
- C^{2+}

best reducing agent
- A^{2+}
- A
- A^{2-}
- B
- B^{2+}
- C
- C^{2+}

reduces B^{2+} but not C^{2+}
- A^{2+}
- A
- A^{2-}
- B
- B^{2+}
- C^{2+}

reduces A
- A^{2+}
- A^{2-}
- B
- B^{2+}
- C
- C^{2+}

oxidizing and reducing agent
- A^{2+}
- A
- A^{2-}
- B
- B^{2+}
- C
- C^{2+}

11.1-13. Redox Couple

An oxidizing agent and the reducing agent it becomes are called a redox couple.

Electron transfer converts a reducing agent (Red_1) into an oxidizing agent (Ox_1) and converts an oxidizing agent (Ox_2) into a reducing agent (Red_2). The oxidizing agent and the reducing agent it becomes form a redox couple. Redox reactions involve two redox couples. A redox couple is written as the oxidized form, a slash, and then the reduced form (Ox/Red). For example, the two redox couples in the reaction of copper(II) and iron are expressed as follows:

- reduction couple: Cu^{2+}/Cu
- oxidation couple: Fe^{2+}/Fe

EXERCISE 11.4:

Consider the following redox reaction:

$$Ag + VO_2{}^{1+} + 2\ H^{1+} \rightarrow Ag^{1+} + VO^{2+} + H_2$$

What atom is oxidized? Give the symbol. __________

The oxidation couple (Ox/Red) is __________

What atom is reduced? Give the symbol. __________

The reduction couple (Ox/Red) is __________

11.2 Half-Reactions

Introduction

Redox reactions can be broken down into two half-reactions, an oxidation and a reduction, that show the loss and gain of electrons explicitly. The total reaction is the sum of the two half-reactions. Using half-reactions simplifies the writing of balanced redox reactions and helps us better quantify the driving force behind a redox reaction.

Objectives

- Identify the half-reaction involved in a redox reaction.
- Write a balanced redox reaction given a table of reduction half-reactions.

11.2-1. Half-Reactions

A redox reaction can be broken down into two ***half-reactions***: an oxidation half-reaction and a reduction half-reaction. The electrons gained are shown as reactants in the reduction half-reaction, and the electrons lost are shown as products in the oxidation half-reaction. The net redox reaction is simply the sum of the two half-reactions. The two half-reactions in the redox reaction between Fe and Cu^{2+} are:

oxidation half-reaction: $Fe \rightarrow Fe^{2+} + \mathbf{2\ e^{1-}}$

reduction half-reaction: $Cu^{2+} + \mathbf{2\ e^{1-}} \rightarrow Cu$

net reaction: $Fe + Cu^{2+} \rightarrow Fe^{2+} + Cu$

Note that the electrons gained in the reduction equals the number lost in the oxidation, so the electrons cancel in the sum to yield the net reaction. The ***net reaction never contains electrons because the number of electrons gained in the reduction must be the same as the number lost in the oxidation***.

EXERCISE 11.5:

Consider the following reaction:

$$3\ \text{Sn} + 2\ \text{Cr}^{3+} \rightarrow 3\ \text{Sn}^{2+} + 2\ \text{Cr}$$

Represent the oxidation half-reaction as z Red → z Ox + n e^{1-}.

$$z\ \text{Red} \rightarrow z\ \text{Ox} + n\ e^{1-}$$

__________ → __________ + __________

Represent the reduction half-reaction as y Ox + n e^{1-} → y Red.

$$y\ \text{Ox} + n\ e^{1-} \rightarrow y\ \text{Red}$$

__________ + __________ → __________

11.2-2. Summing Half-Reactions

Net redox reactions are usually constructed from tabulated half-reactions, which are always in the form of reductions in this course. The procedure is the following:

1. Identify the oxidation and reduction half-reactions.
2. Reverse the tabulated reduction half-reaction that corresponds to the oxidation couple.
3. Determine the lowest common multiple (LCM) of the number of electrons gained in the reduction and lost in the oxidation.
4. Multiply each half-reaction by the integer required to make the electrons gained or lost equal to the LCM determined in Step 3.
5. Add the two half-reactions to obtain the net redox reaction.

Use the following two reduction half-reactions to write the chemical equation that explains what happens when aluminum metal is placed in a strong acid (H^{1+}) to produce H_2 gas.

$$\text{Al}^{3+} + 3\ e^{1-} \rightleftharpoons \text{Al} \qquad \text{Reaction 1}$$

$$2\ \text{H}^{1+} + 2\ e^{1-} \rightleftharpoons \text{H}_2 \qquad \text{Reaction 2}$$

Reduction half-reaction

H^{1+} is a reactant and H_2 is a product, so *we use Reaction 2 as is.*

$$2\ \text{H}^{1+} + 2\ e^{1-} \rightarrow \text{H}_2 \qquad \text{reduction}$$

Protons are reduced to hydrogen gas in the reduction half-reaction. Strong acids are the source of H^{1+} ions, thus strong acids can function as oxidizing agents. Indeed, *this half-reaction represents the redox reaction of most strong acids.* The nitrate ion in nitric acid is a stronger oxidizing agent than H^{1+}, so this half-reaction is not used for nitric acid.

Oxidation half-reaction

Aluminum metal is oxidized to aluminum ion, so the reduction half-reaction given by *Reaction 1 must be reversed to make it an oxidation.*

$$\text{Al} \rightarrow \text{Al}^{3+} + 3\ e^{1-} \qquad \text{oxidation}$$

Aluminum is a good reducing agent, and it reacts vigorously with acid. Most metals are oxidized to their ions by acid and some by water.

Electrons transferred

The reduction half-reaction involves a two-electron gain, while the oxidation half-reaction involves a three-electron loss. The **LCM is therefore 6**. The net equation is a six-electron transfer.

Electrons gained = electrons lost

The reduction half-reaction is multiplied by three, to make it a six-electron gain, and the oxidation half-reaction is multiplied by two to make it a six-electron loss.

$$\begin{array}{llll} \text{reduction} & 3\times & 2\ \mathrm{H}^{1+} + 2\ \mathrm{e}^{1-} & \rightarrow & \mathrm{H}_2 \\ \text{oxidation} & 2\times & \mathrm{Al} & \rightarrow & \mathrm{Al}^{3+} + 3\ \mathrm{e}^{1-} \end{array}$$

Sum half-reactions

Summing the two half-reactions yields the net equation for the reaction. The number of electrons gained equals the number lost, so the electrons cancel in the sum. Note that both the number of atoms and the total charge, which is +6 on each side, balance.

$$\begin{array}{llll} \text{reduction} & 6\ \mathrm{H}^{1+} + 6\ \mathrm{e}^{1-} & \rightarrow & 3\ \mathrm{H}_2 \\ \text{oxidation} & 2\ \mathrm{Al} & \rightarrow & 2\ \mathrm{Al}^{3+} + 6\ \mathrm{e}^{1-} \\ \hline \text{net equation} & 6\ \mathrm{H}^{1+} + 2\ \mathrm{Al} & \rightarrow & 3\ \mathrm{H}_2 + 2\ \mathrm{Al}^{3+} \end{array}$$

11.2-3. Practice Writing Redox Equations

EXERCISE 11.6:

Use the following reduction half-reactions to write balanced redox reactions below:

$\mathrm{Na}^{1+} + \mathrm{e}^{1-} \rightleftharpoons \mathrm{Na}$

$\mathrm{Cr}^{3+} + 3\ \mathrm{e}^{1-} \rightleftharpoons \mathrm{Cr}$

$2\ \mathrm{H_2O} + 2\ \mathrm{e}^{1-} \rightleftharpoons \mathrm{H}_2 + 2\ \mathrm{OH}^{1-}$

$\mathrm{Ni}^{2+} + 2\ \mathrm{e}^{1-} \rightleftharpoons \mathrm{Ni}$

$\mathrm{Ag}^{1+} + \mathrm{e}^{1-} \rightleftharpoons \mathrm{Ag}$

Chromium metal is placed in a solution of Ag^{1+} ions.

Oxidation half reaction:

__________ $\rightleftharpoons$ __________ + __________ e^{1-}

Red. 1 Ox. 1

Reduction half reaction:

__________ + __________ e^{1-} $\rightleftharpoons$ __________

Ox. 2 Red. 2

LCM of transferred electrons:

____

Write the net equation (if any).

________ + ________ → ________ + ________

Red. 1 Ox. 2 Ox. 1 Red. 2

Metallic nickel is placed in a solution of $\mathbf{Ag^{1+}}$ ions.

Oxidation half reaction:

________ ⇌ ________ + ________ e^{1-}

Red. 1 Ox. 1

Reduction half reaction:

________ + ________ e^{1-} ⇌ ________

Ox. 2 Red. 2

LCM of transferred electrons:

____

Write the net equation (if any).

________ + ________ → ________ + ________

Red. 1 Ox. 2 Ox. 1 Red. 2

Chromium metal is placed in a solution of $\mathbf{Ni^{2+}}$ ions.

Oxidation half reaction:

________ ⇌ ________ + ________ e^{1-}

Red. 1 Ox. 1

Reduction half reaction:

________ + ________ e^{1-} ⇌ ________

Ox. 2 Red. 2

LCM of transferred electrons:

____

Write the net equation (if any).

________ + ________ → ________ + ________

Red. 1 Ox. 2 Ox. 1 Red. 2

Metallic sodium is placed in $\mathbf{H_2O}$.

Oxidation half reaction:

________ ⇌ ________ + ________ e^{1-}

Red. 1 Ox. 1

Reduction half reaction:

________ + ________ e^{1-} ⇌ ________ + ________

Ox. 2 Red. 2

LCM of transferred electrons:

____

Write the net equation (if any).

________ + ________ → ________ + ________ + ________

Red. 1 Ox. 2 Ox. 1 Red. 2

11.3 Galvanic Cells

Introduction

We have seen that electrons transfer spontaneously from the donor to the acceptor if the transfer lowers their free energy. Furthermore, the free energy that is released can be used to do work, as is done in a battery. In this section, we show how the relative free energies of the electrons in different redox couples are determined.

Prerequisites

- 9.7 Free Energy (Relate free energy change to spontaneity.)

Objectives

- Define a *galvanic cell* and name its components.
- Explain the purpose of an electrode and distinguish between *active* and *passive* electrodes.
- Explain the function of the anode and write the anode half-reaction for a given galvanic cell.
- Describe the function of the cathode and write the cathode half-reaction of a galvanic cell.
- Explain the role of the junction.
- Explain what a voltmeter measures and relate the cell potential to the two half-cell potentials.
- Describe the movement of ions and electrons in a galvanic cell.

11.3-1. Definitions

Electrons flow spontaneously to the redox couple at higher electrical potential.

We now combine electron transfer reactions and electrical conduction through a circuit, which is the field of ***electrochemistry***. We begin by recalling from Section 9.7 that $-\Delta G$ is the maximum amount of work (w) that can be obtained from any reaction at constant T and P. Extending that to redox reactions, we can write the following:

$$w = -\Delta G \qquad \text{Maximum Work Done by Redox Electrons} \tag{11.1}$$

If the redox reactants are in direct contact, the released free energy is lost as heat. However, the free energy can be harnessed by separating the reactants in an **electrochemical cell** and forcing the electrons through an external circuit. Electrochemical cells in which electrons flow spontaneously ($\Delta G < 0$) are called ***galvanic cells***.

Electrochemical cells were investigated about 60 years prior to the discovery of the electron, but it was known that the **charge** in a cell always moved from a lower or more negative electrical potential toward higher or more positive potential, so the early electrochemists expressed the work done in terms of the flow of charge and electrical potential rather than the flow of negatively charged electrons and energy change. The absolute value of the charge on a mole of electrons is called the faraday ($\mathcal{F}$). A faraday is simply Avogadro's number times the absolute value of the charge on a single electron.

$$1\mathcal{F} = (6.022 \times 10^{23} \text{ electrons/mol})(1.602 \times 10^{-19} \text{ C/electron}) = 96,500 \text{ C/mol}$$

The work done by n moles of electrons (a charge of $n\mathcal{F}$ coulombs) being transferred through an electrical potential $\mathcal{E}$ is given as

$$w = n\mathcal{F}\mathcal{E} \qquad \text{Work and Charge} \tag{11.2}$$

$n\mathcal{F}$ is the magnitude of the charge in coulombs that is transferred, and $\mathcal{E}$ is the electrical potential difference through which the electrons move expressed in volts. A ***volt*** (V) is a joule per coulomb (1V = 1 J/C), so Equation 11.2 gives the work done by the electrons in joules. Rearranging shows that the electrical potential equals the work done by the electrons divided by the number of coulombs. In other words, $\mathcal{E}$ is the work that can be done by each coulomb of charge. Combining Equation 11.2 with Equation 11.1 gives us the following relationship between the free energy of the redox reaction and the voltage that would be measured in the corresponding electrochemical cell:

$$\Delta G = -n\mathcal{F}\mathcal{E} = -96,500n\mathcal{E} \qquad \text{Free Energy in Redox Reactions} \tag{11.3}$$

Equation 11.3 indicates that the cell potential ($\mathcal{E}$) becomes more positive as the free energy change of the redox reaction becomes more negative, which means that the amount of work that can be done by each electron increases as the cell potential becomes more positive.

11.3-2. Half-Cells

Just as a redox reaction is comprised of two half-reactions, an electrochemical cell is divided into two half-cells:

- ***anode***: the half-cell in which oxidation takes place
- ***cathode***: the half-cell in which reduction occurs

These two cells are separated but connected through an electrical circuit, so electrons can flow from the anode to the cathode while keeping the two reactants separated.

The two half-cells each develop an electrical potential, which is know as the ***half-cell potential*** and designated $\mathcal{E}_{\text{anode}}$ and $\mathcal{E}_{\text{cathode}}$. Cell potentials are defined as the final electrical potential of the electron minus its initial electrical potential; i.e.,

$$\mathcal{E}_{\text{cell}} = \mathcal{E}_{\text{final}} - \mathcal{E}_{\text{initial}}$$

During a redox process, the electrons flow from the species that is to be oxidized in the anode to the species that is reduced in the cathode, so $\mathcal{E}_{\text{initial}} = \mathcal{E}_{\text{anode}}$ and $\mathcal{E}_{\text{final}} = \mathcal{E}_{\text{cathode}}$, and we may write

$$\mathcal{E}_{\text{cell}} = \mathcal{E}_{\text{cathode}} - \mathcal{E}_{\text{anode}}$$

That is, the cell potential is the difference in the half-cell potentials. If all substances in the cell are in their standard state, then all potentials are standard potentials, and the standard cell potential can be expressed as the difference between the standard half-cell potentials as shown in Equation 11.4.

$$\mathcal{E}^\circ_{\text{cell}} = \mathcal{E}^\circ_{\text{cathode}} - \mathcal{E}^\circ_{\text{anode}} \qquad \text{Standard Cell Potential} \tag{11.4}$$

The extent of reaction depends upon ΔG°, which can be determined with Equation 11.5.

$$\Delta G^\circ = -n\mathcal{F}\mathcal{E}^\circ \qquad \text{Standard Free Energy} \tag{11.5}$$

$\Delta G^\circ < 0$ if $\mathcal{E}^\circ{}_{\text{cell}} > 0$, so a reaction is extensive if the standard cathode half-cell potential ($\mathcal{E}^\circ{}_{\text{cathode}}$) is greater than the standard anode half-cell potential ($\mathcal{E}^\circ{}_{\text{anode}}$). Thus, we could predict the extent of a redox reaction if we knew the relative values of the standard half-cell potentials of the redox couples.

11.3-3. Cell Description

Galvanic cells convert the chemical potential stored in high-energy electrons into electrical potential that can be used to do work.

A typical galvanic cell consists of four components:

- the anode compartment,
- the cathode compartment,
- a liquid junction, and
- a load.

Each compartment contains the reactants in solution and a piece of metal immersed into a solution. The metal is called an ***electrode***. Electrodes provide a surface at which electrons move between the circuit and the reactant. ***Active electrodes*** participate in the reaction (the atoms are reactants), while ***passive electrodes*** provide only the surface and do not participate in the reaction.

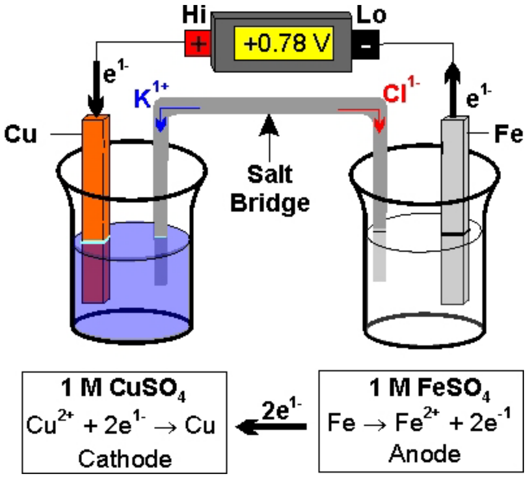


Figure 11.5: An Electrochemical Cell

11.3-4. Anode

The ***anode*** is the oxidation half-cell. A typical anode half-reaction has the following form:

$$\text{Red} \rightarrow \text{Ox} + ne^{1-}$$

The following points should be noted for the anode, which is boxed in red in Figure 11.6.

1 The half-cell reaction is $Fe \rightarrow Fe^{2+} + 2\ e^{1-}$.

2 Electrons are lost by iron atoms in the electrode and enter the external circuit.

3 The loss of electrons by the iron atoms produces iron(II) ions, which enter the solution and increase the Fe^{2+} concentration.

4 The negative charge that is carried out of the compartment with each electron is compensated by a flow of a Cl^{1-} ion into the compartment from the salt bridge.

5 The iron electrode is an active electrode that slowly dissolves as iron atoms are converted into Fe^{2+} ions that enter the solution.

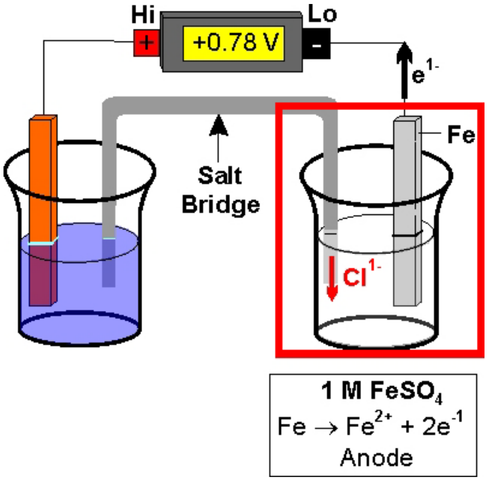


Figure 11.6 The ***anode compartment***, outlined by the red box, consists of a solution of Fe^{2+} ions and a piece of Fe metal.

11.3-5. Cathode

The ***cathode*** is the reduction half-cell. The cathode half-reaction can be expressed as

$$\mathrm{Ox} + ne^{1-} \rightarrow \mathrm{Red}$$

The following points should be noted for the cathode, which is boxed in red in Figure 11.7.

1 The half-cell reaction is $Cu^{2+} + 2\ e^{1-} \rightarrow Cu$.

2 Electrons flowing into the cell from the anode are gained by Cu^{2+} ions that are in solution but at the electrode surface.

3 The gain of electrons by the Cu^{2+} ions produces copper atoms, which become part of the electrode.

4 The negative charge that is gained when each electron enters the compartment is compensated by the flow of a cation, a K^{1+} ion here, into the compartment from the salt bridge.

5 The copper electrode is an active electrode that slowly increases in size as Cu^{2+} ions are converted into copper atoms.

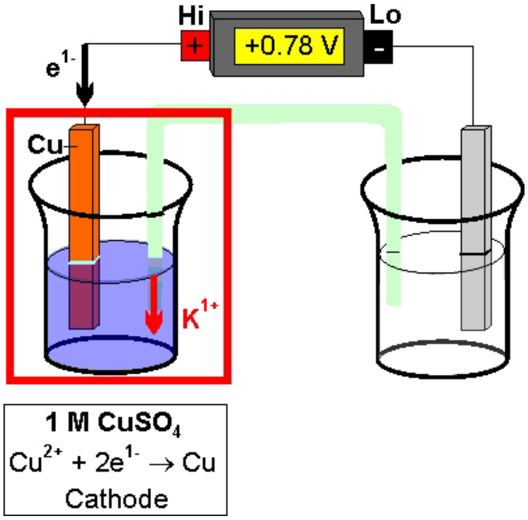


Figure 11.7 The **cathode compartment**, outlined by the red box, consists of a solution of Cu^{2+} ions and a piece of metallic Cu.

11.3-6. Bridge

A ***liquid junction*** or salt bridge completes the circuit of an electrochemical cell by allowing ions to migrate between the compartments.

As reaction proceeds, Cu^{2+} ions are consumed as electrons enter the cathode, and Fe^{2+} ions are created as electrons leave the anode. However, all reaction would cease under these conditions because the two compartments would become electrically charged. The liquid junction maintains electrical neutrality by allowing ions to pass between the two compartments, while separating the oxidant and reductant. A ***salt bridge*** is a liquid junction that contains a saturated solution of a strong electrolyte, such as KCl.

The flow of electrons into the cathode must be balanced by either a flow of anions out of the compartment or cations into the compartment. The charge balance in the cell shown in the figure can be maintained by sulfate ions leaving the cathode and entering the salt bridge or by potassium ions entering the cathode from the bridge. Note that two K^{1+} must enter for every one Cu^{2+} that is consumed.

The flow of electrons out of the anode is balanced by a flow of anions into the compartment or cations out of the compartment. Thus, chloride ions migrate from the salt bridge into the anode or Fe^{2+} ions migrate from the anode into the salt bridge.

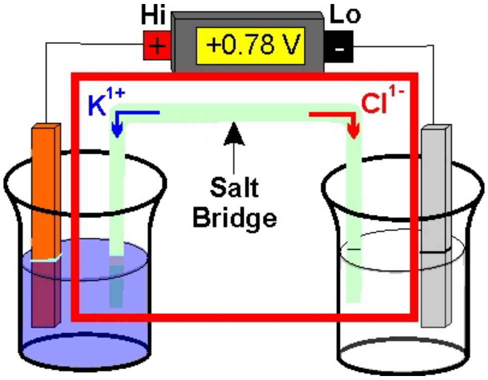


Figure 11.8 The **liquid junction** in this electrochemical cell is a salt bridge, which consists of a saturated solution of KCl.

11.3-7. Load

The ***load*** is a device that uses the energy released by the transferred electrons.

The load might be the filament of a light bulb, a power tool, the starter of an automobile, a toy, or anything that requires a battery to operate. In the experiment discussed here, the load is a voltmeter. A voltmeter measures the electrical potential difference between the two electrodes. The two terminals of a voltmeter are labeled as follows:

- Red = Hi = +. The red terminal is assumed to be at the higher or more positive potential.
- Black = Lo = −. The black terminal is assumed to be at the lower or more negative potential.

Note that a negative cell potential simply means that the terminals have been reversed; i.e., that the red terminal is actually connected to the cell at the more negative potential. In this case the electrons flow from the Hi (+) to the Lo (−) terminal.

The voltage (cell potential) measured by the voltmeter is defined as the following:

$$\mathcal{E}_{\text{cell}} = \mathcal{E}_{\text{Hi}} - \mathcal{E}_{\text{Lo}}$$

Recall that electrons move from lower to higher potential (from more negative toward more positive charge) and from the anode to the cathode. Consequently, the anode should be connected to the black (Lo or −) terminal and the cathode should be connected to the red (Hi or +) terminal to get a positive voltage. Thus, the cell potential can also be expressed as the following.

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

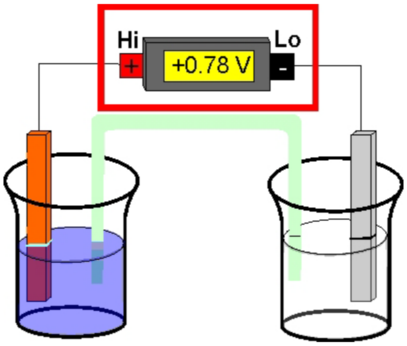


Figure 11.9 The ***load*** in the figure is a voltmeter.

11.3-8. Example

EXERCISE 11.7:

The electrical potential of the Ag^{1+}/Ag couple is about 1 V higher than that of the Ni^{2+}/Ni couple. Indicate the oxidizing and reducing agents in the electron transfer that takes place when Ag^{1+}, Ag, Ni^{2+}, and Ni are mixed.

Oxidizing agent (oxidant)	Reducing agent (reductant)
Ag^{1+}	Ag^{1+}
Ag	Ag
Ni^{2+}	Ni^{2+}
Ni	Ni

Write the reaction.

Oxidation half reaction:

$$\underset{\text{Red. 1}}{\underline{\qquad\qquad}} \rightleftharpoons \underset{\text{Ox. 1}}{\underline{\qquad\qquad}} + \underline{\qquad\qquad}\, e^{1-}$$

Reduction half reaction:

$$\underset{\text{Ox. 2}}{\underline{\qquad\qquad}} + \underline{\qquad\qquad}\, e^{1-} \rightleftharpoons \underset{\text{Red. 2}}{\underline{\qquad\qquad}}$$

The number of electrons transferred (or the LCM) is:

____

Write the net equation (if any).

$$\underset{\text{Red. 1}}{\underline{\qquad\qquad}} + \underset{\text{Ox. 2}}{\underline{\qquad\qquad}} \rightarrow \underset{\text{Ox. 1}}{\underline{\qquad\qquad}} + \underset{\text{Red. 2}}{\underline{\qquad\qquad}}$$

11.4 Standard Reduction Potentials

Introduction

The standard reduction potential of a redox couple is a measure of the electrical potential of the redox electron in that couple relative to the potentials of the redox electrons in other couples under standard conditions. Thus, standard reduction potentials can be used to determine cell potentials and to predict the spontaneity of redox processes.

Objectives

- Compare the electron and ion movement in a cell when the SHE is connected to a couple with a positive standard reduction to one in which it is connected to a couple with a negative standard reduction potential.

11.4-1. Standard Reduction Potentials Video

A video or simulation is available online.

11.4-2. Reference Electrodes

Although we cannot measure a half-cell potential, we can measure the potential difference between two half-cells. Relative half-cell potentials can be obtained by defining one half-cell as a reference against which all other half-cells can be measured. Which half-reaction we choose for the reference half-cell and the value we assign its potential are arbitrary. The decision, made many decades ago, was to use the ***standard hydrogen electrode*** (SHE) as the reference and assign it a value of exactly 0 V. The SHE half-reaction is

$\text{Ox} + ne^{1-}$	$\rightleftharpoons$	Red	$\mathcal{E}°$ (V)
$2\ H^{1+} + 2\ e^{1-}$	$\rightleftharpoons$	H_2	0.00

By convention, the half-cell to be measured is connected to the "Hi" terminal, so it is *assumed* to be the cathode or the reduction half-reaction. The SHE is then connected to the "Lo" terminal, so it is assumed to be the anode or oxidation half-reaction. If both cells are in their standard states, then the resulting cell potential is the ***standard reduction potential*** of the half-cell. It is a "reduction potential" because the half-cell to be measured is connected to the "Hi" terminal. Consider the setup in Figure 11.10.

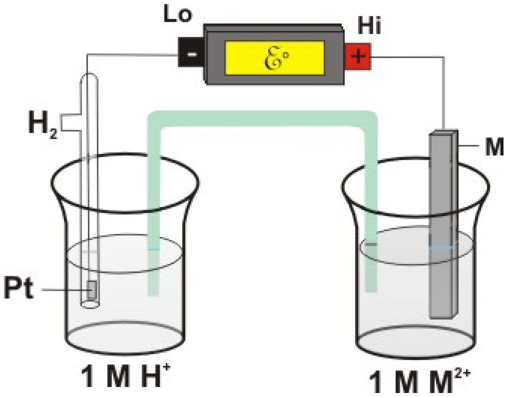


Figure 11.10: Determining the Standard Reduction Potential of M

- If $\mathcal{E}°_\text{M} > 0$, then $M^{2+} + H_2 \rightarrow M + 2\ H^{1+}$.
- If $\mathcal{E}°_\text{M} < 0$, then $M + 2\ H^{1+} \rightarrow M^{2+} + H_2$.

None of the reactants or products of the SHE reaction are solids, so an inert metal is used as the electrode. Platinum is used as the electrode in the figure. Electrons enter and leave the solution on the surface of the Pt.

- $\mathcal{E}°_\text{cell} = \mathcal{E}°_\text{Hi} - \mathcal{E}°_\text{Lo} = \mathcal{E}°_\text{metal} - \mathcal{E}°_\text{SHE}$
- $\mathcal{E}°_\text{SHE} = 0$ V, so $\mathcal{E}°_\text{cell} = \mathcal{E}°_\text{metal}$, which is the standard reduction potential of M.
- $\mathcal{E}°_\text{cell} > 0$ means that $\mathcal{E}°_\text{metal} > \mathcal{E}°_\text{SHE}$. Since the metal is at higher potential, electrons flow to it. Consequently, electrons flow from "Hi" to "Lo" in the circuit, and the metal ions are reduced by H_2.
- $\mathcal{E}°_\text{cell} < 0$ means that $\mathcal{E}°_\text{metal} < \mathcal{E}°_\text{SHE}$, so the metal is at a lower potential, and electrons flow from it to the higher potential of the SHE. Therefore, electrons flow from "Lo" to "Hi" in the circuit as the metal is oxidized by H^{1+}. $\mathcal{E}°_\text{cell}$ is still the standard reduction potential of the metal even though the metal is being oxidized because it was connected to the "Hi" terminal; i.e., the cell was connected as if the metal were the cathode. The negative sign of the cell potential simply indicates that the electrons flow through the circuit in the opposite direction of the connection.

11.4-3. Determining Standard Reduction Potentials

Standard Reduction Potential of Copper

Determining the standard reduction potential of Cu^{2+}:

- The copper half-cell is connected to the "Hi" or "+" terminal so the copper half-reaction is assumed to be the reduction.
- All reactants and products are in their standard state, so the measured voltage (+0.34 V) is the standard reduction potential of the Cu^{2+}/Cu couple.

- The reduction potential of the Cu^{2+}/Cu couple is greater than that of the H^{1+}/H_2 couple, so electrons move spontaneously from H_2 to Cu^{2+}.
- Electrons move spontaneously from higher to lower free energy, so the *transferred electrons are at a lower free energy on copper.*

Ox + ne^{1-}	$\rightleftharpoons$	Red	$\mathcal{E}°$ in V
Cu^{2+} + 2 e^{1-}	$\rightleftharpoons$	Cu	+0.34

When the Cu^{2+}/Cu couple is connected to a half-reaction at a potential that is less than 0.34 V, the electrons move from the lower potential reactant and reduce Cu^{2+} to Cu, but when the couple is connected to a half-reaction at higher potential, the electrons leave the Cu and reduce the species at higher potential.

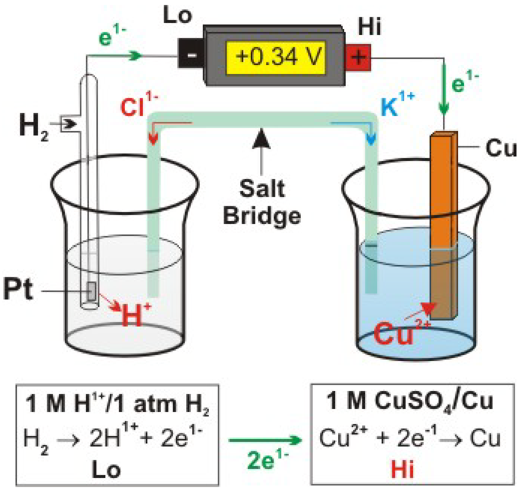


Figure 11.11: Determining the Standard Reduction Potential of Cu

Standard Reduction Potential of Iron

Determining the standard reduction potential of Fe^{2+}:

- The iron half-cell is connected to the "Hi" or "+" terminal so the iron half-reaction is ***assumed*** to be the reduction.
- All reactants and products are in their standard state, so the measured voltage (−0.44 V) is the standard reduction potential of the Fe^{2+}/Fe couple.
- The reduction potential of the Fe^{2+}/Fe couple is less than that of the H^{1+}/H_2 couple, so electrons move spontaneously from Fe to H^{1+}.
- Electrons move spontaneously from higher to lower free energy, so the *transferred electrons are at higher free energy on iron.*
- As is always the case, spontaneous electron flow is to the compartment at higher potential, but, in this case, it is to the compartment connected to the "Lo" terminal. The apparent contradiction results because the cell is constructed to measure its potential when the Fe^{2+}/Fe couple is the cathode, but the Fe^{2+}/Fe couple is actually the anode in the spontaneous cell. It was connected in this manner because the **reduction potential** of the Fe^{2+}/Fe couple was desired, even if Fe is oxidized. What is important is that the Fe^{2+}/Fe couple is at a lower potential (more negative voltage) than the H^{1+}/H_2 couple.

Ox + ne^{1-}	$\rightleftharpoons$	Red	$\mathcal{E}°$ in V
Fe^{2+} + 2 e^{1-}	$\rightleftharpoons$	Fe	−0.44

When the Fe^{2+}/Fe couple is connected to a half-reaction at a potential more negative than −0.44 V, the electrons move from the lower potential reactant and reduce the Fe^{2+} to Fe. When the couple is connected to a half-reaction at a higher potential, the electrons leave the Fe to reduce the species at higher potential. The Fe^{2+}/Fe couple (−0.44 V) is more negative than the H^{1+}/H_2 couple (0 V), so electrons transfer to the H^{1+}/H_2 couple and convert H^{1+} into H_2.

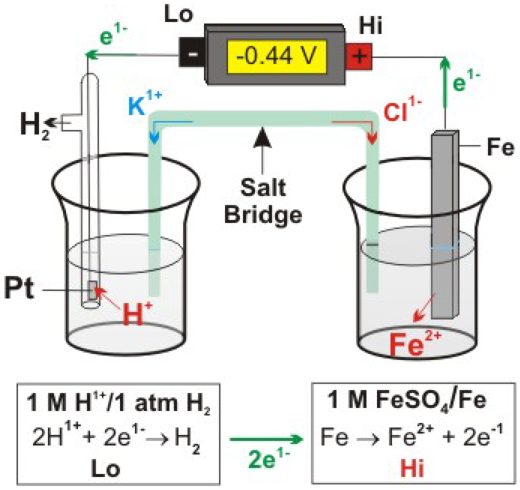


Figure 11.12: Determining the Standard Reduction Potential of Fe

11.4-4. Calculating Cell Potentials

A standard cell potential is the potential difference between the cathode and the anode. The relative potentials of the two half-reactions are given by their standard reduction potentials, so standard reduction potentials can be used to determine the difference. Consequently, the standard cell potential of any electrochemical cell can be expressed as

$$\mathcal{E}^\circ_{\text{cell}} = \mathcal{E}^\circ_{\text{cathode}} - \mathcal{E}^\circ_{\text{anode}}$$

where

- $\mathcal{E}^\circ{}_{\text{cathode}}$ = *standard reduction potential* of reduction couple.
- $\mathcal{E}^\circ{}_{\text{anode}}$ = *standard reduction potential* of the oxidation couple.

Note that the standard reduction potential is a measure of the relative electrical potential of the half-cell. Consequently, ***standard reduction potentials are independent of the number of electrons transferred and the direction in which they are transferred***. The Fe^{2+}/Fe couple is at −0.44 V whether iron atoms are reduced or iron(II) ions are oxidized, i.e., whether it is the cathode or the anode.

To determine the cell potential for the $Fe + Cu^{2+} \rightarrow Fe^{2+} + Cu$ reaction, follow these steps.

1 Determine $\mathcal{E}^\circ{}_{\text{cathode}}$.

Cu^{2+} is reduced, so $\mathcal{E}^\circ{}_{\text{cathode}}$ is the standard reduction potential of the Cu^{2+}/Cu couple: $\boldsymbol{\mathcal{E}^\circ{}_{\textbf{cathode}} = +0.34}$.

2 Determine $\mathcal{E}^\circ{}_{\text{anode}}$.

Fe is oxidized, so $\mathcal{E}^\circ{}_{\text{anode}}$ is the standard reduction potential of Fe^{2+}/Fe couple: $\boldsymbol{\mathcal{E}^\circ{}_{\textbf{anode}} = -0.44}$ **V.**

Note that the sign is NOT changed even though this is the half-reaction for the oxidation couple.

3 Determine the cell potential, $\mathcal{E}^\circ{}_{\text{cell}}$.

$$\begin{aligned}\mathcal{E}^\circ_{\text{cell}} &= \mathcal{E}^\circ_{\text{cathode}} - \mathcal{E}^\circ_{\text{anode}} = \mathcal{E}^\circ_{\text{Cu}} - \mathcal{E}^\circ_{\text{Fe}} \\ \mathcal{E}^\circ_{\text{cell}} &= +0.34 - (-0.44) = +0.78\text{V}\end{aligned}$$

The potential of the cathode is 0.78 V higher than that of the anode. A positive standard cell potential means that the reaction is extensive.

11.4-5. Reduction Potentials

Electron transfer is spontaneous when the standard reduction potential of the reducing agent is more negative than that of the oxidizing agent.

The standard reductions that we have considered thus far are shown in the table of standard reduction potentials below.

Ox + ne^{1-}	$\rightleftharpoons$	Red	$\mathcal{E}°$ (V)
$Fe^{2+} + 2\ e^{1-}$	$\rightleftharpoons$	Fe	−0.44
$2\ H^{1+} + 2\ e^{1-}$	$\rightleftharpoons$	H_2	0.00
$Cu^{2+} + 2\ e^{1-}$	$\rightleftharpoons$	Cu	+0.34

Table 11.2

Note that the half-reactions are listed so that $\mathcal{E}°$ is most negative at the top and most positive at the bottom. This choice places the electrons of greatest free energy at the top. The donor electrons are on the reducing agents (Red), while the acceptor orbitals are on the oxidizing agents (Ox). Spontaneous electron transfer occurs from a donor at higher free energy (lower or more negative potential) to an acceptor at lower free energy (higher or more positive potential). Thus, a redox reaction is spontaneous when the reducing agent lies above the oxidizing agent in a table of standard reduction potentials ordered in this manner.

EXERCISE 11.8:

Use Table 11.2 to answer the following questions.

Which of the following is the best oxidizing agent?

- H_2
- H^{1+}
- Fe
- Fe^{2+}
- Cu
- Cu^{2+}

Which of the following is the best reducing agent?

- H_2
- H^{1+}
- Fe
- Fe^{2+}
- Cu
- Cu^{2+}

11.5 Writing Redox Reactions

Introduction

We now use our understanding of half reactions and standard reduction potentials to write net equations for redox reactions.

Objectives

- Predict relative oxidizing and reducing powers based on the position of the couple in a table of standard reduction potentials.
- Predict whether a redox reaction is extensive from the position of the reacting couples in a table of standard reduction potentials.
- Use a table of standard reduction potentials to predict whether a redox reaction takes place when two substances are mixed.
- Write balanced chemical equations for redox reactions from the tabulated half-reactions.

11.5-1. Reactivity and Standard Reduction Potentials Video

A video or simulation is available online.

11.5-2. Writing REDOX Chemical Equations Video

A video or simulation is available online.

11.5-3. Standard Reduction Potentials

Electrons transfer spontaneously from a reducing agent that is above and to the right of the oxidizing agent.

Electron transfer is spontaneous when the reactants are the stronger oxidizing and reducing agents and the products are the weaker reducing and oxidizing agents. In this discussion, we will express a general redox reaction between species 1 and 2 as:

$$\mathrm{Red_1 + Ox_2 \rightarrow Ox_1 + Red_2}$$

The two half-reactions have the relative positions in a Table of Standard Reduction Potentials that are shown in Figure 11.13.

$$\mathrm{Ox_1 + n_1e^{-1} \rightleftharpoons Red_1} \quad \mathcal{E}^\circ_1$$

$$\mathrm{Ox_2 + n_2e^{-1} \rightleftharpoons Red_2} \quad \mathcal{E}^\circ_2$$

Figure 11.13: Relative positions of the Ox_1/Red_1 and Ox_2/Red_2 couples in a Table of Standard Reduction Potentials.

Ox_1 is above Ox_2 in the table of standard reduction potentials, so we can conclude that

- $\mathcal{E}^\circ{}_2 > \mathcal{E}^\circ{}_1$
- The redox electrons on Red_1 are higher in energy than those on Red_2.
- Red_1 is a better reducing agent than Red_2.
- Ox_2 is a better oxidizing agent than Ox_1.
- Electron transfer from Red_1 to Ox_2 is extensive because Red_1 is above Ox_2, which implies that electron transfer would be to higher electrical potential and lower free energy.
- $\mathcal{E}^\circ{}_{\text{cell}} = \mathcal{E}^\circ{}_{\text{cathode}} - \mathcal{E}^\circ{}_{\text{anode}} = \mathcal{E}^\circ{}_2 - \mathcal{E}^\circ{}_1 > 0$. The positive value of $\mathcal{E}^\circ{}_{\text{cell}}$ also indicates that the electron transfer is extensive.

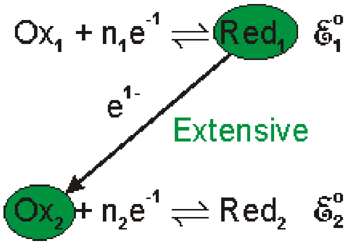


Figure 11.14: Electron transfer from upper right to lower left is extensive.

We also conclude that

- Ox_1 is below Ox_2 in the table, so $\mathcal{E}^\circ{}_2 < \mathcal{E}^\circ{}_1$.
- The Redox electrons on Red_1 are at higher electrical potential and lower in energy than those on Red_2.
- Electron transfer from Red_2 to Ox_1 is NOT extensive as electrons do not transfer extensively to lower potential or higher free energy (lower right to upper left in the table).

- $\mathcal{E}°_{\text{cell}} = \mathcal{E}°_{\text{cathode}} - \mathcal{E}°_{\text{anode}} = \mathcal{E}°_2 - \mathcal{E}°_1 < 0$. The negative value of $\mathcal{E}°_{\text{cell}}$ also indicates that the electron transfer is NOT extensive.

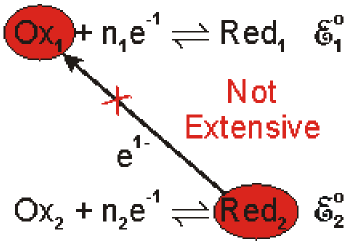


Figure 11.15: Electron transfer from lower right to upper left is NOT extensive.

11.5-4. Predicting Reactions Exercise

EXERCISE 11.9:

Note: sulfate ion is a common spectator ion in redox reactions, so ignore it in the following. Also, "metallic" implies that the metal is in the zero oxidation state, so it can be oxidized but not reduced. Use the Table of Standard Reduction Potentials to determine whether a reaction takes place when the following are mixed.

Metallic tin is added to 1 M $CuSO_4$.
  Yes
  No
Metallic tin is added to 1 M $FeSO_4$.
  Yes
  No
Metallic copper is added to water.
  Yes
  No
Metallic copper is added to 1 M HCl (hydrochloric acid).
  Yes
  No

Metallic silver is added to 1 M $CuSO_4$.
  Yes
  No
Metallic iron is added to 1 M $NiSO_4$.
  Yes
  No
Metallic sodium is added to water.
  Yes
  No
Metallic copper is added to 1 M HNO_3 (nitric acid).
  Yes
  No

11.5-5. Net Equations

EXERCISE 11.10:

Use the Table of Standard Reduction Potentials to write the net equation for the process described below and determine its standard cell potential.

Metallic tin is placed in 1 M $CuSO_4$.

Oxidation half reaction:

________ $\rightleftharpoons$ ________ + ________ e^{1-}

Red. 1 Ox. 1

Reduction half reaction:

________ + ________ e^{1-} $\rightleftharpoons$ ________

Ox. 2 Red. 2

The number of electrons transferred (or the LCM) is:

____

Write the net equation (if any).

________ + ________ → ________ + ________

Red. 1 Ox. 2 Ox. 1 Red. 2

The standard cell potential in volts is:

________ V

Try another exercise online.

11.6 Common Batteries

Introduction

Batteries are devices that utilize the free energy from spontaneous redox reactions to generate electrical energy, i.e., they are electrochemical cells. Three of the more common batteries are described in this section.

Objectives

- Describe the common alkaline battery.
- Describe a button of silver oxide battery.
- Describe a car battery.

11.6-1. Alkaline Battery

All batteries are galvanic cells.

The alkaline battery is commonly used in flashlights. The half-reactions are:

- **Anode:** $Zn \rightarrow Zn^{2+} + 2\ e^{1-}$
- **Cathode:** $2\ MnO_2 + H_2O + 2\ e^{1-} \rightarrow Mn_2O_3 + 2\ OH^{1-}$

$\mathcal{E}_{cell} = 1.5\ V$

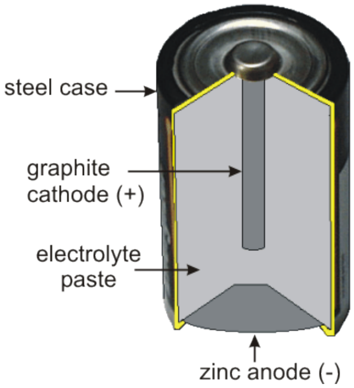


Figure 11.16: Alkaline Battery

The cathode reaction shown above is simply representative of a much more complicated process involving manganese species. The zinc base is an active anode, and a graphite rod serves as a passive cathode. The MnO_2 is present in a moist paste of electrolyte (KOH, H_2O, and KOH).

11.6-2. Silver (Button) Battery

The button battery is used in calculators, cameras, watches, etc. The half-reactions are:

- **Anode:** $Zn \rightarrow Zn^{2+} + 2\ e^{1-}$
- **Cathode:** $Ag_2O + H_2O + 2\ e^{1-} \rightarrow 2\ Ag + 2\ OH^{1-}$

Note: Hg is sometimes used in place of Ag, in which case the cathode reaction is $HgO+H_2O+2e^{1-} \rightarrow Hg+2OH^{1-}$.

$\mathcal{E}_{cell} = 1.6$ V when Ag_2O is the oxidizing agent and 1.3 V when HgO is the oxidizing agent. The porous separator serves as the liquid junction.

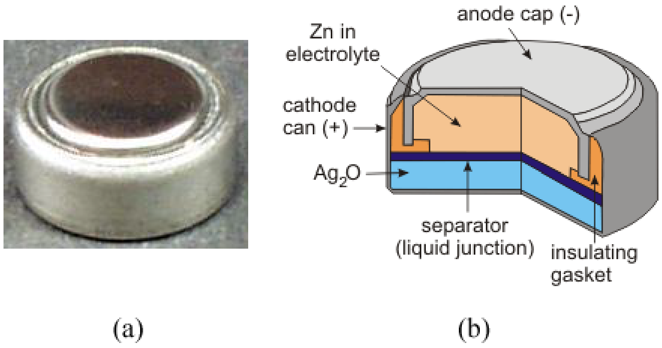


Figure 11.17: Button Battery

11.6-3 Lead Acid Battery

Almost all automobiles are started with the power of the lead-acid battery. A 12 V battery actually contains six identical electrochemical cells, each producing 2.0 V. The two half-reactions of each cell are

- **Anode:** $Pb + SO_4{}^{2-} \rightarrow PbSO_4 + 2\ e^{1-}$

- **Cathode:** $PbO_2 + 4\ H^{1+} + SO_4{}^{2-} + 2\ e^{1-} \rightarrow 2\ PbSO_4 + 2\ H_2O$

The electrodes, spongy lead anodes, and powdered PbO_2 cathodes, are immersed in ~4.5 M H_2SO_4.

A major advantage of the lead-acid battery is that it can be recharged by reversing the half-reactions with an external power supply. The alternator in an automobile, which is driven by the car's engine, generates electrical energy that is applied across the battery in the reverse direction. The electrical energy is used to drive the reactions in the reverse direction. Consequently, the starting materials are regenerated for the next time the car is started. We take up the recharging process in more detail in our discussion of electrolytic cells.

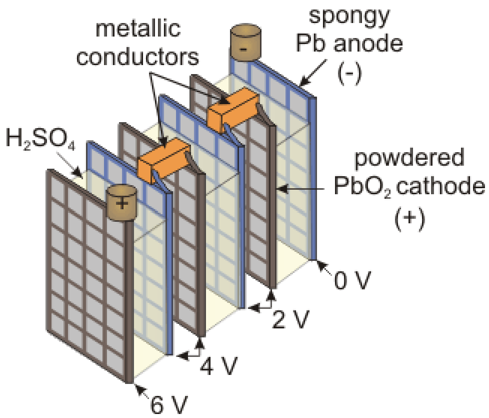


Figure 11.18: Lead Storage Battery The potential of the cathode of each cell is 2 V higher than that of its anode, but metallic conductors keeps the anode of each cell at the same potential as that of the previous cell. Consequently, the potential of the cathode increases by 2 V in each cell. The figure shows a battery with three cells, so it is a 6 V battery. A 12 V battery would have six such cells.

11.7 Corrosion

Introduction

Corrosion is the unwanted oxidation of a metal. Approximately 25% of new steel production is devoted to the replacement of corroded steel. This very costly process is a series of electrochemical reactions that take place in the iron and the water that is on it.

Objectives

- Distinguish between galvanization and passivation.
- Use standard reduction potentials to choose a metal that would protect a given metal from corrosion.

11.7-1. Definition and Example

Corrosion is the unwanted oxidation of a metal. Consider the following observations regarding the corrosion of iron.

1 Regions of pitting (holes in the iron surface) and rusting are often separated.

2 Water is required. Iron does not rust in dry climates.

3 Oxygen is required. Iron will not rust in water that contains no O_2.

4 Acid promotes rusting.

These observations are explained in the figure, which shows the rusting of iron as an electrochemical cell in which the iron is both an active anode and a passive cathode.

Note that oxygen and other gases from the atmosphere dissolve in rain drops, and some of these gases react with water to produce H^{1+}, which makes the drops acidic. For example, SO_3, which is an industrial pollutant, reacts with water to produce sulfuric acid (H_2SO_4), and CO_2 reacts in a similar manner to produce carbonic acid (H_2CO_3).

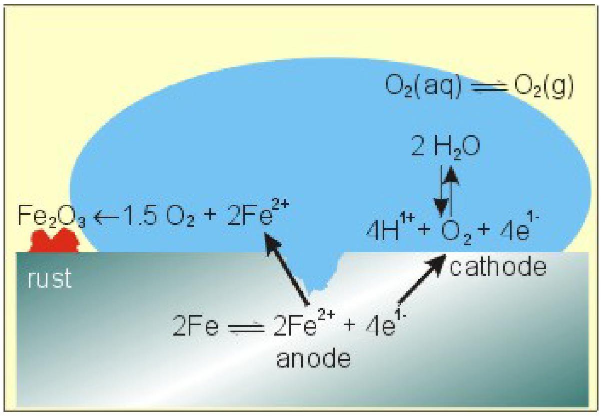


Figure 11.19: Corrosion of Iron A drop of water with dissolved oxygen and some acid sitting on a piece of iron is an electrochemical cell.

- Anode (pit): Fe → Fe^{2+} + 2 e^{1-}. The ion dissolves in the water. The loss of Fe atoms causes the iron surface to pit.
- Cathode: 4 H^{1+} + O_2 + 4 e^{1-} → 2 H_2O. This reaction explains the need for both oxygen and acid.
- $\mathcal{E}°_{\text{cell}} = \mathcal{E}°_{\text{cathode}} - \mathcal{E}°_{\text{anode}} = 1.23 - (-0.44) = +1.67$ V, an extensive reaction.
- Oxygen in solution further oxidizes the Fe^{2+} in solution to Fe^{3+}, which forms insoluble Fe_2O_3 (rust).

11.7-2. Protection Against Corrosion

Metals can be protected from corrosion by being galvanized or passivated.

Process	Definition	Examples
Galvanization	Protecting one metal by sacrificing another more reactive metal, which reacts instead of the protected metal.	• The standard reduction potentials of iron and zinc are -0.44 and $-0.76V$, respectively, so zinc is oxidized more easily than iron. Consequently, automobile bodies are galvanized with a zinc coating, which prevents the corrosion of the iron frame. • Magnesium ($\mathcal{E}° = -2.36$V) and aluminum ($\mathcal{E}° = -1.66$V) rods are connected to underground iron ($\mathcal{E}° = -0.44$V) pipes to protect them. The reactive metals are sacrificed before the iron corrodes.
Passivation	Protection of a reactive metal by the formation of an oxide layer. Some of the metal at the surface reacts, but the product of the oxidation is an oxide layer that is impervious to further attack.	• Aluminum is a reactive metal, but an aluminum chair can be left outdoors because the reactive metal forms a coating of aluminum oxide on the surface. The layer protects the underlying metal. • The iron in an automobile body is also passivated by ZnO, which forms from the sacrificial Zn that was added in the galvanization process. The ZnO coating further protects the underlying iron.

11.8 Electrolytic Cells

Introduction

We have seen that spontaneous redox reactions can be used to generate electrical energy in an electrochemical cell, and, in this section, we demonstrate the reverse of that process, using electrical energy to drive redox reactions that are not spontaneous.

Objectives

- Distinguish between electrolytic and galvanic cells.
- Explain how the lead storage battery can be either a galvanic cell or an electrolytic cell.

11.8-1. Electrolytic Cells

Electrolytic cells convert electrical potential energy into chemical potential energy.

Thus far, we have concerned ourselves with galvanic cells, i.e., cells in which the electron transfer is spontaneous. However, a major advantage of electrochemistry is that we can vary the free energy of the electrons in the electrodes and force electrons to transfer uphill in free energy. The cell potential is a measure of the amount of work we can get out of a galvanic cell ($\mathcal{E}_{\text{cell}} > 0$), but if it's negative it indicates the amount of work that an external power source must provide to an electrolytic cell ($\mathcal{E}_{\text{cell}} < 0$) in order to force the reaction. That is, galvanic cells convert chemical potential energy into electrical potential energy, while electrolytic cells convert electrical potential energy into chemical potential energy.

Forcing a nonspontaneous reaction to take place by the application of a voltage from an external source is called ***electrolysis***. Electrolysis is used to extract many metals from their ores, and to coat one metal (frequently iron) with another in a process called plating (silver and gold plated jewelry, and chrome or nickel plated sink fixtures).

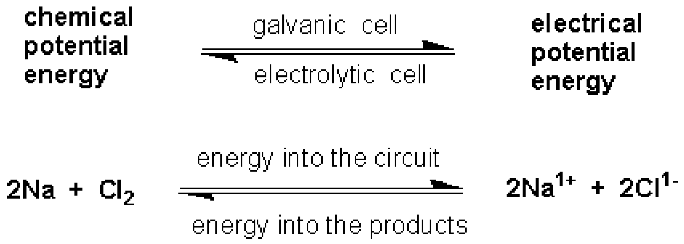


Figure 11.20

For example, the redox electrons are at much higher potential energy on Na than on Cl^{1-}. Consequently, the reaction of Na with Cl_2 in an electrochemical cell would produce a large voltage as the chemical potential energy of the electrons is converted to electrical potential energy. When Na^{1+} and Cl^{1-} are brought into contact no reaction takes place unless electrical potential energy from a power supply is added to drive the electrons from the lower potential energy of the chloride ion to the higher potential energy of the sodium atom. The nonspontaneous reaction is called electrolysis. In this example, NaCl is electrolyzed to Na and Cl_2.

11.8-2. Lead Storage Batteries

A car battery operates like a galvanic cell when it starts a car and like an electrolytic cell when it is recharging.

Recharging batteries is also a function of electrolytic cells. The lead-acid battery is one of the most common examples. Cranking power is given in amps, which is a measure of the rate at which electrons flow through the circuit, and every two moles of electrons that flow through the circuit produce two moles of $PbSO_4$. A battery with 550 amp of cranking power produces 1.7 g $PbSO_4$ per second. At this rate, the battery would run out of reactants after only a few starts. However, cars are equipped with generators (or alternators) that force the spontaneous discharge reaction to reverse while the car is running, i.e., they recharge the battery. Thus, lead-acid batteries are *galvanic* while a car is starting and *electrolytic* while it is running.

Starting	Galvanic	• **Anode**: $Pb + SO_4^{2-} \rightarrow PbSO_4 + 2\ e^{1-}$ • **Cathode**: $PbO_2 + 4\ H^{1+} + SO_4^{2-} + 2\ e^{1-} \rightarrow PbSO_4 + 2\ H_2O$ Electron transfer is spontaneous and develops 2 V per cell. Electrons move through the starter to get from the anode to the cathode. The free energy change of the electrons is used to start the car.
Driving	Electrolytic	• **Anode**: $PbSO_4 + 2\ H_2O \rightarrow PbO_2 + 4\ H^{1+} + SO_4^{2-} + 2\ e^{1-}$ • **Cathode**: $PbSO_4 + 2\ e^{1-} \rightarrow Pb + SO_4^{2-}$ Electrons must be forced from the anode to the cathode because the cathode is now at lower potential (higher free energy). In this case, electrons flow through the alternator to get from the anode to the cathode, and the battery recharges.

11.9 Exercises and Solutions

Links to view either the end-of-chapter exercises or the solutions to the odd exercises are available in the HTML version of the chapter.

Chapter 12 – Acid-Base Chemistry

Introduction

The terms *acid* and *base* have been used for several hundred years. **Acids** were substances that had a sour taste, were corrosive, and reacted with substances called bases. Substances that had a bitter taste, made skin slippery on contact, and reacted with acids were called **bases**. However, these simple definitions had to be refined as the chemical properties of acids and bases became better understood.

The first chemical definition of acids and bases was made by Svante Arrhenius. An Arrhenius acid is a substance that produces H^{1+} ions when it is dissolved in water, and an Arrhenius base is a substance that produces OH^{1-} ions when dissolved in water. In this theory, an acid *ionizes* in water much as an ionic substance, and the equilibrium constant for the reaction is called the ***acid ionization constant***. For example, the ionization of the Arrhenius acid HCl in water is represented as follows:

$$\mathrm{HCl} \rightarrow \mathrm{H}^{1+} + \mathrm{Cl}^{1-}$$

Neutralization is the reaction of an acid and a base to produce water and a **salt**.

$$\mathrm{HCl} + \mathrm{NaOH} \rightarrow \mathrm{H_2O} + \mathrm{NaCl}$$

NaCl is a ***salt***. Note that the cation of a salt is derived from the base and the anion from the acid.

Arrhenius acid-base theory is very limited because its definitions are restricted to behavior in water. Consequently, broader definitions for these very important classes of compounds were developed. In this chapter, we examine the Lewis and the Brønsted-Lowry theories of acid-base chemistry. The Lewis theory is the broadest and is discussed first.

12.1 Lewis Acids and Bases

Introduction

The broadest definition of acids and bases is that of Lewis. By this definition, a large number of reactions can be classified as acid-base reactions. In this section, we introduce Lewis acids and bases and the use of curved arrows to show the mechanism of a Lewis acid-base reaction. These topics will be used again in Chapter 13, Organic Chemistry.

Prerequisites

- 5.6 Determining Lewis Structures (Draw Lewis structures.)
- 5.4 Lewis Symbols of the Elements (Identify lone pairs in a Lewis structure.)
- 6.1 Molecular Shapes (Determine the number of electron regions around each atom in a Lewis structure.)

Objectives

- Define a Lewis acid and a Lewis base.
- Describe a Lewis acid-base reaction.
- Identify Lewis acids and bases.
- Explain how curved arrows are used to show the mechanism of a Lewis acid-base reaction.
- Distinguish between an electron transfer and a Lewis acid-base reaction.

12.1-1. Definitions

A Lewis acid-base reaction converts a lone pair on a base and an empty orbital on an acid into a covalent bond.

- A ***Lewis acid*** is a substance that has an empty orbital that it can use to share a lone pair to form a bond.
- A ***Lewis base*** is a substance that has a lone pair that it can share in a covalent bond.
- A ***Lewis acid-base reaction*** is the conversion of the lone pair on the base and the empty orbital of the acid into a covalent bond between the acid and the base.

The product of a Lewis acid-base reaction is a covalent bond between the acid and the base. Both bonding electrons come from the base, so it is a coordinate covalent bond. A curved arrow from the lone pair to the atom with the empty orbital is used to show that the lone pair will become the bonding pair between the two atoms.

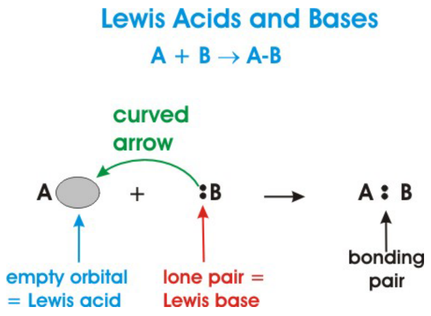


Figure 12.1

12.1-2. Lewis Acids and Bases

Lewis Bases

- A Lewis base must contain at least one lone pair of electrons.
- All anions are Lewis bases, but not all Lewis bases are anions.
- The lone pair is frequently, but not always, located on oxygen or nitrogen atoms.
- The strength of a base is increased by electron density.

The strength of the base depends upon the electron density in the region of the lone pair, the greater the electron density the stronger the base. Consequently, the strength of a base depends upon the groups around the lone pair. For example, consider the relative base strengths of the following, which are basic due to the lone pairs on the oxygen atom.

$$CH_3O^{1-} > HO^{1-} > ClO^{1-}$$

CH_3O^{1-} is the strongest base because the CH_3 group pushes electron density onto the oxygen atom. ClO^{1-} is the weakest because the electronegative chlorine atom removes electron density from the oxygen.

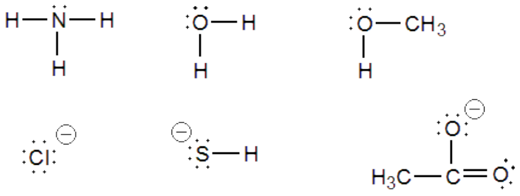


Figure 12.2: Examples of Lewis Bases

The top row of Figure 12.2 shows some Lewis bases that are molecules. In each case the lone pair resides on a nitrogen or oxygen atom, a common occurrence in Lewis bases that are molecules. Anions are also Lewis basic. The chloride anion is a very weak Lewis base, while the hydrogen sulfide ion (HS^{1-}) and the acetate ion (${C_2H_3O_2}^{1-}$) are common weak Lewis bases.

Lewis Acids

Lewis acids are often more difficult to identify. The following should help.

- A Lewis acid must be able to accommodate an additional electron region (the new bond), so, if it obeys the octet rule, a Lewis acidic atom must have less than four regions.
- Attack by a lone pair is facilitated by positive charge, so Lewis acidity is strengthened by positive charge.
- All cations are Lewis acids, but not all Lewis acids are cations.

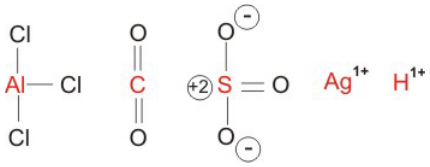


Figure 12.3: Examples of Lewis Acids

The Lewis acidic sites in Figure 12.3, each of which contains less than four electron regions, are shown in red. $AlCl_3$ is electron deficient because aluminum has only six valence electrons. Molecules with electron deficient atoms are strong Lewis acids. SO_3 and CO_2 are not electron deficient, but the central atom in each has less than four electron regions (three around S and two around C), so they are Lewis acids. Their acidity is strengthened by positive formal charge. Cations such as Ag^{1+} and H^{1+} that have fairly low-energy empty orbitals are also good Lewis acids.

12.1-3. Lewis Acidity and Basicity and Orbital Energy

The bond between two atoms is covalent only when the interacting orbitals have similar energies because large energy separations favor ionic bonds. Thus, the formation of a coordinate covalent bond in a Lewis acid-base reaction is facilitated when the energy of the empty orbital of the Lewis acid is close to that of the lone pair of the Lewis base. The energies of lone pairs are typically lower than those of empty orbitals, so the strongest interactions occur when the energy of the lone pair is high for a lone pair and the energy of the empty orbital is low for an empty orbital. For example, consider the cases of Na^{1+} and Ag^{1+} as shown in the figure. The energy of the empty orbital of Ag^{1+} is much lower than that of Na^{1+}; i.e., the energy of the empty orbital of Ag^{1+} is low for an empty orbital. Thus, the empty orbital on Ag^{1+} is sufficiently close to that of the lone pair on the Br^{1-} ion that the Ag–Br bond is covalent. However, the energy of the empty orbital on Na^{1+} is so high that the Na–Br bond is ionic. Thus, Ag^{1+} is a sufficiently strong Lewis acid to react with Br^{1-} ion, but the acidity of Na^{1+} is so weak that it does not. Indeed, Na^{1+} is such a weak Lewis acid (its orbitals are so high in energy) that it does not function as an acid in aqueous solutions. In general, H^{1+} and cations of metals with high effective nuclear charge (metals such as Ag and Pb that lie low and to the right of the periodic table) have empty orbitals that are relatively low in energy, so they are Lewis acidic, but the cations of metals on the left side of the periodic table are such weak Lewis acids that their acidity can be ignored in most cases. We conclude the following.

Strong Lewis acids have low-energy empty orbitals, and strong Lewis bases have high-energy lone pairs.

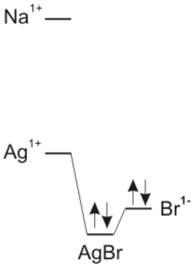


Figure 12.4: Lewis Acidity and Orbital Energy The empty orbital on Ag is relatively low in energy, so it forms a covalent bond with the lone pair on Br^{1-} ion. The empty orbital on Na^{1+} is very high in energy, so its bonds to anions are ionic. Therefore, Ag^{1+} is a much stronger Lewis acid than Na^{1+}, which is so weak that its acidity can usually be ignored.

12.1-4. Oxidants and Acids

Oxidizing agents and Lewis acids are both characterized by empty valence orbitals that are low in energy, while reducing agents and Lewis bases both have high-energy electrons. Consequently, many Lewis acids are also oxidants and many Lewis bases are also reductants. Indeed, oxidants and Lewis acids are often defined as electron acceptors, and reductants and Lewis bases as electron donors. The obvious question becomes, “What determines whether electrons are transferred or shared when a lone pair comes into contact with an empty orbital?” As has been the case so often in our study of chemistry, the answer lies in their relative energies: electrons do whatever is most efficient at increasing their electrical potential in order to lower their energy. If the energy of the empty orbital is lower than that of the lone pair, the electrons simply transfer from the reductant to the more positive electrical potential on the oxidant in a redox reaction. However, if the empty orbital is at higher energy, the electrons lower their energy by

forming a covalent bond between an acid and a base, which increases their electrical potential by exposing them to part of the nuclear charge on the acid. The example of H^{1+}, which is both an oxidant and an acid, is considered in Figure 12.5. If H^{1+} encounters a zinc atom, it behaves as an oxidant and accepts the higher energy electrons from the reductant zinc. However, electrons will not flow from a Br^{1-} ion to the higher energy orbital on H^{1+}, so the lone pair on Br^{1-} ion lowers its energy by forming an H–Br covalent bond. Br^{1-} is a base in the presence of H^{1+}, but it is a reductant in the presence of something like Cl_2 that has an empty orbital at lower energy
($2\ Br^{1-} + Cl_2 \rightarrow Br_2 + 2\ Cl^{1-}$).

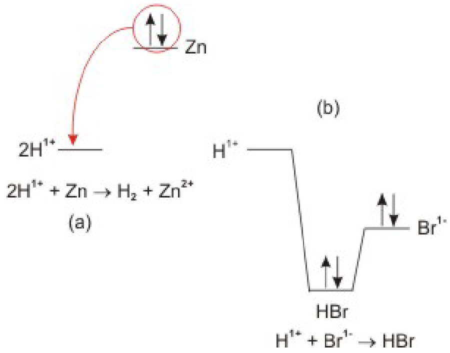


Figure 12.5: Protons as Oxidants and Reductants (a) H^{1+} is an oxidizing agent in the presence of Zn because the electrons on Zn are higher in energy; i.e., the electrons transfer to lower orbitals; (b) H^{1+} is an acid in the presence of Br^{1-} because the lone pair on Br^{1-} is lower in energy; i.e., the electrons are shared with higher orbitals.

12.1-5. Curved Arrows in Lewis Acid-Base Reactions

Curved arrows pointing from a lone pair to an atom indicate that the lone pair is converted into a bonding pair, while curved arrows pointing from a bond to an atom are used to show that a bonding pair is converted into a lone pair on the atom.

Curved arrows always start on an electron pair and end on an atom, but their meaning depends upon whether the electron pair is a lone pair or a bonding pair.

Start of a Curved Arrow	End of a Curved Arrow	Reactant	Product	Effect
lone pair on atom B	atom A		A—B	The lone pair becomes an A–B bond.
A–B bonding pair	atom A		A: B	The A–B bond becomes a lone pair on atom A.

Table 12.1

Curved arrows will be used extensively in this chapter and the next chapter to explain the mechanisms of Lewis acid-base reactions.

12.1-6. Examples of Metals as Lewis Acids

Ag^{1+} ions have relatively low-energy empty orbitals, so they are good Lewis acids. Cl^{1-} ions have lone pairs, so they are Lewis bases. In Figure 12.6a, a curved arrow from Cl^{1-} to Ag^{1+} is used to show the conversion of a lone pair on the Cl^{1-} ion into the AgCl bond in this Lewis acid-base reaction.

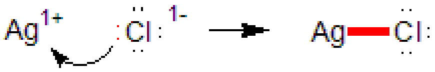


Figure 12.6a: Metal Ions as Lewis Acids: Precipitation of AgCl

Silver ions also react with ammonia. Note that the red lone pair on the nitrogen in each ammonia is converted into a red Ag–N bond in Figure 12.6b.

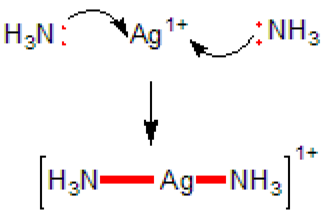


Figure 12.6b: Metal Ions as Lewis Acids: Formation of $Ag(NH_3)_2{}^{1+}$

In Figure 12.6c, the aluminum atom of $AlCl_3$ has only six valence electrons and three electron regions surrounding it, so $AlCl_3$ is a strong Lewis acid. Note that during this reaction, Al goes from three electron regions and sp^2 hybridization to four electron regions and sp^3 hybridization.

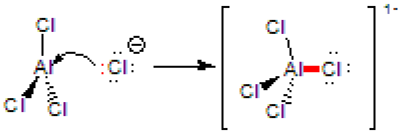


Figure 12.6c: Metal Ions as Lewis Acids: Formation of $AlCl_4{}^{1-}$

The hybridization change from sp^2 to sp^3 results in a geometry change from trigonal planar to tetrahedral. The following animation shows the geometry change.

A video or simulation is available online.

We conclude the following.

The number of electron groups around the Lewis acidic atom changes with the formation of a bond, which changes the geometry and hybridization of the atom.

12.1-7. Curved Arrows in a Mechanism–an Example

A video or simulation is available online.

The Lewis acid-base reaction between SO_3 and H_2O to form H_2SO_4 is the reaction that is the primary cause of acid rain. The oxygen atom of the water molecule contains two lone pairs, so water is a Lewis base, while the sulfur atom in SO_3 has only three electron regions, which makes SO_3 Lewis acidic. As shown in Figure 12.7a, a lone pair on the oxygen atom in water is shared with the sulfur atom to form a new S–O bond. Simultaneously, the the pi electrons in the S=O bond are converted into a lone pair on the oxygen (curved arrow from the bond to the atom), and the hybridization of the sulfur atom goes from sp^2 to sp^3 (from trigonal planar to tetrahedral).

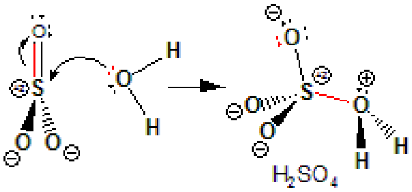


Figure 12.7a: $SO_3 + H_2O$ Mechanism: Step 1 A lone pair on water is converted to an S–O bond and the π electrons of the S=O bond are converted into a lone pair. Lone pairs on other oxygen atoms have been omitted for clarity.

The resulting structure places positive formal charge on the oxygen atom, which is eliminated by transferring a proton from that oxygen atom to one that carries negative formal charge. The proton transfer is accomplished with two acid-base reactions with the solvent. In the first, a proton is transferred from the oxygen atom with positive formal charge to a solvent molecule (water) as shown in Figure 12.7b.

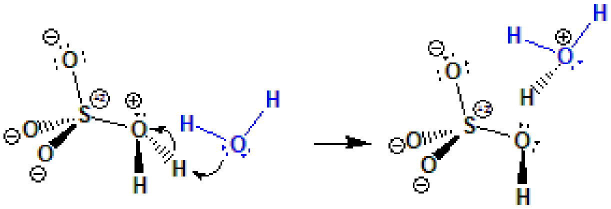


Figure 12.7b: SO_3 + H_2O Mechanism: Step 2 A proton is transferred from the oxygen with positive formal charge to a water molecule.

In the final step, a proton is transferred from the solvent to an oxygen atom with negative formal charge as shown in Figure 12.7c. The H_3O^{1+} produced in step 2 and the OH^{1-} produced in this step would then undergo proton transfer reactions to produce 2 H_2O. The final product has the correct structure of sulfuric acid.

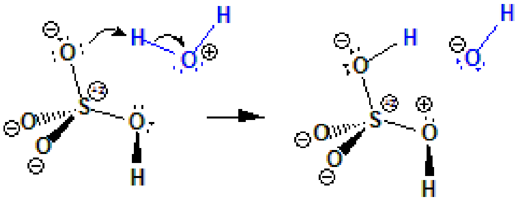


Figure 12.7c: SO_3 + H_2O Mechanism: Step 3 A proton is transferred from a solvent molecule to an oxygen atom with negative formal charge.

12.1-8. Comparing Redox and Lewis Acid-Base Reactions

A video or simulation is available online.

A video or simulation is available online.

An electron pair behaves like a reducing agent when an empty orbital is much lower in energy, but like a Lewis base when the empty orbital is higher in energy.

Compare the definitions of the reactants involved in Lewis acid-base and redox reactions.

- Reductant: a substance that can transfer electrons to another substance. Good reducing agents are characterized by high-energy electrons.
- Lewis base: a substance that can donate an electron pair to a covalent bond with another substance. Good Lewis bases are characterized by high-energy electron pairs.
- Oxidant: a substance that can accept electrons from another substance. Good oxidizing agents are characterized by low-energy, empty orbitals.
- Lewis acid: a substance that can accept an electron pair into an empty orbital to form a covalent bond. Good Lewis acids are characterized by low-energy, empty orbitals.

The only difference between the two reaction types is that one transfers, while the other shares electrons between the two reactants.

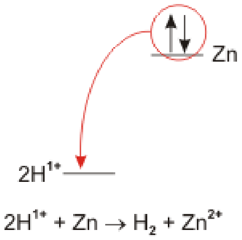


Figure 12.8: H^{1+} as oxidant

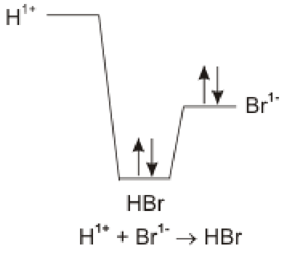


Figure 12.9: H^{1+} as an acid

12.2 Brønsted Acids

Introduction

Although the Lewis definition is the broadest, the Brønsted-Lowry (or simply Brønsted) definition is the most frequently used acid-base definition in aqueous solutions. In this section, we define Brønsted acids and bases and introduce Brønsted acid-base reactions.

Prerequisites

- 10.5 Electrolytes (Differentiate between strong electrolytes and nonelectrolytes based upon the ability of their aqueous solutions to conduct electricity.)

Objectives

- Write the name of an acid from its formula or the formula from its name.

12.2-1. Brønsted Definition

Brønsted acid-base reactions are proton transfer reactions.

A ***Brønsted acid*** **is a proton donor, a** ***Brønsted base*** **is a proton acceptor, and a Brønsted acid-base reaction is a proton transfer from the acid to the base.** Thus, the electron pair is the point of reference in Lewis theory, while the proton is the point of reference in Brønsted theory.

The Brønsted definition is a special case of the Lewis definition. In each, a base contains a lone pair that it shares with the acid to form a covalent bond. Any Brønsted base is a Lewis base and vice versa. However, a Lewis acid is any species that can accept a lone pair, but the lone pair acceptor must be a proton in the Brønsted definition, and the substance that contains the proton is a Brønsted acid.

12.2-2. Aqueous Solutions of Acids and Base

$[H_3O^{1+}]$ dictates the acidity and $[OH^{1-}]$ dictates the basicity of an aqueous solution.

In the Brønsted definition, acids transfer a proton to water, which is a weak Brønsted base, to produce hydronium ions (H_3O^{1+}).

$$HX + H_2O \rightleftharpoons H_3O^{1+} + X^{1-}$$

It is the concentration of H_3O^{1+} that dictates how acidic an aqueous solution is. Thus, if the above reaction with water is extensive, the concentration of H_3O^{1+} is relatively high as essentially all of the HX is converted to H_3O^{1+}. Such acids are strong acids. If its reaction with water is not extensive,the concentration of H_3O^{1+} is relatively low as only a small portion of the acid is converted into H_3O^{1+}, and such acids are called weak acids.

Similar considerations can be made for bases. It is the hydroxide ion concentration that determines the basicity of an aqueous solution. Thus, a ***strong base***, such as KOH, is one that is converted extensively into hydroxide ions in water: $KOH \rightarrow K^{1+} + OH^{1-}$. A ***weak base***, such as fluoride ion, reacts only slightly with water to produce hydroxide ions: $F^{1-} + H_2O \leftrightharpoons HF + OH^{1-}$.

12.2-3. Acids and Bases are Electrolytes

Strong acids and bases are strong electrolytes, while weak acids and bases are weak electrolytes.

If HX is a strong acid, then it is converted completely into H_3O^{1+} and X^{1-} ions in water. The presence of these ions makes the acid a strong electrolyte. However, if HX does not react completely with water, then only small concentrations of the ions are produced. In this case, HX is a ***weak electrolyte***. Similarly, strong bases are strong electrolytes and weak bases are weak electrolytes.

Recall from Section 10.5 that electricity is conducted through a solution of an electrolyte but not through a solution of a nonelectrolyte. Indeed, the brightness of the light is indicative of the ion concentration in solution. Consider the following possibilities for an acid or base.

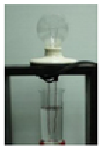
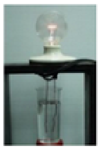
	The light bulb does not glow, so there are no ions in solution. The fact that HX produces no ions in solution indicates that HX is a **nonelectrolyte**. An aqueous solution is represented as HX to show that the molecules do not ionize in water.
	The light shines brightly, which means that the concentration of H_3O^{1+} ions in solution is relatively high. Acids that ionize completely in water to produce high concentrations of H_3O^{1+} ions are called **strong acids**. An aqueous solution is represented as $H_3O^{1+} + X^{1-}$ to show that the molecules ionize completely in water.
	The light shines, so HX is an electrolyte, but the intensity of the light is much less than for a strong acid. The dimness of the light indicates that the H_3O^{1+} ion concentration is low. Thus, only a fraction of the HX molecules in water ionize. Acids that ionize only partially in water are called **weak acids**. An aqueous solution is represented as HX because HX is the predominant species in solution.

Table 12.2: Determining the Relative Concentrations of H_3O^{1+} Ions in a 0.1 M of HX

12.2-4. Examples

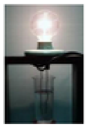
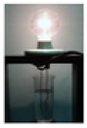
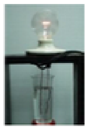
pure H_2O		Water is a nonelectrolyte and represented as H_2O. There are ions in water, but their concentrations are very small.
0.10 M HNO_3		Nitric acid is a strong acid, and its aqueous solution is represented as $\mathbf{H_3O^{1+}(H^{1+}) + NO_3{}^{1-}}$. The following reaction is so extensive that there are essentially no nitric acid molecules in solution. Recall that extensive reactions are expressed with single arrows as in the following. $HNO_3 + H_2O \rightarrow H_3O^{1+} + NO_3{}^{1-}$
0.10 M KOH		KOH ionizes completely in water and is a strong electrolyte. It is a strong base because one of the ions that it produces is the OH^{1-} ion. Thus, aqueous KOH is written as $\mathbf{K^{1+} + OH^{1-}}$.
0.10 M CH_3OH		CH_3OH is a nonelectrolyte. It is neither an acid nor a base—it is an alcohol (wood alcohol). An aqueous solution of methanol is written as $\mathbf{CH_3OH}$.
0.10 M HNO_2		The light bulb glows dimly, so nitrous acid is a weak acid and its aqueous solutions are represented as $\mathbf{HNO_2}$, not as hydronium ion and nitrite ion, to show the predominant form. The following reaction is not extensive (only about 5% of the HNO_2 molecules react), so double arrows are used. $HNO_2 + H_2O \leftrightharpoons H_3O^{1+} + NO_2{}^{1-}$
0.10 M NH_3		The light bulb glows dimly, so $\mathbf{NH_3}$ is a weak electrolyte. About 1% of the ammonia molecules react with water to produce ions, so an aqueous solution is represented as NH_3 molecules, not as the ions. Double arrows are used in the reaction. $NH_3 + H_2O \leftrightharpoons NH_4{}^{1+} + OH^{1-}$ The proton is transferred from water to ammonia, so NH_3 is a **weak base**.

Table 12.3

12.2-5. Brønsted Acids

An acidic proton must be bound to an electronegative atom, which is oxygen in most acids that contain an oxygen atom.

In order for HX to be acidic, the H–X bond must break to produce H^{1+} and X^{1-} ions, but that can happen only if it is a polar bond. Thus, a hydrogen atom must be covalently bound to a highly electronegative atom to be acidic. There are a great number of compounds with hydrogen atoms covalently bound to atoms that are not very electronegative, but these compounds are not Brønsted acids. The most common examples are organic compounds because the C–H bond is not polar (C and H have very similar electronegativities). For example, the C–H bonds in CH_4 do not produce H^{1+} when they break, so CH_4 cannot be a Brønsted acid. The H–Cl bond is very polar, so breaking the H–Cl bond does produce H^{1+} ions, which makes HCl a Brønsted acid.

Acidic protons are usually written first in the formula of acids to indicate that they are acidic.

For example, the chemical formulas of the hydrogen sulfate ion and perchloric acid are written as $HSO_4{}^{1-}$ and $HClO_4$ to demonstrate that they are acids, while the formulas of methane and ammonia are written CH_4 and NH_3 to indicate that they have no acidic protons. However, writing the formulas this way can be misleading because it often places the proton next to an atom to which it is not bound. The acidic protons in $HSO_4{}^{1-}$ and $HClO_4$ are both attached to oxygen atoms. Acetic acid is written $HC_2H_3O_2$ to indicate that it is an acid that has only one acidic proton. Once again, the acidic proton is also bound to an oxygen atom, not the carbon, while the other hydrogen atoms are attached to the carbon and are not acidic. Consequently, acetic acid is often written as CH_3COOH, which indicates an O–H bond and better represents the true structure of the acid. Similarly, H_2SO_4 contains two O–H bonds but no S–H bonds.

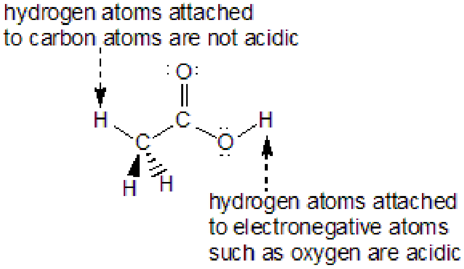


Figure 12.10: Only Protons Bound to Highly Electronegative Atoms are Acidic Acetic acid contains three hydrogen atoms bound to carbon that are not acidic because carbon is not highly electronegative and the C–H bond is not polar. It also contains one hydrogen atom attached to highly electronegative oxygen that is acidic because the O–H bond is very polar.

12.2-6. Binary Acids and Oxoacids

Binary Acids

Binary acids have a proton and only one other element. HCl, HBr, and HI are strong acids, but HF is a weak acid. Note: these acids plus NH_4^{1+}, H_2S, and $H{-}C{\equiv}N$ are the only acids that we deal with that do not have O–H bonds.

- Note that HCN is not a binary acid because it contains atoms from three different elements. However, HCN is a gas and its name (hydrogen cyanide) ends in -ide, so it is treated as a binary compound.

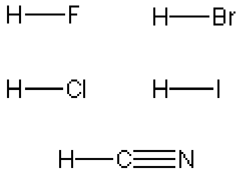


Figure 12.11: Some Binary Acids

Oxoacids

Most acidic protons are bound to an oxygen atom. Such acids are called oxoacids. The acidic protons are shown in blue in Figure 12.12.

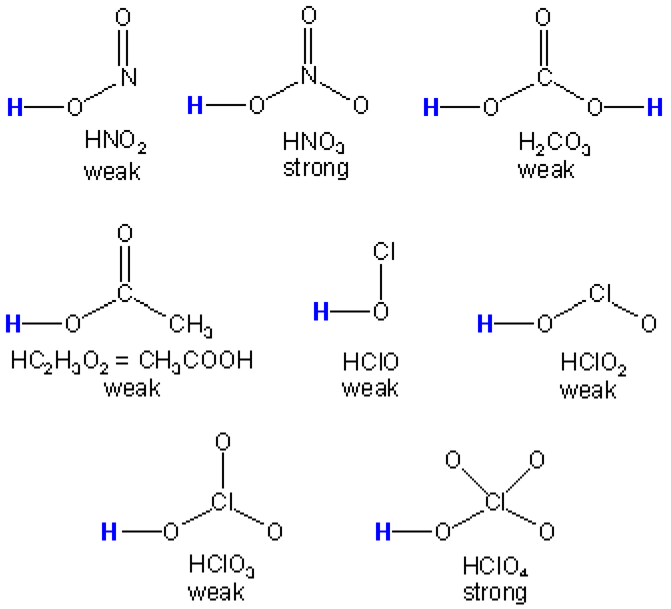


Figure 12.12: Some Common Oxoacids

Naming Acids

12.2-7. Binary Acids

The pure compounds that produce binary acids are named using the rules outlined in Section 4.6 until they are dissolved in water. For example, HCl is hydrogen chloride and H_2S is hydrogen sulfide. However, when these substances are dissolved in water, they produce acidic solutions that are named in the following manner.

- Replace hydrogen with hydro.
- Change the -ide ending to -ic.
- Add the word acid.

Formula	Name as Pure Substance
$HF(g)$	hydrogen fluoride
$HCl(g)$	hydrogen chloride
$HI(g)$	hydrogen iodide
$HCN(g)$	hydrogen cyanide
$H_2S(g)$	hydrogen sulfide

Formula	Name as Aqueous Solution
$HF(aq)$	hydrofluoric acid
$HCl(aq)$	hydrochloric acid
$HI(aq)$	hydroiodic acid
$HCN(aq)$	hydrocyanic acid
$H_2S(aq)$	hydrosulfuric acid

Table 12.4: Names of Some Common Binary Acids

12.2-8. Polyatomic Acids

Polyatomic acids are derived from polyatomic ions and are named by

- changing the -ate ending of the polyatomic ion to -ic or
- changing the -ite ending of the polyatomic ion to -ous and
- adding the word acid.

If the acid is also an ion, its name is unchanged. For example, the $HPO_4{}^{2-}$ and $H_2PO_4{}^{1-}$ ions are the monohydrogen phosphate ion and dihydrogen phosphate ion, respectively. In an older, but still common, method, ions with acidic protons are named by using the prefix ‘bi’ instead of the word ‘hydrogen.’ Thus, $HSO_4{}^{1-}$ is either hydrogen sulfate or bisulfate.

Ion Formula	Ion Name	Acid Formula	Acid Name
$C_2H_3O_2{}^{1-}$	acetate ion	$HC_2H_3O_2$	acetic acid
$SO_3{}^{2-}$	sulfite ion	H_2SO_3	sulfurous acid
$SO_4{}^{2-}$	sulfate ion	H_2SO_4	sulfuric acid
$NO_2{}^{1-}$	nitrite ion	HNO_2	nitrous acid
$NO_3{}^{1-}$	nitrate ion	HNO_3	nitric acid
ClO^{1-}	hypochlorite ion	$HClO$	hypochlorous acid
$ClO_2{}^{1-}$	chlorite ion	$HClO_2$	chlorous acid
$ClO_3{}^{1-}$	chlorate ion	$HClO_3$	chloric acid
$ClO_4{}^{1-}$	perchlorate ion	$HClO_4$	perchloric acid
$PO_4{}^{3-}$	phosphate ion	H_3PO_4	phosphoric acid

Table 12.5: Acids Derived from Polyatomic Anions

12.2-9. Acid Naming Exercise

EXERCISE 12.1:

Name the following acids.

H_2CO_3 ______________

$HCO_3{}^{1-}$ ______________

Write formulas for the following acids.

selenous acid ______________

hydroselenic acid ______________

12.3 Brønsted Acid-Base Reactions

Introduction

Brønsted acid-base reactions all involve transferring a single proton from the acid to the base. In this section, we see how to predict the products of a Brønsted acid-base reaction.

Objectives

- Identify the conjugate base of an acid.
- Identify the conjugate acid of a base.
- Describe a Brønsted acid-base reaction in terms of the proton transfer.

12.3-1. Conjugate Base

The conjugate base of an acid is formed by removing one, and only one, proton from the acid.

After the acid loses a proton, it becomes a base because the species it becomes can gain the proton back. The loss of a single proton converts an acid into its **conjugate base**. It is important to realize that ***an acid and its***

conjugate base differ by one, and only one proton. All Brønsted reactions involve the transfer of a single proton. Thus, the acid is always converted to it conjugate base in a Brønsted reaction.

The charge on the conjugate base is always lower than that on the acid by one because the acid loses H^{1+}.

EXERCISE 12.2:

Use the above definition to determine the conjugate base of each of the following.

NH_3 ______________

H_2O ______________

$HSO_3{}^{1-}$ ______________

$HC_2H_3O_2$ ______________

12.3-2. Conjugate Acid

The conjugate acid of a base is formed by adding one proton to the base.

After the base gains a proton, it becomes an acid because the species it becomes can donate the proton back. The gain of a single proton converts a base into its **conjugate acid**. All Brønsted reactions involve the transfer of a single proton. Thus, the base is always converted into its conjugate acid in a Brønsted reaction.

The charge on the conjugate acid is always greater than that on the base by one because the base gains H^{1+}. A base and an acid that differ by one, and only one proton, are said to be a ***conjugate acid-base pair***.

EXERCISE 12.3:

Determine the conjugate acid of each of the following.

NH_3 ______________

H_2O ______________

$HSO_3{}^{1-}$ ______________

$CO_3{}^{2-}$ ______________

12.3-3. Brønsted Acid-Base Reactions

The chemical equation for a Brønsted acid-base reaction consists of two conjugate acid-base pairs and nothing else.

Brønsted acid-base reactions convert the reacting acid into its conjugate base and the reacting base into its conjugate acid. The chemical equation for a Brønsted acid-base reaction consists of two conjugate acid-base pairs and nothing else.

Consider the following proton transfer reaction: $HCN + NH_3 \rightarrow CN^{1-} + NH_4{}^{1+}$.

The proton transfer converts the reacting acid (HCN) into its conjugate base (CN^{1-}) and the reacting base (NH_3) into its conjugate acid ($NH_4{}^{1+}$).

The products of an acid-base reaction are also an acid and a base, so the substances on the right of the chemical equation also react to produce those on the left: $CN^{1-} + NH_4{}^{1+} \rightarrow HCN + NH_3$.

In this particular reaction, the probability that a collision between the acid and the base results in an acid-base reaction is about the same in either direction. The fact that the back reaction is important is demonstrated with the use of double arrows in the chemical equation: $HCN + NH_3 \rightleftharpoons CN^{1-} + NH_4{}^{1+}$.

12.4 Extent of Proton Transfer

Introduction

Not all acids and bases react very well with one another, and the degree to which they do react is referred to as the **extent of proton transfer**. If the extent of proton transfer is great, the reaction is usually written with a single arrow, but if the transfer is not extensive, the reaction is written with double arrows.

Prerequisites

- 9.11 Equilibrium and the Equilibrium Constant

Objectives

- Write the chemical equation for the reaction of a strong acid, a weak acid, or a weak base with water.

12.4-1. Comparing Conjugate Acid-Base Strengths

The weaker an acid is, the stronger is its conjugate base.

The strength of an acid is related to the ease with which it donates its proton to become its conjugate base, and the strength of a base is related to its ability to accept a proton to become its conjugate acid. **If A^{1-} is a strong base**, then it must bind a proton strongly when it forms HA, and if its proton is bound strongly, **then HA must be a weak acid**. We conclude that the strength of a base varies inversely with the strength of its conjugate acid, i.e., strong acids have weak conjugate bases and *vice versa*.

Consider the following acid-base reaction.

$$\mathrm{HA} + \mathrm{B}^{1-} \rightleftharpoons \mathrm{A}^{1-} + \mathrm{HB}$$

If HA is the stronger of the two acids, then A^{1-} must be the weaker of the two bases due to the inverse relationship between conjugate acid-base strengths. This means that **the stronger acid is always on the same side of the chemical equation as the stronger base**. Similarly, the weaker acid and base are also on the same side of the equation. Consequently, there are only three possible combinations in Brønsted acid-base reactions:

1 stronger acid + stronger base → weaker base + weaker acid

2 reacting and produces acids of comparable strengths and reacting and produced bases of comparable strengths

3 weaker acid + weaker base → stronger base + stronger acid

12.4-2. Extent as a Function of Relative Acid Strengths

If the reacting acid is the stronger acid, then the reacting base is the stronger base, and the reaction is extensive.

- Forward Reaction: stronger acid + stronger base is extensive.
- Reverse Reaction: weaker acid + weaker base produces little of the stronger acid and base.
- Equilibrium: almost exclusively the weaker acid and base, which are the products in this reaction type.
- A single arrow typically used to indicate that very little of the limiting reactant is present at equilibrium.

If the acid strengths are comparable then the concentrations of substances on both sides of the equilibrium are comparable.

- Forward Reaction: moderate acid + moderate base produces moderate amounts of products.
- Reverse Reaction: moderate acid + moderate base produces moderate amounts of reactants.
- Equilibrium: moderate amounts of all species.
- All species present in significant amounts at equilibrium, so reaction is not extensive and double arrows should be used.

If the reacting acid is much weaker than the produced acid then little product is formed.

- Forward Reaction: weaker acid + weaker base produces little of the stronger base and stronger acid.
- Reverse Reaction: stronger acid + stronger base react extensively to produce weaker acid and base.
- Equilibrium: almost exclusively the weaker acid and base, which are the reactants in this reaction type.

- Little product, but some product is formed as there is some reaction, and double arrows would have to be used when writing the chemical equation.

12.4-3. Relative Acid Strength Exercise

EXERCISE 12.4:

Solutions containing equal concentrations of HA, A^{1-}, HB, and B^{1-} are mixed. After reaction, the resulting solution is composed almost exclusively of HA and B^{1-} determine relative acid and base strengths.

Which is the stronger acid?
- HA
- A^{1-}
- HB
- B^{1-}

Which is the stronger base?
- HA
- A^{1-}
- HB
- B^{1-}

Which is the weaker base?
- HA
- A^{1-}
- HB
- B^{1-}

Which is the weaker acid?
- HA
- A^{1-}
- HB
- B^{1-}

12.4-4. Equilibrium Constant Expression

The equilibrium mixture is always dominated by the weaker acid and base.

We now examine the equilibrium mixture that results from mixing equal amounts of HA and B^{1-} as a function of the relative acid strengths of HA and HB.

Chemical Equation: $HA + B^{1-} \rightleftharpoons A^{1-} + HB$

Equilibrium Constant Expression: $K = \dfrac{[A^{1-}][HB]}{[HA][B^{1-}]}$

HA >> HB; $K >> 1$

Stronger Acid		**Stronger Base**		*Weaker Base*		*Weaker Acid*
HA	+	B^{1-}	$\rightarrow$	A^{1-}	+	HB

At equilibrium, $[A^{1-}][HB] >> [HA][B^{1-}]$, so $K >> 1$, consistent with an extensive reaction. Note: A^{1-} is the weaker base and HB is the weaker acid!

HA ~ HB; $K \sim 1$

Acid		Base		Base		Acid
HA	+	B^{1-}	$\leftrightharpoons$	A^{1-}	+	HB

$[A^{1-}][HB] \sim [HA][B^{1-}]$ at equilibrium, so $K \sim 1$ when the reacting and produced acids are of similar strengths.

HA << HB; $K << 1$

Weaker Acid		*Weaker Base*		**Stronger Base**		**Stronger Acid**
HA	+	B^{1-}	$\leftrightharpoons$	A^{1-}	+	HB

At equilibrium, $[HA][B^{1-}] >> [A^{1-}][HB]$, so $K << 1$, consistent with a reaction that in not extensive. Note that HA is the weaker acid and B^{1-} is the weaker base.

In each case where the acid strengths are much different, the product of the equilibrium concentrations of the weaker acid and base are always much greater than the product of the concentrations of the stronger acid and base. That is, the equilibrium mixture is dominated by the weaker acid and base.

12.4-5. Single vs. Double Arrows

Single arrows are sometimes used to indicate that a reaction is extensive. We arbitrarily assume that $K > 1000$ for such reactions.

When $K >> 1$, the amount of product formed can be determined without use of the equilibrium constant because the equilibrium concentration of at least one of the reactants will be negligible. Reactions of this type are frequently written with single arrows (→) rather than the double equilibrium arrows to emphasize that the reverse reaction occurs only to a negligible extent.

Although the value of K at which the reverse reaction can be ignored varies with the concentrations of the reactants, we will use a value of ∼1000 in our discussions. Thus, a single arrow can be used for reactions in which $K >\sim 1000$. If $K < 1000$, the reverse reaction cannot be ignored, and the value of K must be used when determining the amount of product that is formed. Equations for reactions of this type should be written with double arrows ($\rightleftharpoons$) to emphasize the importance of the reverse reaction. An example of each case is provided in the following table.

$HF + ClO^{1-} \rightarrow F^{1-} + HOCl$	$K = \dfrac{[F^{1-}][HOCl]}{[HF][OCl^{1-}]} = 2 \times 10^4$	$K >> 1$ so, • The reaction (or proton transfer) is extensive. • The reacting acid (HF) is a much stronger acid than the produced acid (HClO). • The equilibrium concentrations of F^{1-} and HClO are much greater than those of HF + OCl^{1-}. • The reaction is frequently written with a single arrow.
$HF + NO_2{}^{1-} \rightleftharpoons F^{1-} + HNO_2$	$K = \dfrac{[F^{1-}][HNO_2]}{[HF][NO_2{}^{1-}]} = 2$	$K \sim 1$ so, • The reaction is not extensive in either direction. • The strengths of the reacting and produced acids are comparable. • The equilibrium concentrations of reactants and products are similar. • The reaction is written with double arrows.
$HCN + F^{1-} \rightleftharpoons CN^{1-} + HF$	$K = \dfrac{[CN^{1-}][HF]}{[HCN][F^{1-}]} = 6 \times 10^{-7}$	$K << 1$ so, • The forward reaction is not extensive, but the reverse reaction is. • The reacting acid (HCN) is much weaker than the produced acid (HF). • The equilibrium concentrations of HF and F^{1-} are much greater than those of CN^{1-} and HF. • The reaction is written with double arrows.

Table 12.6

12.4-6. Proton Transfer Exercise

EXERCISE 12.5:

Consider the following acid-base equilibrium.

$$\mathrm{HOCl} + \mathrm{CN}^{1-} \leftrightharpoons \mathrm{OCl}^{1-} + \mathrm{HCN} \quad K \sim 100$$

stronger acid ______________ stronger base ______________

weaker base ______________ weaker acid ______________

Acid-Base Reactions Involving Water

12.4-7. The Role of Water

All of the remaining acid-base reactions in this chapter occur in water, which can act as both as an acid and a base. Thus, the reaction with water is an important consideration in acid-base chemistry. The general reaction of an acid and water can be represented as the following.

$$\mathrm{HA} + \mathrm{H_2O} \rightleftharpoons \mathrm{A}^{1-} + \mathrm{H_3O}^{1+}$$

- **Strong acids**: Strong acids react extensively with water. In order for the reaction to be extensive, HA must be a stronger acid than H_3O^{1+}. In other words, any acid stronger than hydronium ion is considered to be a strong acid.
- **Weak acids**: Weak acids do not react extensively with water. Thus, weak acids are weaker acids than H_3O^{1+} ions.

12.4-8. Strong Acids in Water

Strong acids are represented as H_3O^{1+} in acid-base reactions in water.

The strong acids are those that are stronger than H_3O^{1+}. Thus, their reaction with water is one where the reacting acid is stronger than the produced acid, i.e., the reaction is so extensive that it is usually written with a single arrow. The common strong acids are $HClO_4$, HCl, HBr, HI, HNO_3, and H_2SO_4. Hydronium ion is the strongest acid that can exist in water because any acid stronger than hydronium reacts extensively with the water to produce hydronium ion. This effect is known as the ***leveling effect*** because the strengths of the strong acids are all leveled to that of hydronium ion. **Due to the leveling effect, strong acids are all represented by H_3O^{1+} in acid-base reactions in water.**

The conjugate bases of the strong acids are all too weak to react as Brønsted bases in aqueous solution. Thus, the **$ClO_4{}^{1-}$, Cl^{1-}, Br^{1-}, I^{1-}, and $NO_3{}^{1-}$ ions should be treated as spectator ions in aqueous Brønsted acid-base reactions**. The $HSO_4{}^{1-}$ does not react as a Brønsted base in water, but it can react as a weak acid.

Hydrochloric acid, which is an aqueous solution of HCl, is a strong acid, but there are essentially no HCl molecules in hydrochloric acid solution because the above reaction is so extensive. Hydronium ion is a strong acid, but chloride ion is such a weak Brønsted base that it can be ignored in Brønsted acid-base reactions. Consequently, hydrochloric acid is represented as H_3O^{1+} + Cl^{1-} ions in aqueous solutions.

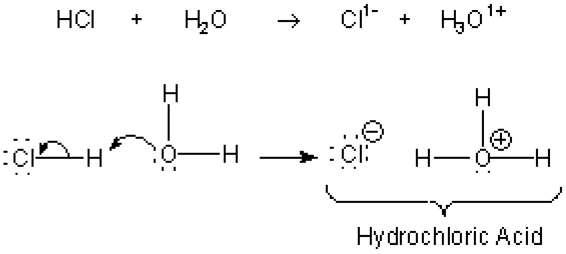


Figure 12.13

12.4-9. Weak Acids in Water

Weak acids are represented by the formula of the acid not by H_3O^{1+} in acid-base reactions.

Weak acids are those acids weaker than H_3O^{1+}. Thus, their reaction with water is one in which the produced acid is stronger than the reacting acid, i.e., the following reaction is not extensive.

$$HA + H_2O \rightleftharpoons A^{1-} + H_3O^{1+}$$

The reverse reaction between hydronium ion and the conjugate base of the weak acid is the extensive reaction, so $K < 1$. The reactions are written with double arrows to emphasize the importance of the back reaction. The concentration of HA is much greater than that of A^{1-} or H_3O^{1+} in a solution of a weak acid. Consequently, weak acids are represented by the formula of the acid not by H_3O^{1+} in acid-base reactions. The example of hydrofluoric acid is considered below.

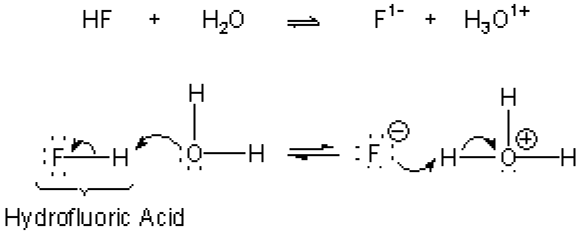


Figure 12.14

The hydronium ion is a much stronger acid than HF, so the reverse reaction is much more extensive than the forward reaction. Consequently, $K < 1$, and very little HF reacts. Less than 10% of the HF molecules in a typical HF solution react to produce H_3O^{1+} ions, so the solution is represented by HF not by H_3O^{1+}.

12.4-10. Bases in Water

All anions are bases because an anion can always accept a proton.

Water is also used as the reference acid in determining relative base strengths. The reaction of a base (A^{1-}, the conjugate base of HA) with water can be represented as follows: $A^{1-} + H_2O \rightleftharpoons HA + OH^{1-}$.

- **Strong Bases**: A^{1-} is a strong base if the above reaction is extensive, which is the case when the base is a stronger base than hydroxide ion.
- **Weak Bases**: A^{1-} is a weaker base than hydroxide ion, so it does not react extensively with water.

O^{2-} and ${NH_2}^{1-}$ are strong bases. However, OH^{1-} is the strongest base that can exist in water because the above reaction is extensive when A^{1-} is a strong base. Metal hydroxides are the most common strong bases. All anions are bases because an anion can always accept a proton. However some bases are molecular and the common example of ammonia is considered below.

$$NH_3 + H_2O \rightleftharpoons NH_4^{1+} + OH^{1-}$$

The above reaction is not extensive in the forward direction, which is demonstrated with the use of double arrows, because ammonia is a weak base. Only about 1% of NH_3 molecules in a typical aqueous solution react with water to produce ${NH_4}^{1+} + OH^{1-}$, so an aqueous solution of ammonia is represented as NH_3.

12.5 Acid and Base Strengths

Introduction

We have now seen that the extent of an acid-base reaction depends upon the relative strengths of the reacting and produced acids. In this section, we show how the relative strengths of acids are measured and tabulated.

Prerequisites

- 4.4 Oxidation States
- 5.1 The Covalent Bond

Objectives

- Relate acid strength of HA to the strength of the H–A bond.
- Explain why the acid strength of HA also depends upon the electronegativity of A.
- Predict the stronger of two acids with comparable bond strengths from the electronegativity of the atom to which the H is bound.
- Rate the relative strengths a series of oxoacids (HOX) based on the electron withdrawing or donating abilities of X.

12.5-1. Bond Strengths

Knowledge of the relative acid strengths of the reacting and produced acids allow us to predict the extent of reaction, so we now examine the factors that dictate those strengths. The acid strength of HA is related to the ease with which the H–A bond is broken. If the H–A bond is weaker, then HA gives up the proton more easily and is a stronger acid, but if the bond is stronger, then it does not give up the proton as readily and is a weaker acid. Other factors being equal, we can conclude the following.

If the H–A bond is strong, then HA is a weak acid.

EXERCISE 12.6:

List the acids HF, HCl, and HBr in order of increasing acid strength given that $D_{HF} = 565$ kJ/mol, $D_{HCl} = 431$ kJ/mol, and $D_{HBr} = 366$ kJ/mol.

________________ < ________________ < ________________

List the conjugate bases in order of increasing base strength.

________________ < ________________ < ________________

12.5-2. Bond Breaking

Bond energies are not sufficient to explain relative acid strengths because the tabulated values are for the bonds in the gas phase, not in solution. In addition, the bonding pair is divided between the bound atoms to produce atoms, not ions. The bond energy process is compared to the solution process for HF, HCl, and CH_4 in Figures 12.15a and 12.15b.

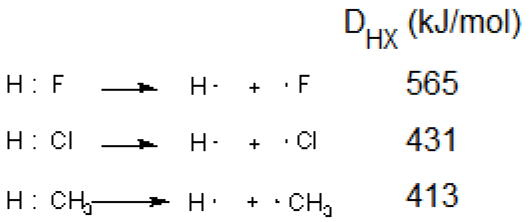


Figure 12.15a: Two Ways to Break Bonds–Gas Phase In the gas phase, the bonding pair is split so that each atom gets one electron to produce atoms, not ions.

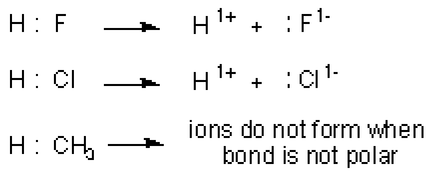


Figure 12.15b: Two Ways to Break Bonds–Solution Phase In the solution phase, the bonding pair remains on the more electronegative atom to produce ions, not atoms.

Note that the H–C bond is not polar, so it cannot break to produce ions, which is why hydrogen atoms attached to carbon are not acidic. We conclude that **the hydrogen atom must be attached to an atom that is more electronegative than carbon in order to be acidic**.

12.5-3. Electronegativity

Breaking the H–A bond in an acid-base reaction produces the ions, and ion formation is favored by large electronegativity differences between the bound atoms. Thus, **acid strengths also increase as the electronegativity of the atom to which the hydrogen is bound increases**.

EXERCISE 12.7:

You are given the following compounds and the bond energies of the bonds to hydrogen.

HF	HCl	CH_4
D_{HF} = 565 kJ/mol	D_{HCl} = 431 kJ/mol	D_{CH} = 413 kJ/mol

Fill in the following.

strongest of the three acids ________________

weakest acid ________________

12.5-4. Oxoacid Strengths

Oxoacids are acids in which the acidic hydrogen is attached to an oxygen atom. The strength of the oxoacid H–O–X depends upon the strength of the H–O bond. Anything that withdraws electron density from the H–O bond, weakens the bond and makes the acid stronger. Thus, **the strength of the acid increases with increases in the electronegativity or oxidation state of X.**

- If X is highly electronegative, it withdraws electron density of the O–H bond, which weakens the bond and makes the acid stronger. Thus, H_2SO_4 is a stronger acid than H_2SeO_4 because S is more electronegative than Se.
- The ability of X to withdraw electron density from the O–H bond also increases as its oxidation state increases. Thus, H_2SO_4 is a stronger acid than H_2SO_3 because the oxidation state of S is higher in H_2SO_4.

In Table 12.7, we consider four compounds with the general X–OH, where X = H, CH_3, Cl, and ClO. There are two lone pairs and a proton on the oxygen atom, so XOH can function as either an acid or a base depending upon the properties of X.

HOH	H–O–H (water) is both a very weak acid and a very weak base. In fact its acid and base strengths are equal.
$HOCH_3$	CH_3 groups are electron donating, so the oxygen atom is more electron rich than in water. Consequently, CH_3OH is a better base than water. Alternatively, the added electron density in the O–H bond strengthens the bond, which makes CH_3OH a weaker acid than water.
HOCl	Cl is electron withdrawing and is more electronegative than H. Removing electron density from OH has two effects: the oxygen is not as electron rich, so HOCl is a weaker base, and the O–H bond is weakened, so HOCl is a stronger acid. Thus, HOCl is a stronger acid and weaker base than water.
HOClO	OClOH ($HClO_2$) is the strongest acid and weakest base in this group. This is because the additional oxygen atom removes even more electron density than the single Cl, so it is a stronger acid than HOCl. Alternatively, the oxidation state of Cl goes from +1 in HClO to +3 in $HClO_2$. The increase in oxidation state withdraws electron density from OH, which makes it a weaker base and a stronger acid.

Table 12.7

12.5-5. Example

EXERCISE 12.8:

Use the following rules to determine whether each of the reactions is extensive or not.

- Extensive acid-base reactions occur when the reacting acid and base are much stronger than the produced acid and base.
- The stronger oxoacid is the one in which the central atom is more electronegative and/or in the higher oxidation state.

$HSO_4^{1-} + H_2SO_3 \rightleftharpoons H_2SO_4 + HSO_3^{1-}$

extensive

not extensive

$H_3PO_4 + H_2AsO_4^{1-} \rightleftharpoons H_2PO_4^{1-} + H_3AsO_4$

extensive

not extensive

12.6 Acid Dissociation Constant, K_a

Introduction

The extent of an acid-base reaction depends upon the strengths of the reacting and produced acids, and the acid dissociation constants of the acids give us those relative strengths.

Prerequisites

- 9.11-2. Examples of Equilibrium Constant Expressions (Write the equilibrium constant expression for a reaction that involves both aqueous solutes liquid water.)
- 9.11 Equilibrium and the Equilibrium Constant

Objectives

- Write the acid dissociation constant expression for an Arrhenius acid and the chemical equation to which it applies.
- Rate the relative acid strengths of series of Arrhenius acids given their acid dissociation constants.
- Write the acid dissociation constant expression for a Brønsted acid and the chemical equation to which it applies.
- Rate the relative acid strengths of series of Brønsted acids given their acid dissociation constants.
- Determine the equilibrium constant for an acid-base reaction from the acid dissociation constants of the reacting and produced acids.

12.6-1. Arrhenius Definition

Arrhenius acids ionize in water rather than react with it. Consequently, H^{1+} is produced rather than H_3O^{1+}.

An ***Arrhenius acid*** is a substance that contains H atoms and produces H^{1+} in water, and an ***Arrhenius base*** is a substance that contains OH and produces OH^{1-} in water. All Arrhenius acids and bases are also Brønsted acids and bases, but the Brønsted definition is slightly broader, so not all Brønsted acids and bases are classified as Arrhenius acids and bases. For example, NH_3 is a Brønsted base but not an Arrhenius base.

Arrhenius acids "ionize" in water to produce H^{1+} rather than react with it to produce H_3O^{1+}.

$$HA \rightleftharpoons H^{1+} + A^{1-}$$

The extent of the reaction is dictated by the strength of the acid and is measured by the equilibrium constant, which is called the ***acid dissociation*** or **acid ionization constant** and given the symbol K_a.

$$K_a = \frac{[H^{1+}][A^{1-}]}{[HA]}$$

12.6-2. Brønsted K_a

The dissociation constant of an acid, K_a, is the equilibrium constant for the reaction of the acid with water.

Brønsted Definition of Acid Strength

Brønsted acids do not dissociate in water, they react with it, so the equilibrium reaction becomes $HA + H_2O \leftrightharpoons H_3O^{1+} + A^{1-}$. The equilibrium constant for the reaction is the following.

$$K_a = \frac{[H_3O^{1+}][A^{1-}]}{[HA]}$$

Water is the solvent and considered to be a pure liquid, so it enters the equilibrium expression as 1 (one). Note that this is the same dissociation constant (K_a) as given for Arrhenius acids except that H_3O^{1+} appears instead of H^{1+}, but H_3O^{1+} and H^{1+} are just two way of representing the same species in the two different theories. The important thing to remember is that **acids with large K_a values are stronger than acids with smaller K_a values, regardless of whether the acid is treated as an Arrhenius acid or as a Brønsted acid**.

HCl is a strong acid ($K_a >> 1$). There are essentially no HCl molecules in a 0.1 *M* solution of HCl. The reverse reaction can be ignored when calculating the concentration of H_3O^{1+} or Cl^{1-} because K_a is so large. Consequently, the reaction is usually indicated with a single arrow.

$$HCl + H_2O \rightarrow H_3O^{1+} + Cl^{1-} \quad K_a = \frac{[H_3O^{1+}][Cl^{1-}]}{[HCl]} =>> 1$$

HClO is a weak acid. In a 0.1 *M* solution of HClO, $[H_3O^{1+}] = 10^{-4}$ *M*. The reverse reaction is important in determining the concentrations of H^{1+} and Cl^{1-}, so the double equilibrium arrows are used when writing the K_a equation.

$$HClO + H_2O \rightleftharpoons H_3O^{1+} + ClO^{1-} \quad K_a = \frac{[H_3O^{1+}][ClO^{1-}]}{[HClO]} = 3.5 \times 10^{-8}$$

H_2SO_3 is a weak diprotic (contains two protons) acid. In a 0.1 *M* solution of H_2SO_3,
$[H_3O^{1+}] = 0.04$ *M*. The importance of the reverse reaction is indicated with the double arrows. Note that only one proton is removed in the K_a equation. The conjugate base of H_2SO_3 is $HSO_3{}^{1-}$, which is also an acid with its own K_a (1.0×10^{-7}).

$$H_2SO_3 + H_2O \rightleftharpoons H_3O^{1+} + HSO_3^{1-} \quad K_a = \frac{[H_3O^{1+}][HSO_3^{1-}]}{[H_2SO_3]} = 1.5 \times 10^{-2}$$

HS^{1-} is a very weak acid. In a 0.1 *M* solution of HS^{1-}, $[H_3O^{1+}] = 10^{-7}$ *M*.

$$HS^{1-} + H_2O \rightleftharpoons H_3O^{1+} + S^{2-} \quad K_a = \frac{[H_3O^{1+}][S^{2-}]}{[HS^{1-}]} = 1.3 \times 10^{-13}$$

Hydronium ion is the strongest acid that can exist in water. HCl is a stronger acid, but it cannot exist in water because it reacts so extensively with the water.

$$H_3O^{1+} + H_2O \rightleftharpoons H_2O + H_3O^{1+} \quad K_a = \frac{[H_3O^{1+}]}{[H_3O^{1+}]} = 1$$

12.6-3. Determining *K* for an Acid-Base Reaction

The equilibrium constant for an acid-base reaction equals the acid dissociation constant of the reacting acid divided by that of the produced acid.

The equilibrium constant for any acid-base reaction can be determined from the K_a values of the reacting and produced acids as shown in Equation 12.1.

$$K = \frac{K_a \text{ of reacting acid}}{K_a \text{ of produced acid}} \qquad \text{Equilibrium Constant, } K \tag{12.1}$$

Recall that we are using the general guideline that acid-base reactions in which $K > \sim 1000$ are so extensive that the back reaction can be ignored in calculations, and they can be written with single arrows. This means that the reacting acid must be about 1000 times stronger than the produced acid if an acid-base reaction is considered to be so extensive that the back reaction can be ignored in calculations.

12.6-4. Determining *K* Exercise

EXERCISE 12.9:

Use the following K_a values to answer the questions.

Acid	K_a
HF	7.2×10^{-4}
HNO_2	4.0×10^{-4}
NH_4^{1+}	5.6×10^{-10}
HCN	4.0×10^{-10}

What is the strongest acid?

____

What is the acid with the strongest conjugate base?

____

Are the following reactions extensive enough to be expressed with single arrows?

$HCN + NH_3 \rightleftharpoons CN^{1-} + NH_4{}^{1+}$
Yes
No

$HF + CN^{1-} \rightleftharpoons F^{1-} + HCN$
Yes
No

12.6-5. Predicting Extent Exercise

EXERCISE 12.10:

Use the following K_a values to determine the equilibrium constant for the reaction of each of the acids with ClO^{1-} and indicate whether a single arrow can be used to describe the reaction.

Acid	$\boldsymbol{K_a}$	**Base**
HF	7.2×10^{-4}	F^{1-}
H_2S	1.0×10^{-7}	HS^{1-}
HClO	3.5×10^{-8}	ClO^{1-}
HCN	4.0×10^{-10}	CH^{1-}
HS^{1-}	1.3×10^{-13}	S^{2-}

HF
$K =$ ______________

$\rightarrow$
$\rightleftharpoons$

H_2S
$K =$ ______________

$\rightarrow$
$\rightleftharpoons$

HCN
$K =$ ______________

$\rightarrow$
$\rightleftharpoons$

HS^{1-}
$K =$ ______________

$\rightarrow$
$\rightleftharpoons$

12.7 Solutions of Weak Bases

Introduction

Water is also an acid, so it can react with weak bases to produce hydroxide ion and the conjugate acid of the weak base.

12.7-1. Most Anions are Weak Bases

Weak bases react with water to produce hydroxide ion and their conjugate acid.

Consider the reaction of hypochlorite ion, a weak base, with water: $ClO^{1-} + H_2O(l) \rightleftharpoons HClO(aq) + OH^{1-}$.

The reaction of a base with water breaks an O–H bond in water in a process called hydrolysis. Most weak bases are found as salts, so salts such as KClO, NaF, KCN, and $LiNO_2$ all form basic solutions in water because their anions react with water to produce hydroxide ion.

12.8 Acid Base Table

Introduction

Acid-base reactions are extensive when the reacting acid is stronger than the produced acid. Acid strengths are measured by the acid dissociation constants for the acids. Combining these two facts, we can now write equations for acid-base reactions and determine if they are extensive.

Objectives

- Predict whether an acid-base reactions is extensive based on the positions of the acid and base in the acid-base table.
- Identify the reactants to be used in a net equation for an acid-base reaction.

- Use the acid base table to write equations for acid-base reactions and to determine the equilibrium constant for the reaction.
- Decide whether an acid-base reaction is better represented with a single or a double arrow.

12.8-1. Using an Acid-Base Table Video

A video or simulation is available online.

12.8-2. Using the Acid-Base Table to Write Chemical Equations

A video or simulation is available online.

12.8-3. Acid-Base Table

Acid base reactions are extensive when the reacting acid is stronger than the produced acid, and the relative acid strengths can be deduced from the acid dissociation constants. Consequently, tables of acids and their K_a values are common. The acid-base table used in the text includes the acid, its K_a, and its conjugate base. Thus, both the reactants and the products of an acid-base reaction can be found in the table.

The acid-base table used in this text is given in the Acid-Base Table resource. It lists the acids in the left column, their K_as in the center column, and their conjugate bases in the right column. Acid strengths decrease and base strengths increase going down the table. This arrangement puts the strongest acid ($HClO_4$) in the upper left corner and the strongest base (O^{2-} ion) in the lower right corner. Therefore, consider the following.

Acid-base reactions are extensive when the reacting acid is above (stronger than) the produced acid in the table.

The following examples show how the relative positions of the acid and base allow us to predict whether an acid-base reaction is extensive.

HA is a stronger acid than HB, so it lies above HB in the acid-base table. B^{1-} is a stronger base than A^{1-}, so it lies below A^{1-} in the acid-base table.

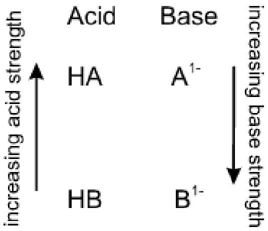


Figure 12.16a: Reactivity from the Relative Positions of Reactants and Products

Reaction of the stronger acid (HA) with the stronger base (B^{1-}) is favorable ($K > 1$). Note that this arrangement guarantees that the reacting acid is stronger than the produced acid. If the reacting acid is well above the reacting base (or produced acid), the reaction is so extensive that it can be written with a single arrow. For example, $HF + OH^{1-} \rightarrow F^{1-} + H_2O$.

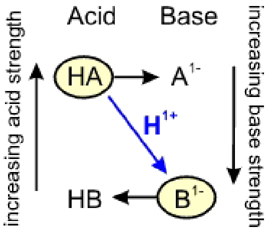


Figure 12.16b: Reactivity from the Relative Positions of Reactants and Products

Reaction of the weaker acid (HB) with the weaker base (A^{1-}) is not extensive. Note that the reacting acid is below (weaker than) the produced acid. Only a small fraction of the acid is converted to its conjugate base (B^{1-}), and only a small fraction of the base is converted to its conjugate acid (HA). The back reaction of the stronger acid and base is important in determining the concentrations of B^{1-} and HA, so the net equation is usually written with double arrows. For example, $HCN + F^{1-} \rightleftharpoons CN^{1-} + HF$.

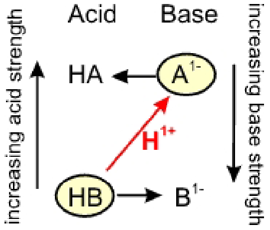


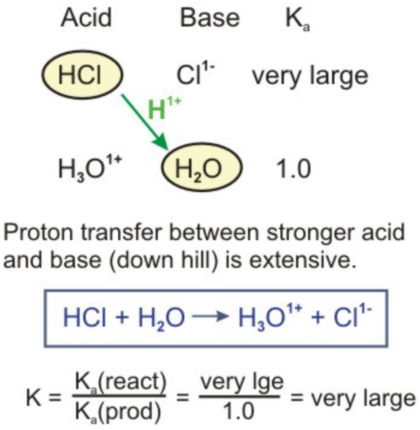
Figure 12.16c: Reactivity from the Relative Positions of Reactants and Products

12.8-4. Acid-Base Table Examples

We now use the acid-base table to write chemical equations for the acid-base reactions that result when the following solutions are mixed and use Equation 12.1 to determine their equilibrium constants. We use the relative positions of the reactants in the table and the equilibrium constants to indicate whether the reactions are extensive. Remember that the acid strengths increase going up the table, but base strengths increase going down the table. View the Acid-Base Table resource.

Hydrogen chloride gas is bubbled into water.

The relative reactant positions and their K_a values from the table in the resources are given in Figure 12.17a. Note that the reactant is hydrogen chloride, not hydrochloric acid, so the reacting acid is HCl. The reacting base is then water. The products of the reaction are Cl^{1-}, the conjugate base of the reacting acid, and H_3O^{1+}, the conjugate acid of the reacting base. The acid is above the base, so we expect a favorable reaction. Note that the K_a values of the strong acids are given simply as << 1 because they are so large that they cannot be determined accurately. We use Equation 12.1 to determine that the value of the equilibrium constant is very large, so a single arrow should be used. Thus, dissolving HCl(g) in water produces hydrochloric acid, which is a solution of hydronium and chloride ions.



Proton transfer between stronger acid and base (down hill) is extensive.

$$\boxed{HCl + H_2O \longrightarrow H_3O^{1+} + Cl^{1-}}$$

$$K = \frac{K_a(\text{react})}{K_a(\text{prod})} = \frac{\text{very lge}}{1.0} = \text{very large}$$

Figure 12.17a

Solutions of hydrocyanic acid and potassium nitrite are mixed.

We identify HCN as the reacting acid, K^{1+} as a spectator ion, and the $NO_2{}^{1-}$ ion as the reacting base. The reactants and their K_a values as determined from the acid-base table are given in Figure 12.17b. The reacting acid is below the reacting base, so little proton transfer is expected. Using Equation 12.1, we determine that the equilibrium constant is only 1.0×10^{-6}, so very little product would form and double arrows would have to be used in the chemical equation.

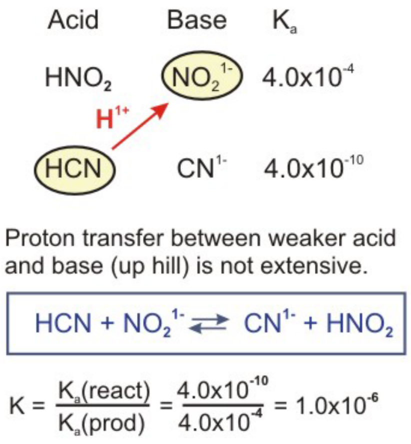


Figure 12.17b

A solution of potassium hypochlorite is added to hydrochloric acid.

We identify the K^{1+} ion as a spectator ion and the ClO^{1-} ion as the reacting base. HCl is leveled to $H_3O^{1+} + Cl^{1-}$ in water, so H_3O^{1+} is the reacting acid, while Cl^{1-} is also a spectator ion. We retrieve the reacting acid and base from the acid-base table as shown in Figure 12.17c. The acid is well above the base, so an extensive proton transfer is expected, and using Equation 12.1, we determine that $K = 2.9 \times 10^7$. Thus, the reaction can be written with a single arrow.

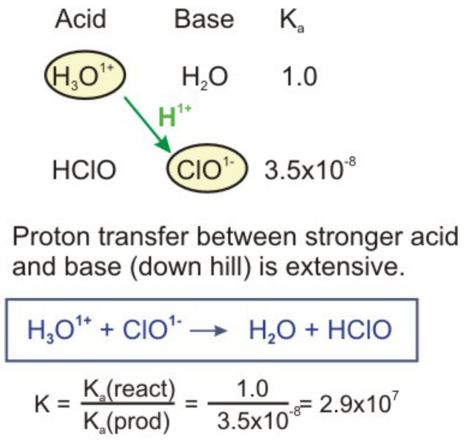


Figure 12.17c

Ammonia is added to water.

We identify NH_3 as the reacting base and H_2O as the reacting acid. The relative positions and K_a values of the reactants as given in the acid-base table are shown in Figure 12.17d. The base is well above the acid, so little proton transfer is expected. Indeed, $K = 1.8 \times 10^{-5}$ for the reaction, so double arrows should be used for the reaction of this weak base with water.

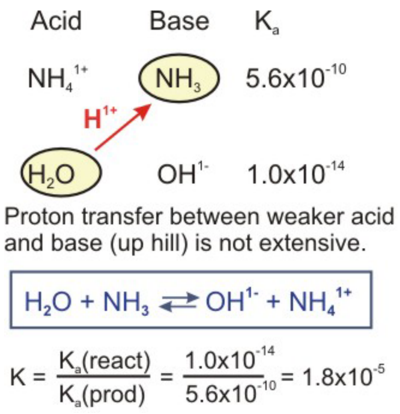


Figure 12.17d

Hydrofluoric acid is added to a solution of potassium hydrogen sulfide.

HF is the reacting acid and K^{1+} is a spectator ion. The HS^{1-} ion has a proton and is an anion, so it can behave as either and acid or a base, but the HF will not react with another acid, so HS^{1-} is the reacting base in this reaction. The acid is above the base so the transfer is favorable with an equilibrium constant of 7.2×10^3, so a single arrow can be used in the net equation to show that essentially all of at least one of the reactants disappears.

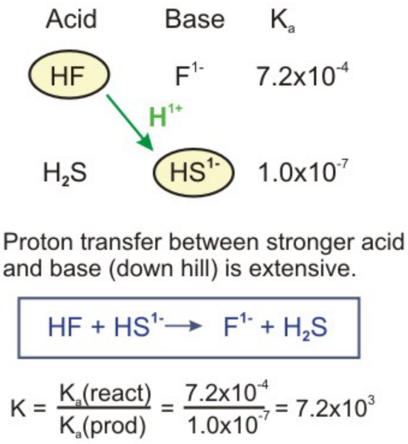


Figure 12.17e

12.8-5. Identifying the Reactants

Identifying the reacting species is the first thing you must do when writing the net ionic equation for an acid-base equation. Remember the following:

- Strong acids are written as H_3O^{1+} and weak acids as the formula of the acid.
- Most bases and a few acids are anions, but they are usually found as salts. However, the cation is usually a spectator ion in these cases. Thus, the base in a solution of KF is the F^{1-} ion.
- $NH_4{}^{1+}$ is an acid, but it is normally found as a salt. Be careful with the anion because anions are also bases. If the anion is the conjugate base of a strong acid, it is a spectator ion in an acid-base reaction, otherwise, the anion may be a reactive base.
- Anions with acidic protons, such as $HSO_3{}^-$, are amphiprotic. They behave like acids in the presence of bases, but they function as bases in the presence of acids.

EXERCISE 12.11:

Indicate how the reacting acids and bases would be represented in the net ionic equations for the acid-base reactions that occur when solutions of the following are mixed. Refer to the Acid-Base Table resource.

nitric acid and potassium sulfide	ammonium chloride and sodium cyanide
acid _______________	acid _______________
base _______________	base _______________
sodium carbonate and hydrofluoric acid	ammonia and perchloric acid
acid _______________	acid _______________
base _______________	base _______________

12.8-6. Net Equations

EXERCISE 12.12:

Use the Acid-Base Table resource to write net equations for the reactions described below. Use a single arrow to indicate that a reaction is extensive and double arrows to indicate that it is not. Assume that a reaction is extensive only when the reacting acid is at least 1000 times stronger than the produced acid. That is, **use a single arrow if the following is true**.

- K_a(reacting acid) $> 1000 \times K_a$(produced acid)

Indicate the extent of the reaction by choosing the single or double arrows.

Barium hydroxide and **nitric acid** are mixed.

_______________ (acid 1) + _______________ (base 2)

$\rightarrow$

$\rightleftharpoons$

_______________ (base 1) + _______________ (acid 2)

Sodium acetate and **hydrochloric acid** are mixed.

_______________ (acid 1) + _______________ (base 2)

$\rightarrow$

$\rightleftharpoons$

_______________ (base 1) + _______________ (acid 2)

Sodium hydroxide and **hydrofluoric acid** are mixed.

_______________ (acid 1) + _______________ (base 2)

$\rightarrow$

$\rightleftharpoons$

_______________ (base 1) + _______________ (acid 2)

Ammonium chloride and **sodium cyanide** are mixed.

______________ (acid 1) + ______________ (base 2)

→
⇌
______________ (base 1) + ______________ (acid 2)

Ammonium chloride and **sodium fluoride** are mixed.

______________ (acid 1) + ______________ (base 2)

→
⇌
______________ (base 1) + ______________ (acid 2)

12.9 pH and pK_a

Introduction

The hydronium ion concentration is an important property of an aqueous solution, but it can be very small, so it is often given on the p-scale to avoid writing exponents.

Objectives

- Write the expression for the ion product constant of water and give its value at 25 °C.
- Determine the hydronium (or hydroxide) ion concentration in aqueous solution given the hydroxide (or hydronium) ion concentration.
- Define pK_a and determine relative acid strengths based on the acid pK_a.

12.9-1. The Ion Product Constant of Water

Water is both a very weak acid and a very weak base, so it can react with itself.

$$\mathrm{H_2O + H_2O \rightleftharpoons H_3O^{1+} + OH^{1-}}$$

Remember that water is the solvent and is treated as a pure liquid, so it enters the equilibrium expression as unity to produce the following equilibrium constant expression.

$$K_\text{w} = [\mathrm{H_3O^{1+}}][\mathrm{OH^{1-}}] = 1.0 \times 10^{-14} \qquad \text{Ion Product of Water} \qquad (12.2)$$

The equilibrium constant for the reaction is called the ***ion product constant of water*** and given the symbol K_w. The value given for the equilibrium constant is the value at 25 °C. Equation 12.2 can be used to determine either $[\mathrm{H_3O^{1+}}]$ or $[\mathrm{OH^{1-}}]$ if the other is known.

In pure water, the hydronium and hydroxide ion concentrations are the same because they are produced in a 1:1 ratio from water. Consequently, in pure water at 25 °C, the following is true.

$$\begin{aligned} [\mathrm{H_3O^{1+}}] &= [\mathrm{OH^{1-}}] = (K_\text{w})^{1/2} \\ &= 1.0 \times 10^{-7} M \end{aligned} \qquad \text{Concentrations in Pure Water} \qquad (12.3)$$

Solutions for which Equation 12.3 is valid are called neutral; solutions in which $[\mathrm{H_3O^{1+}}] > [\mathrm{OH^{1-}}]$ are called acidic; and solutions in which $[\mathrm{H_3O^{1+}}] < [\mathrm{OH^{1-}}]$ are called basic or alkaline.

12.9-2. pH

The hydronium ion concentration is an important characteristic of the solution, but it is normally a small number. To avoid the use of exponentials in discussions of hydronium ion concentrations, we define ***pH***.

$$\text{pH} = -\log[\text{H}_3\text{O}^{1+}] \qquad \text{pH Defined} \tag{12.4}$$

The exponent of $[\text{H}_3\text{O}^{1+}]$ is usually negative, so the sign of log $[\text{H}_3\text{O}^{1+}]$ is usually negative. The negative sign in Equation 12.4 assures that the pH is usually positive. Because of the negative sign, a high pH implies a low hydronium ion concentration, and a low pH implies a high hydronium ion concentration.

Equation 12.2 can be rearranged as follows to show how the hydronium ion concentration, and therefore the pH, of a basic solution can be determined.

$$\begin{aligned}[\text{H}_3\text{O}^{1+}] &= \frac{K_\text{w}}{[\text{OH}^{1-}]} \qquad \text{Hydronium and Hydroxide Ion Concentrations} \\ &= \frac{1.0\times 10^{-14}}{[\text{OH}^{1-}]}\end{aligned} \tag{12.5}$$

Equation 12.5 shows that solutions with high hydroxide ion concentrations have low hydronium ion concentrations, so a high pH also implies a high hydroxide ion concentration and a low pH implies a low hydroxide ion concentration. A neutral solution is one in which $[\text{H}_3\text{O}^{1+}] = [\text{OH}^{1-}] = 1.0\times 10^{-7}M$, so the pH of a neutral solution is determined to be $\text{pH} = -\log(1.0\times 10^{-7}) = 7.0$. The hydronium ion concentration is greater in an acidic solution, so the pH of an acidic solution is less than 7.0. The hydronium ion concentration is less in a basic solution, so the pH of a basic solution is greater than 7.0. These conclusions are summarized in the following table.

Solution pH	**Solution Type**
above 7	basic
equal to 7	neutral
below 7	acidic

Table 12.8: Solution Type Versus pH

12.9-3. Hydronium Ion Concentration Exercise

EXERCISE 12.13:

What is the hydronium ion concentration in the following solutions? Use e-format for exponentials:
$1\times 10^{-4} = 1\text{e}-04$.

pure water ______________ M

$[\text{OH}^{1-}] = 2.5\text{e}-04\ M$ ______________ M

$[\text{OH}^{1-}] = 6.2\text{e}-12\ M$ ______________ M

12.9-4. pH Exercises

EXERCISE 12.14:

What is the pH if $[H_3O^{1+}] = 1.3 \times 10^{-5}$ M?

____

What is the pH of 0.10 M HCl?

____

Pick the stronger acid given the pHs of their 0.1 M solutions.

The pH of 0.1 M HBrO is 4.8.
The pH of 0.1 M HClO is 4.3.

What is the pH of a 0.022 M $Ba(OH)_2$ solution? Hint: the hydroxide ion concentration is not 0.022M.

____

12.9-5. pK_a

A high pK_a implies a weak acid.

The K_a of an acid is a commonly used property of acids because it describes the acid strength, but it is frequently given as the **pK_a** to avoid using negative exponents in discussions of acid strength. The pK_a of an acid is the negative base 10 logarithm of the K_a.

$$\mathrm{p}K_a = -\log K_a \qquad \mathrm{p}K_a \tag{12.6}$$

Acids with high pK_as are weak acids because of the negative sign in the pK_a definition. The following table lists some acids, their K_as and their pK_as.

Acid	K_a	pK_a
HF	7.2×10^{-4}	3.14
HOCl	3.5×10^{-8}	7.46
HCN	4.0×10^{-10}	9.40

Table 12.9

Note that the pK_a increases as the acid strength decreases.

12.9-6. pK_a Exercise

EXERCISE 12.15:

A 0.1 M solution of which of the following acids has the higher pH?

phenol (pK_a = 10.0)
HSO_3^{1-} (pK_a = 7.0)

12.9-7. Selecting the Solution with the Lower pH Exercise

EXERCISE 12.16:

Indicate the solution in each pair that has the lower pH.

0.10 *M* HNO_2
0.15 *M* HNO_2

0.10 *M* KF
0.15 *M* KF

0.05 *M* benzoic acid (pK_a = 4.19)
0.05 *M* lactic acid (pK_a = 3.85)

0.1 *M* $Ba(OH)_2$
0.15 *M* KOH

12.10 Exercises and Solutions

Links to view either the end-of-chapter exercises or the solutions to the odd exercises are available in the HTML version of the chapter.

Chapter 13 – Organic Chemistry

Introduction

Organic chemistry is the study of carbon based compounds. The structural and genetic materials of living organisms are organic compounds. Many of the substances that we encounter on a daily basis are organic compounds: drugs, plastics, textiles, dyes, paper, food, vitamins, etc. Because of the manner in which carbon atoms can bond to one another, the number of organic compounds is enormous. In this chapter, we explore some of the fundamental topics of the structure and reactivity of several classes of organic compounds by applying our knowledge of Lewis structures, resonance, and Lewis acid-base theory.

13.1 Hydrocarbons

Introduction

We begin our study of organic chemistry with two classes of compounds that contain only carbon and hydrogen.

Prerequisites

- 5.8 Formal Charge and Oxidation State (Draw Lewis structures.)

Objectives

- Name and draw the two simplest alkanes.
- Draw line-wedge-dash, Lewis, condensed, and skeletal structures of alkanes.
- Convert skeletal structures into molecular formulas.
- Distinguish between a straight or continuous chain and a branched chain.
- Write the equation for the combustion of an alkane.
- Define an alkene and draw and name the two simplest alkenes.
- Draw the isomers of an alkene.
- Define a polyene and explain why many polyenes absorb visible light.
- Define alkynes and discuss their isomers.
- Distinguish between saturated and unsaturated hydrocarbons.

Alkanes

13.1-1. Definition

Carbon atoms always have four bonds: four single bonds, two single and one double bond, two double bonds, or a single bond and a triple bond. Although carbon is the basic building block, organic compounds usually have hydrogen atoms as well. Oxygen and nitrogen are also common, but almost any other element can be found in organic compounds. In this section, we deal with the class of compounds known as ***hydrocarbons***, which are compounds that contain only carbon and hydrogen.

Alkanes are the simplest organic compounds. All of the carbon atoms in an alkane are sp^3 hybridized and tetrahedral, and all bonds are sigma bonds, which makes alkanes relatively unreactive. They have the general formula C_nH_{2n+2}, where n is an integer. Table 13.1 shows the three simplest alkanes.

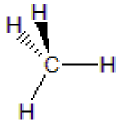
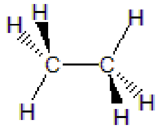
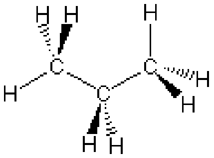
Alkane	Structure
Methane, CH_4	
Ethane, C_2H_6	
Propane, C_3H_8	

Table 13.1: The Simplest Alkanes

13.1-2. Structures

Carbon atoms always have four bonds in their compounds.

There are times when the line-wedge-dash representation is used to show the three-dimensional structure of organic compounds, but the structures of alkanes are very dynamic because ***groups attached by a single bond can rotate relative to one another (much like the wheels on an axle)***. Consequently, other shorthand notations are frequently used. These other methods, shown in Figures 13.1a, 13.1b, 13.1c, and 13.1d, are based on the following points that are common to most organic molecules.

- Carbon atoms form their backbone.
- Carbon atoms always have four bonds to them.
- There are usually many C–H bonds present.

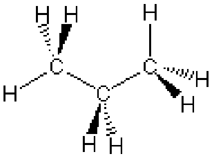


Figure 13.1a: Representations of Propane: Wedge-Dash

Propane is C_3H_8. Figure 13.1a shows the line-wedge-dash representation of the three-dimensional structure.

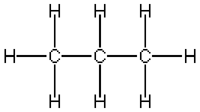
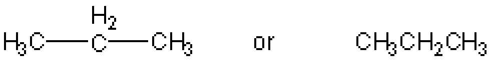


Figure 13.1b: Representations of Propane: Lewis Structure

In a **Lewis structure** of an organic compound, all of the bonds and atoms are shown explicitly, but the bond angles are often shown as 90°.



$$H_3C\text{—}\overset{H_2}{C}\text{—}CH_3 \quad \text{or} \quad CH_3CH_2CH_3$$

Figure 13.1c: Representations of Propane: Condensed Structure

A **condensed structure** shows the atoms, but not all of the bonds. Sometimes the C–C bonds are shown, but frequently they are not.

Figure 13.1d: Representations of Propane: Skeletal Structure

A **skeletal structure** does not show carbon or hydrogen atoms explicitly, nor does it show the C–H bonds. The positions of the carbon atoms in a skeletal structure are indicated by the ends and intersections of lines. Thus, the structure of propane shows three carbon atoms: one at each end and one at the intersection of the two line segments. The positions of the hydrogen atoms are inferred from the number of bonds shown to each carbon. Each carbon atom must have four bonds (a double bond counts as two bonds and a triple bond counts as three), so ***the number of C–H bonds to any carbon atom equals four minus the number of bonds shown to the carbon atom in the skeletal structure***. For example, the skeletal structure shows only one bond to each of the terminal carbon atoms, so there must also be three C–H bonds to each of the end carbons. The structure shows two bonds to the middle carbon, so there must also be two C–H bonds.

13.1-3. Molecular Formulas for Skeletal Structures

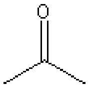
Neither carbon nor hydrogen atoms are shown explicitly in a skeletal structure.

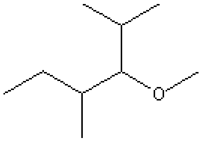
Use the following rules to convert the skeletal structures into molecular formulas.

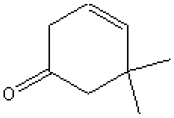
- Carbon atoms are represented as intersections or ends of lines.
- The number of hydrogen atoms attached to a carbon atom is equal to four minus the number of bonds involving the carbon atom because carbon atoms are always involved in four bonds. Note that double and triple bonds count as 2 and 3 bonds, respectively.

EXERCISE 13.1:

Write the molecular formula for the given skeletal structures. **Note that the order of elements in the formula should be C then H then O**.







13.1-4. Chains

Isomers are different molecules with the same formula.

There is only one way to connect the carbon atoms in each of the alkanes discussed so far, but there are multiple ways to connect the carbon atoms in all of the alkanes with more than three carbon atoms. The way in which the carbon atoms are connected is called the ***connectivity***. The molecules with the same formula but different connectivities are different molecules, and different molecules with the same formula are called ***isomers***.

Molecules in which no carbon is connected to more than two other carbons are called ***straight chains*** or ***continuous chains***, while molecules that contain with at least one carbon with three or four carbon atoms attached to it are called ***branched chains***. Butane (C_4H_{10}) exists as two isomers, one straight chain and one branched chain.

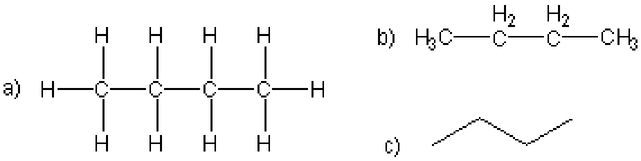


Figure 13.2a: Isomers of Butane: Straight Chain Lewis (a), condensed (b), and skeletal (c) representations of the straight or continuous chain isomer: It is a straight chain isomer because none of the carbon atoms are connected to more than two other carbon atoms.

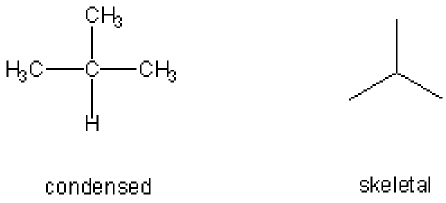

condensed skeletal

Figure 13.2b: Isomers of Butane: Branched Chain It is a branched isomer because there are three carbon atoms connected to the central carbon atom, so the chain branches at that position.

13.1-5. Combustion

Alkanes are found primarily in natural gas (mainly CH_4 and C_2H_6) and petroleum. They are relatively unreactive, but they do burn well. Burning is a rapid combustion, i.e., the reaction with oxygen. The products of the combustion of an alkane are CO_2 and H_2O. Table 13.2 shows the heats of combustion for four common alkanes.

Alkane	**Use**	**Combustion Reaction**	**Heat of Combustion (kJ/mol)**
methane	natural gas furnace	$CH_4 + 2\ O_2 \rightarrow CO_2 + 2\ H_2O$	−891
propane	propane tank	$C_3H_8 + 5\ O_2 \rightarrow 3\ CO_2 + 4\ H_2O$	−2220
butane	cigarette lighters	$C_4H_{10} + 6.5\ O_2 \rightarrow 4\ CO_2 + 5\ H_2O$	−2855
octane	automobile fuel	$C_8H_{18} + 12.5\ O_2 \rightarrow 8\ CO_2 + 9\ H_2O$	−5494

Table 13.2: Combustion of Some Common Alkanes

13.1-6. Octane Ratings

Each atom in a C–H or C–C bond retains one of the bonding electrons during combustion. The result is two species, called free radicals, that have unpaired electrons. Free radicals are highly reactive, but they are stabilized when the unpaired electron is on an atom that is attached to other carbon-containing groups. Thus, free radicals formed from highly branched carbon atoms are more stable and less reactive than those formed from straight chain hydrocarbons.

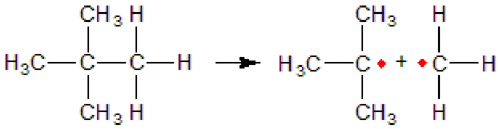


Figure 13.3: Free Radicals Bond cleavage of a C–C bond during combusion produces two free radicals. The radicals are stabilized when the carbon atom with the unpaired electron is bound to one or more carbon atoms, so $(CH_3)_3C\cdot$ is more stable and less reactive than $H_3C\cdot$.

Indeed, straight chain hydrocarbons react so fast and violently that they can cause an engine to “knock.” The octane rating of a gasoline indicates the extent of knocking it causes. The reference molecules are shown in Figure 13.4. The straight chain hydrocarbon C_7H_{16} causes substantial knocking and is assigned an octane rating of 0, while the highly branched alkane C_8H_{18} (an isomer of octane) causes little knocking and is assigned an octane rating of 100. A gasoline with an octane rating of 87 causes the same knocking as a mixture that is 87% in the branched alkane and 13% of the straight chain alkane.

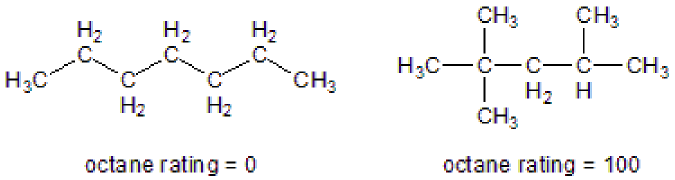


Figure 13.4: Reference Molecules Used to Determine Octane Ratings

Alkenes

13.1-7. Definition

Organic compounds that contain carbon-carbon double bonds are called ***alkenes***. The carbon atoms involved in the double bond are sp^2 hybridized. The two simplest alkenes are ethene (C_2H_4) and propene (C_3H_6).

Alkenes in which the position of the double bond is different are different molecules. However, care must be taken to be certain that the two positions are indeed different and not just a different view of the same molecule.

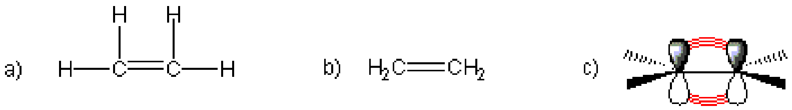


Figure 13.5a: a) Lewis, b) Condensed, and c) Line-Wedge Representations of Ethene

Note that the p orbitals and the pi interaction are shown in the line-wedge structure.

The two carbon atoms are each sp^2 hybridized, and the molecule is planar. Figure 13.5a(c) shows the pi bond (represented in red) as the overlap of the two p orbitals that are not used to make the hybrid orbitals. The electron density of the pi bond lies above and below the molecular plane. Consequently, the pi electrons can attack other substances, i.e., alkenes are weak Lewis bases.

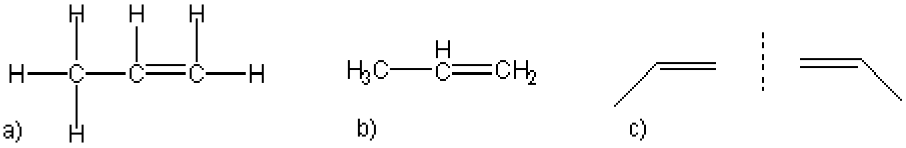


Figure 13.5b: a) Lewis, b) Condensed, and c) Skeletal Structures of Propene

It might appear that the double bond in C_3H_6 could be placed after the first carbon or before the last carbon. However, these two positions are identical because one can be converted into the other by a rotation of the molecule. Thus, the two skeletal structures shown in Figure 13.5b(c) are identical, not isomers. Simply rotate one about the dotted line to get the other.

13.1-8. Butene

The double bond in C_4H_8 can be placed in three different positions (after the first or second carbon in a straight chain or after the first carbon of a branched chain) to produce three isomers. In addition, groups cannot rotate about double bonds like they can about single bonds because the rotation would break the pi bond. Consequently, the butene with two carbon atoms (two CH_3 groups) on the same side of the double bond is different than the one with the two carbon atoms on opposite sides. We will discuss this type of isomer in more detail later.

The four isomers of C_4H_8 are derived below by starting with propene as follows.

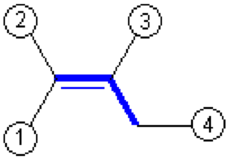


Figure 13.6: Possible Positions of the Fourth Carbon Atom in Butene The skeleton of C_3H_6 is highlighted in blue. The fourth carbon (CH_3 group) of C_4H_8 can be placed in any of the labeled positions to produce a total of four different molecules (isomers).

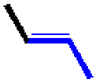
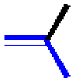
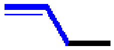
Position of 4th C	**Skeletal Structure**	**Comments**
1		Propane is C_3H_8. This is a straight chain alkene with double bond after the second carbon atom. In this isomer, the two CH_3 groups are on the *same side* of the double bond.
2		This is also a straight chain alkene with double bond after the second carbon atom. In this isomer, the two CH_3 groups are on *opposite sides* of the double bond.
3		This isomer is the only branched isomer.
4		This is the only straight chain isomer in which the double bond involves one of the end carbons.

Table 13.3: The Isomers of Butene

13.1-9. Polyenes

Organic dyes are polyenes with alternating single and double bonds.

The names of alkenes all end in -*ene*, and compounds with many double bonds are called ***polyenes***. An extended pi system results when double bonds of a polyene alternate with single bonds (as in —═—═—═—═) and the pi electrons are delocalized over the alternating single and double bonds. Recall from our discussion of band theory (Chapter 8.6), that electronic energy levels get closer together as electrons become spread out over many bonds. Also recall from Chapter 6.5 that pi electrons can be delocalized over many carbon atoms. Thus, while most organic compounds are white or colorless because their electronic energy levels are too far apart to absorb visible light, many polyenes with alternating single and double bonds absorb visible light and are colored. Consequently, they are often used to make dyes. As we shall see later in this chapter, it is the absorption of a visible photon by a polyene that initiates the vision process. Two common polyene dyes are considered in Figures 13.7a and 13.7b.

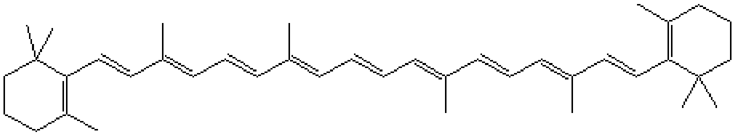


Figure 13.7a: Skeletal Structures of Two Polyenes: Beta Carotene Beta carotene gives carrots their orange color and is oxidized to vitamin A in the body. Its color is due to the large number of alternating single and double bonds (21).

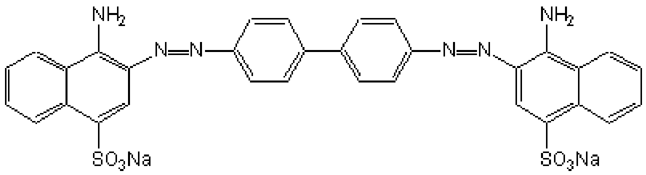


Figure 13.7b: Skeletal Structures of Two Polyenes: Congo Red Congo red was one of the first dyes for cotton. It has 41 bonds involved in the pi system. The polar NH_2 and $SO_3{}^{1-}$ groups form hydrogen bonds to the cellulose in the cotton fiber, which keeps the dye from washing out.

Alkynes

13.1-10. Definition

Alkynes are hydrocarbons that contain at least one triple bond. The simplest alkyne is C_2H_2, which is ethyne, or more commonly acetylene.

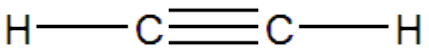


Figure 13.8

Carbon atoms involved in triple bonds have only two electron regions, are sp hybridized, and have 180° bond angles. The presence of π electrons makes them Lewis basic as well, and their chemistry is similar to that described above for alkenes.

13.1-11. Isomers

As with alkenes, different positions of the multiple bond can lead to different isomers. However, the positions must be different viewed from either end of the molecule. For example, there are three ways to draw butyne, but there are only two isomers. The two molecules on the left of Figure 13.9 are the same molecule as the triple bond in each is located on a terminal carbon atom. The molecule on the right is the isomer of the molecule on the left.

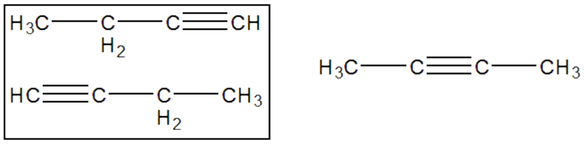
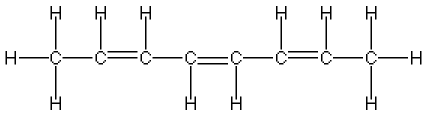
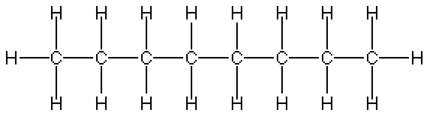


Figure 13.9: Isomers of Butyne

13.1-12. Hydrogenation and Saturation

Carbon atoms with four sigma bonds are ***saturated carbons***, while those with less than four sigma bonds are ***unsaturated carbons***.

All of the carbon atoms in alkanes are saturated because they have the maximum number of sigma bonds (four). However, carbon atoms involved in multiple (double or triple) bonds are unsaturated because their pi bonds can be replaced with sigma bonds, which increases the number of electron regions. Compounds with many multiple bonds are said to be ***polyunsaturated***. An unsaturated compound can be saturated by ***hydrogenation***, i.e., by reaction with hydrogen. In a hydrogenation, H_2 adds across the double bond, forming two C–H bonds, i.e., the pi bond between the carbon atom is replaced by two C–H sigma bonds.

unsaturated hydrocarbon	+	**hydrogen**	→	**saturated hydrocarbon**
 unsaturated alkene	+	3 H_2	→	 saturated alkane
Multiple bonds (double and triple) are unsaturated. The more multiple bonds a compound has, the higher is its degree of unsaturation. Unsaturated compounds can be saturated by hydrogenation.		One H_2 is required for each double bond.		All C–C bonds are single bonds in the hydrocarbon above, so it is saturated.

13.2 Naming Simple Hydrocarbons

Introduction

Understanding the nomenclature of alkanes, alkenes, and alkynes will help you understand some of the diversity in organic molecules that will be discussed later in the chapter.

Prerequisites

- 5.8 Formal Charge and Oxidation State (Draw Lewis structures.)
- 6.4: Valence Bond Theory and Hybridization (Determine the hybridization of an atom in a Lewis structure.)

Objectives

- Give the common root names and the endings for alkanes and alkenes.
- Name straight chain alkanes.
- Identify and name the two simplest alkyl groups.
- Name branched alkanes with a single alkyl group.
- Name branched alkanes with two alkyl groups.
- Name straight chain alkenes and alkynes.

13.2-1. Root Names

The name of a hydrocarbon is based on the name of the longest continuous chain it contains.

The name of an organic compound must indicate the number of carbon atoms in the longest continuous chain, which is given by the **root name** of the chain as given in Table 13.4, and the type of compound, which is designated by the ending of the name as shown below.

- Alkanes end in **ane**.
- Alkenes end in **ene**.
- Alkynes end in **yne**.

For example, a hexane is an alkane that contains a six-carbon chain, while a pentene is an alkene with a five-carbon chain, and butyne is an alkyne with a four-carbon chain.

# C atoms	Root Name	Name of Alkane	Name of Alkene
1	meth	methane	
2	eth	ethane	ethene
3	prop	propane	propene
4	but	butane	butene
5	pent	pentane	pentene
6	hex	hexane	hexene
7	hept	heptane	heptene
8	oct	octane	octene
9	non	nonane	nonene
10	dec	decane	decene

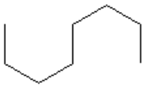
Table 13.4: Root Names for Organic Compounds

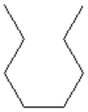
13.2-2. Naming Organic Molecules

EXERCISE 13.2:

To name a straight or continuous chain alkane, ***indicate the number of carbon atoms it contains with the appropriate root name and add -ane***. For example, $C_{10}H_{22}$ contains ten carbon atoms, so its root name is dec, and it is an alkane, so -ane is added to the root name. Thus, $C_{10}H_{22}$ is decane.

Name the following straight or continuous chain alkanes.





13.2-3. Alkyl Groups

An alkyl group is formed by removing an H atom from an alkane. They are the side chains (not on the longest continuous chain) of a hydrocarbon.

All of the carbon atoms are not in the longest continuous chain of a branched hydrocarbon. Instead, these carbon atoms are in groups called *side chains*, which are attached to the longest continuous chain. Side chains can be any type of group, but we restrict our discussion to ***alkyl groups***. Alkyl groups are formed by removing one hydrogen atom from an alkane. The resulting alkyl group binds to a longer chain at the position of the removed hydrogen. Alkyl groups are parts of compounds; they are not compounds themselves. The name of the alkyl group is obtained by adding -yl to the root name The two simplest alkyl groups are given in Table 13.5.

Formula of Alkyl Group	Name of Alkyl Group
$-CH_3$	methyl
$-C_2H_5$	ethyl

Table 13.5: The Simplest Alkyl Groups

The dash before the formula indicates where they bond to a longer chain. Propyl, butyl, pentyl, etc., groups also exist, but there are more than one of each of these alkyl groups. For example, there are two different propyl groups that differ by the position of the removed hydrogen, which can come from a terminal carbon atom or from the middle carbon atom. We restrict our discussion of naming organic compounds to compounds that contain methyl and/or ethyl groups to avoid this complexity.

13.2-4. Naming Alkanes

Branched alkanes have side chains, so the name of a branched alkane specifies the longest continuous chain and the identity and position of the side chains (alkyl groups). Although there can be many side chains of varying lengths, we restrict our discussion of branched alkanes to those with one or two side chains, which will be either a methyl or an ethyl group. The position of the alkyl group is indicated by the number of the carbon atom to which it is attached. Thus, the carbon atoms in the longest chain must be numbered. To number the longest continuous chain, start at the end that produces the smallest number for the side chain.

To name branched alkanes:

1 Identify the longest chain, select the appropriate root name, and add *ane* to indicate an alkane.

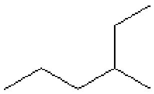
2 Number the carbon atoms of the longest continuous chain starting at the end that produces the smaller number for the carbon atom to which the alkyl group is attached.

3 Identify the side chain and its position.

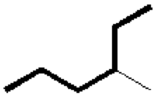
4 Name the alkane as the number of the position of the side chain, a hyphen, and then the name of the alkyl group followed by the name obtained in step 1.

Note that the name of the alkyl group and the name of the longest chain are combined into one word. For example, 2-methylhexane has a six-carbon chain with a CH_3 group attached to the second carbon from the end (either end).

As an example, we will follow the steps above to name the following compound.

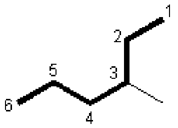


1 Identify the longest continuous chain.



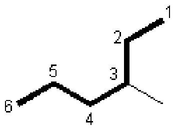
The longest chain contains six carbon atoms, so this is a **hexane**.

2 Number the longest continuous chain so that the side chain has the lowest number.



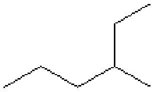
Numbering the chain from left to right places the side chain on carbon 4, but numbering it from right to left puts the side chain on carbon 3. Thus, the chain is numbered from right to left to produce the smaller number for the alkyl group.

3 Identify the side chain and its position.



The side chain contains a single carbon atom, so it is a methyl group. It is attached to carbon number 3.

4 Name the compound by combining the name of the longest chain with the position and identity of the side chain.



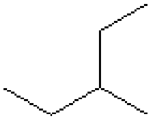
3-methylhexane

13.2-5. Naming Alkanes Exercise

Practice naming branched alkanes by naming the three organic compounds in Exercise 13.3. The root names can be found in Table 13.4.

EXERCISE 13.3:

Answer the questions for each of the branched alkanes.



How many carbon atoms are in the longest continuous chain?

____

What is the name of the longest continuous chain?

____

What is the name of the alkyl group on the longest chain?

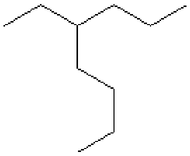
____

What is the position of the alkyl group (number of carbon)?

____

What is the name of the compound?

____



How many carbon atoms are in the longest continuous chain?

____

What is the name of the longest continuous chain?

____

What is the name of the alkyl group on the longest chain?

What is the position of the alkyl group (number of carbon)?

What is the name of the compound?

How many carbon atoms are in the longest continuous chain?

What is the name of the longest continuous chain?

What is the name of the alkyl group on the longest chain?

What is the position of the alkyl group (number of carbon)?

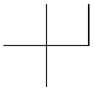
What is the name of the compound?

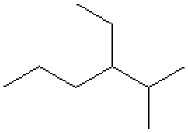
13.2-6. Naming Alkanes with Multiple Alkyl Groups

To name alkanes with more than one side chain, simply place the names of the alkyl groups in alphabetical order separated by hyphens in front of the root name. For example, 3-ethyl-2-methylheptane is a seven carbon continuous chain with a C_2H_5 group on the third carbon and a CH_3 group attached to the second carbon. If two identical groups are attached to the same carbon, the number of the position is repeated with a comma separator, and the number of groups is given by a prefix, as in 2,2-dimethylheptane.

<u>EXERCISE 13.4</u>:

Name the following compounds.





13.2-7. Naming Alkenes and Alkynes

Alkenes are numbered so that the C=C double bond has the lowest number possible.

To name a straight or continuous chain alkene:

1. Number the chain so as to give the carbon atoms in the double or triple bond the lowest number.
2. Specify the chain length with the appropriate root name and add -ene to indicate an alkene or -yne to indicate an alkyne.
3. Indicate the position of the double or triple bond by the number of the carbon atom in the bond with the lower number in the chain.
4. The name is the position of the bond as determined in step 3 followed by a hyphen and then the root name determined in step 2.

For example, 1-pentene is a five-carbon alkene with a double bond between carbon atoms 1 and 2, and 2-hexyne is a six-carbon alkyne with a triple bond between carbons 2 and 3.

EXERCISE 13.5:

Name the following straight or continuous chain alkenes.

13.3 Isomers

Introduction

We have seen that there can be several organic compounds with the same formula. Compounds with the same formula are called isomers. Isomers can have very different chemical and physical properties. In this section, we introduce two broad classifications of isomers.

Prerequisites

- 6.1 Molecular Shapes

Objectives

- Draw the constitutional isomers with a given molecular formula.
- Draw all of the constitutional isomers of an alkane.
- Identify stereoisomers.
- Name the two types of stereoisomers.
- Distinguish between cis and trans isomers.
- Describe the molecular process responsible for vision.
- Identify stereocenters.
- Identify enantiomers.

Constitutional

13.3-1. Constitutional Isomers

Constitutional isomers differ in their connectivities.

The number of constitutional isomers increases with the number of carbon atoms. C_3H_8O has three constitutional isomers, but there are six isomers of $C_4H_{10}O$ and well over a hundred isomers of $C_{12}H_{26}O$. Constitutional isomers can be the same type of molecule with similar properties. For example, there are over 100 isomers of $C_{10}H_{22}$, but they are all alkanes. However, constitutional isomers can also be totally different types of molecules with very different properties. As shown in Figure 13.10, there are three isomers of C_3H_8O. Two are alcohols and one is an ether.

- **Ethers** contain the C–O–C connectivity.
- **Alcohols** contain the C–O–H connectivity.

Ethers do not hydrogen bond to one another, while alcohols do because they contain O–H bonds. Consequently, alcohols have much higher boiling points than their corresponding ether isomers. For example, the isomer of C_3H_8O that is an ether boils at −23 °C, while the two isomers that are alcohols boil at +78 °C and +83 °C.

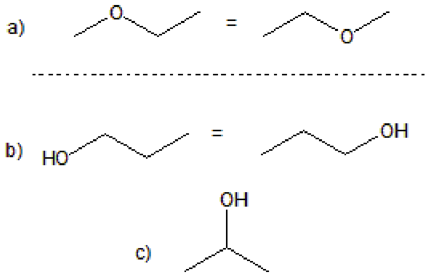


Figure 13.10: Isomers of C_3H_8O The three isomers of C_3H_8O: Isomer (a) is an ether, and isomers (b) and (c) are alcohols.

Now consider the six structures for molecules having the formula $C_4H_{10}O$. Figures 13.11(a) and 13.11(b) contain a C–O–C linkage, so they are ethers, while the remaining structures all contain a hydroxyl group, which makes each of them alcohols. For $C_{12}H_{26}O$, there are well over one hundred isomers! The existence of so many constitutional isomers gives rise to a wealth of structural diversity in organic chemistry. While there is no simple mathematical relationship between the molecular formula and the number of constitutional isomers, you can be certain that molecules with a large number of carbon atoms will have a large number of constitutional isomers.

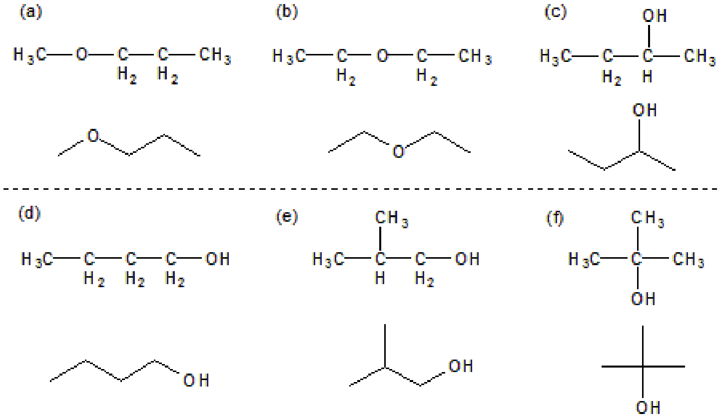


Figure 13.11: Isomers of $C_4H_{10}O$ The six isomers of $C_4H_{10}O$: Isomers (a) and (b) are ethers, but the others are alcohols.

13.3-2. Isomers of Hexane

Follow these steps to determine the constitutional isomers of an alkane.

1 Start by drawing the straight chain isomer.

2 Remove one carbon atom from the straight chain produced above and place the removed carbon (methyl group) on each carbon of the resulting chain that produces a different isomer.
    - The methyl group cannot be placed on a terminal carbon atom as that would lead to the same chain as in the previous step.
    - It does not matter which way the carbon atoms are numbered, so placing a methyl group on each of the carbon atoms that are next to the end carbon produces the same compound.

3 Remove a second carbon atom and place the two methyl groups or one ethyl group on the remaining chain. The ethyl group cannot be placed on a terminal carbon as that would produce the longest chain obtained in step 1, and it cannot be placed on the second carbon as that would produce one of the isomers produced in step 2.

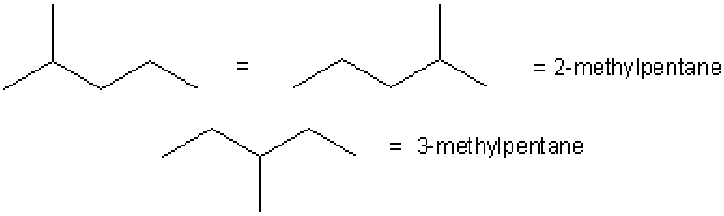
4 Keep removing one carbon atom until you get to a length where no new isomers can be obtained.

We now follow these steps to draw the constitutional isomers of C_6H_{14}.

1 6-carbon chain

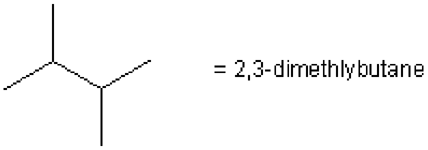
The straight chain isomer is hexane.

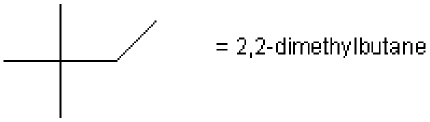
2 5-carbon chains



The methyl group can be placed on a carbon that is next to the end or in the middle to produce two isomers.

3 4-carbon chains





Two carbons must be added to a four-carbon chain. An ethyl group cannot be used because no matter where it is placed, it lengthens the chain and produces one of the isomers of the 5- or 6-carbon chains. The two methyl groups can be placed in two ways: one group on each of the two interior carbons or both groups on the same interior carbon.

4 3-carbon chains

There are no isomers of C_6H_{14} with longest chains of less than four carbons. Thus, there are five isomers of C_6H_{14}.

13.3-3. Isomers of Heptane - an Exercise

Draw the eight isomers of the alkane C_7H_{16} by adding methyl groups to the longest chain.

A video or simulation is available online.

Stereoisomers

13.3-4. Definitions

Stereoisomers have the same connectivities, but they differ in the spatial arrangement of their atoms. There are two types of stereoisomers.

- ***Geometric isomers***: Different spatial arrangement of atoms occurs due to the presence of a bond that cannot be twisted completely. We consider only the case of the double bond.
- ***Enantiomers***: Different spatial arrangement of atoms occurs due to the presence of a carbon atom that has four different groups attached to it.

We take up geometric isomers first, then turn to a discussion of enantiomers.

13.3-5. Bond Twisting

Groups can rotate relative to one another about a single bond, but not about a double or triple bond.

Sigma bonds are cylindrical, and the groups bound by them rotate around the bond to adopt different relative positions. Figure 13.12(a) shows the rotation about the sigma bond. However, groups connected by double bonds cannot rotate relative to one another without breaking the π bond because the rotation would move the two p orbitals used in the π bond away from one another and remove their overlap.

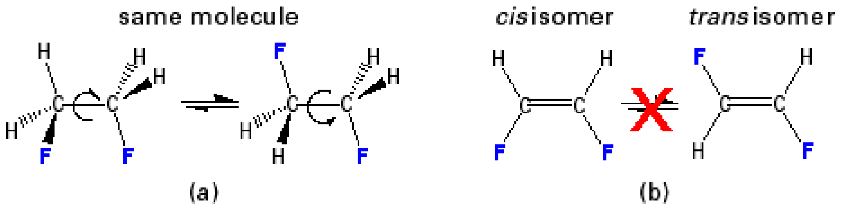


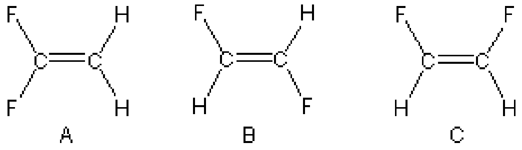
Figure 13.12: Rotation can occur about single bonds, but not about double bonds. (a) The two structures of $C_2H_4F_2$ are not isomers because the groups can rotate around the single bond. (b) The two structures of $C_2H_2F_2$ are isomers because the groups cannot rotate around a double bond.

13.3-6. Cis and Trans Isomers

Two atoms on the same side of a double bond are said to be ***cis***, while two atoms on opposite sides of the double bond are said to be ***trans***.

<u>EXERCISE 13.6</u>:

Consider the following three isomers of $C_2H_2F_2$.



One has no geometric isomer but is a constitutional isomer of the other two. The other two are geometric isomers of one another—one is cis and one is trans. Indicate which is the constitutional isomer and identify the cis and trans geometric isomers.

Isomer A:	Isomer B:	Isomer C:
constitutional	constitutional	constitutional
cis isomer	cis isomer	cis isomer
trans isomer	trans isomer	trans isomer

13.3-7. Retinal

The vision process is initiated by a cis-trans isomerization.

The trans form of an alkene can be twisted into the cis form if the pi bond is broken. Indeed, it is a trans → cis conversion that initiates the vision process. Protein molecules in the eye hold retinal molecules in a structure where one double bond is in the less stable cis configuration. The retinal molecule can absorb a photon of visible light due to the presence of alternating single and double bonds. The energy of the photon breaks the pi bond at the cis double bond. Once the pi bond is broken, the molecule springs back to the more stable trans configuration. This trans → cis conversion initiates a cascade of events that results in vision.

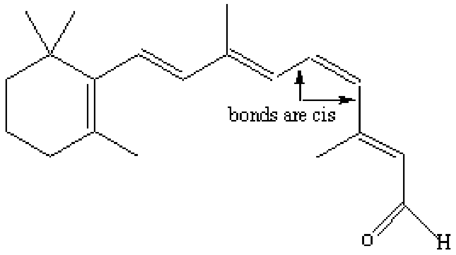


Figure 13.13a: Cis-Trans Isomerization in Retinal: Cis Isomer The cis isomer of retinal is found in the eye when it is dark.

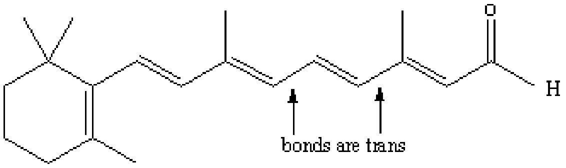


Figure 13.13b: Cis-Trans Isomerization in Retinal: Trans Isomer Absorption of a photon promotes a $\pi \rightarrow \pi^*$ transition, so the bond order is reduced in the excited state. The weakened bond can then rotate to convert the cis isomer into the trans isomer shown.

13.3-8. Naming Cis and Trans Isomers Exercise

To indicate the isomer of an alkene, place "cis-" or "trans-" in front of the name of the alkene.

EXERCISE 13.7:

Name the following compounds.

number of carbon atoms in longest chain

____

position of double bond

____

isomer (cis or trans)

____

name

____

number of carbon atoms in longest chain

____

position of double bond

____

isomer (cis or trans)

____

name

____

number of carbon atoms in longest chain

____

position of double bond

____

isomer (cis or trans)

____

name

____

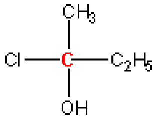
13.3-9. Stereocenters

A carbon atom with four different groups attached to it is called a ***stereocenter***.

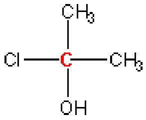
The atoms attached to a stereocenter do not have to be different, but the groups do. For example, a CH_3 group is different than a C_2H_5 group, but both involve a carbon atom attached to the stereocenter. The following exercise should help.

EXERCISE 13.8:

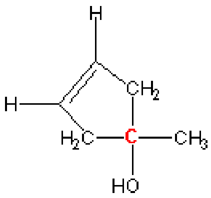
Is the carbon labeled in red a stereocenter?



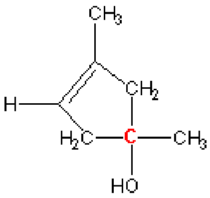
Yes
No



Yes
No



Yes
No



Yes
No

13.3-10. Enantiomers

Enantiomers are isomers that contain stereocenters and are mirror images of one another.

There is additional complexity in the structures of organic molecules that possess carbon atoms with four different groups attached to them. Such carbon atoms are said to be stereocenters. The central carbon shown in red in molecule A in Figure 13.14 is a stereocenter because it contains four different groups: H, OH, CH_3, and Cl. Molecule B in Figure 13.14 is its mirror image. Molecules A and B are different molecules! That they are different can be seen by rotating molecule B by 180° about the C–C bond ($B_1 \rightarrow B_2$). The rotation makes the OH and CH_3 groups of the two molecules (A and B_2) superimposable. However, the H and the Cl groups are still reversed in the two molecules. Consequently, molecules A and B are not superimposable. Note that your right and left hands are also mirror images that are not superimposable. Molecules with a stereocenter cannot be superimposed on their mirror images. Pairs of molecules that are nonsuperimposable mirror images are called enantiomers. Enantiomers are stereoisomers because their spatial arrangements are different while their connectivities are identical. Molecules A and B are enantiomers.

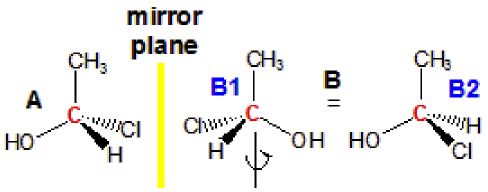
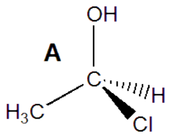


Figure 13.14: Enantiomers The two molecules each contain a stereocenter, and they are mirror images of one another. Consequently, they are enantiomers.

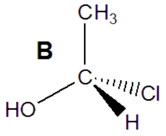
13.3-11. Enantiomer Exercise

EXERCISE 13.9:

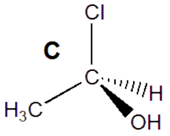
The following molecule has a stereocenter.



Indicate whether each of the following molecules is the same molecule or its enantiomer.



same
enantiomer



same
enantiomer

13.3-12. Enantiomeric Compounds

Enantiomers have the same melting and boiling points, but they often have dramatically different biological activities because biological activities are often based on the structures of the reacting molecules. Thus, one compound may cause one effect, but its enantiomer may cause a very different effect or have no effect at all. All of the biologically active amino acids except one have stereocenters, and in each case, only one enantiomer is active. The following are a couple of examples.

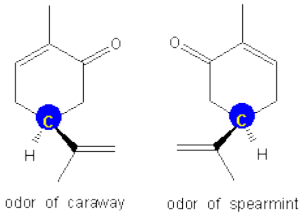


Figure 13.15: Carvone Carvone contains one stereocenter (the yellow carbon on a blue field). The enantiomer on the left is recognized by the olfactory receptors in the nose as the odor of caraway, while the one on the right is recognized as the odor of spearmint.

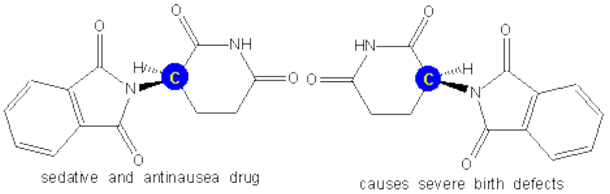


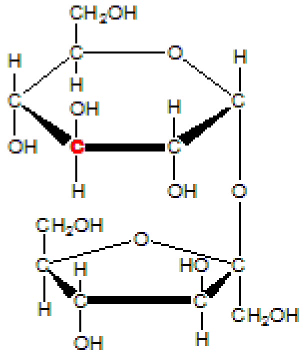
Figure 13.16: Thalidomide Thalidomide contains one stereocenter (the yellow carbon on a blue field). One stereoisomer acts as a sedative and antinausea drug, while the other causes severe birth defects. A drug that contained both enantiomers was marketed in Europe between 1959 and 1962 and resulted in thousands of badly deformed babies. Today, the enantiomer that caused birth defects is being studied as a possible treatment for leprosy, AIDS, and cancer.

13.3-13. Counting Mirror Images

A large structural diversity can occur in molecules that contain several stereocenters. In general, there are 2^n stereoisomers of a molecule with n stereocenters. Thus, there are 2 stereoisomers of a molecule with only one stereocenter, $2^2 = 4$ stereoisomers of a molecule with two stereocenters, and $2^{15} = 32{,}768$ stereoisomers of a molecule with 15 stereocenters.

EXERCISE 13.10:

Consider the sucrose molecule, table sugar. The red highlight of one carbon atom is there for discussion purposes only. It is not special in any other way.



How many stereocenters does a molecule of sucrose contain?

____

How many stereoisomers of sucrose are there?

____

13.4 Functional Groups

Introduction

Organic molecules are designed with specific sizes, shapes, and functional groups to perform specific functions (e.g., a better drug or a stronger plastic). Once a molecule is designed, organic chemists develop procedures to make it. These procedures, which can involve many steps, can be developed because so many organic reactions proceed by a few well understood mechanisms. Organic mechanisms are based on the principles of the octet rule, resonance, and Lewis acid-base theory. Reactions occur at specific groups within the molecule called ***functional groups***. Functional groups have specific reactivities that can be utilized to produce desired reactions. In this section, we introduce some of the functional groups and the fundamental types of reactions they undergo.

Objectives

- Identify some common functional groups.

13.4-1. Alcohols

Alcohols can behave as Brønsted acids because they contain a hydrogen atom attached to an electronegative atom, but they are also Lewis bases because the oxygen atom contains two lone pairs. Alkyl groups are usually electron donating, so alcohols in which R is an alkyl group function more as Lewis bases than acids.

Alcohols have the general formula R–OH, where R is a generic group of atoms and OH is the hydroxyl group.

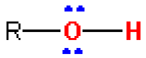


Figure 13.17: Generic Alcohol

Alcohols in which R is an alkyl group are named by adding -anol to the root name of the alkyl group. The position of the hydroxyl group is indicated with the number of the carbon atom to which it is attached.

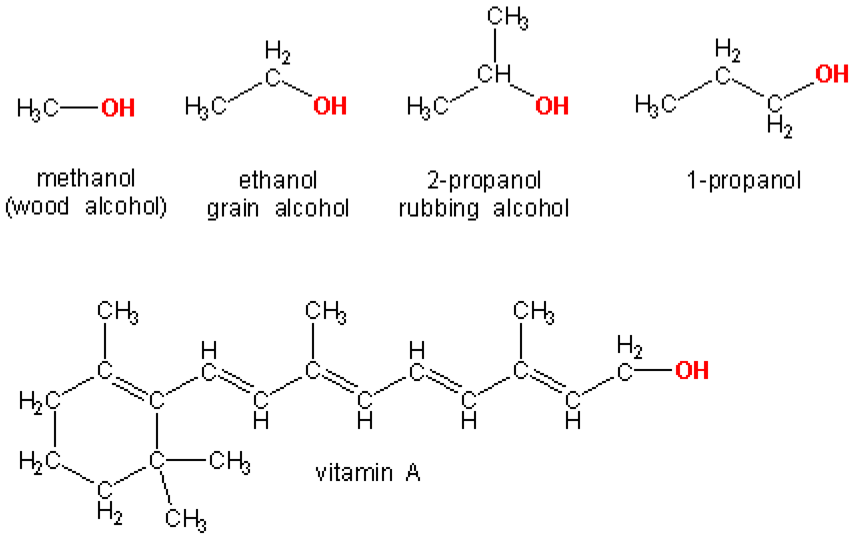


Figure 13.18: Some Common Alcohols

13.4-2. Carbonyls

The ***carbonyl group*** is C=O.

The carbon atom is sp^2 hybridized and is surrounded by only three electron regions. In addition, the electronegative oxygen places a partial positive charge on the carbon atom. These two properties make the carbon atom of a carbonyl a Lewis acid. In Figure 13.19, the one on the left shows the resonance form of a carbonyl that describes the bonding, and the one on the right describes the reactivity of the carbonyl—the carbon atom of the carbonyl can be attacked by the lone pair of a Lewis base. The Lewis acidity of carbonyl groups gives rise to dozens of types of chemical reactions that differ only in the species serving as the Lewis base.

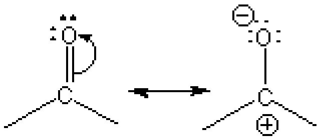


Figure 13.19: Resonance Forms of a Carbonyl Group

13.4-3. Carboxylic Acids

A ***carboxyl group*** is the combination of a carbonyl and a hydroxyl group.

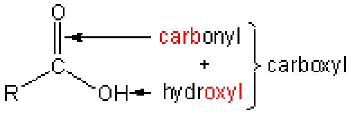


Figure 13.20: Carboxylic Acid

The carbonyl oxygen removes electron density from the O–H bond, which makes carboxyl groups acidic.

A molecule with a carboxyl group is called a ***carboxylic acid*** (RCOOH).

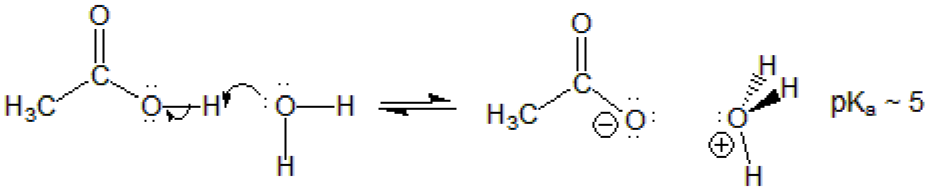


Figure 13.21: Acidity of Acetic Acid

Carboxylic acids in which R is an alkyl group are named by identifying the longest continuous chain that contains the carboxyl carbon and adding "anoic" to the root name of the chain. For example, HCOOH is methanoic (or formic) acid, CH_3COOH is ethanoic (or acetic) acid, and C_2H_5COOH is propanoic acid. The conjugate base of the acid is named by changing the "ic" to "ate." Thus, $C_2H_5COO^{1-}$ is the propanoate ion.

Replacing the O–H hydrogen of a carboxylic acid with an alkyl group results in an ***ester*** (RCOOR').

Esters are named as the name of the alkyl group followed by the name of the group to which it is attached. Consider Figure 13.22, which shows the example of acetic acid (active ingredient of vinegar), which loses a proton to form the acetate ion. Adding an ethyl group to the acetate ion produces the ester ethyl acetate (active ingredient of fingernail polish remover).

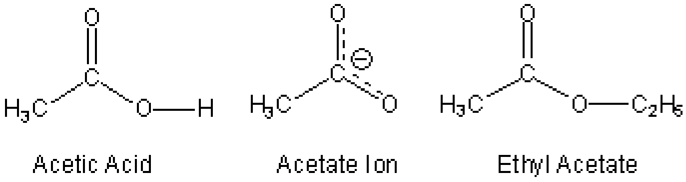


Figure 13.22

The carbon atom of a carbonyl is Lewis acidic, so both carboxylic acids and esters are Lewis acids. In addition, the carbonyl group is electron withdrawing (electronegative oxygen atom), so the O–H bond in a carboxyl group is weakened, which makes carboxylic acids Brønsted acids.

When R is a long alkyl chain, the acid is a **fatty acid**. Fatty acids are found in cells. The R group in fatty acids derived from animal cells is saturated, but those obtained from vegetables are unsaturated (they contain double bonds). Stearic acid (Figure 13.23), a fatty acid derived from animals (it is saturated), is used in making soaps and candles.

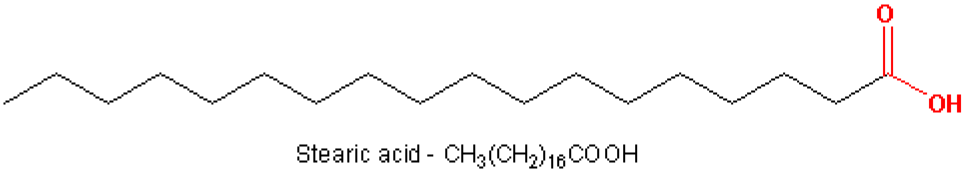


Figure 13.23

13.4-4. Amines and Amides

An ***amine*** is an ammonia molecule in which one or more of the hydrogens have been replaced with R groups. If the nitrogen is attached to a carbonyl, the group becomes an ***amide*** group.

Organic derivatives of ammonia that are not bound to a carbonyl group are called amines. Two examples of simple amines are methyl amine, CH_3NH_2, and dimethyl amine, $(CH_3)_2NH$, are shown in Figure 13.24.

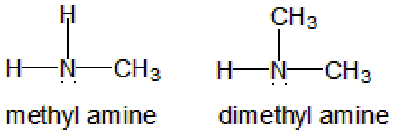


Figure 13.24

Compounds in which a nitrogen atom is bound to a carbonyl carbon are called amides. The groups around the N atom in amides are coplanar, so the N is sp^2 hybridized. The planarity of the amide group is accounted for with the resonance structure in Figure 13.25.

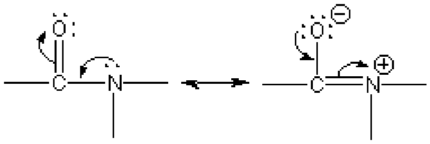


Figure 13.25: Amides

Caffeine contains two amide nitrogens (red), one amine nitrogen (blue), and one nitrogen that is neither an amine nor an amide because it is involved in a double bond.

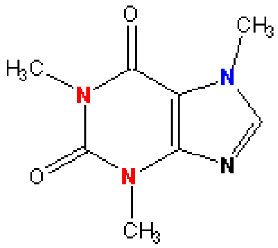


Figure 13.26: Caffeine

13.4-5. Amino Acids

Amino acids contain an amine and a carboxylic acid.

The amine is a good Lewis base, so it can react with the carboxylic acid to produce a charge-separated species, which is the most common form of amino acids in the human body. For example, consider the structure of alanine in Figure 13.27.

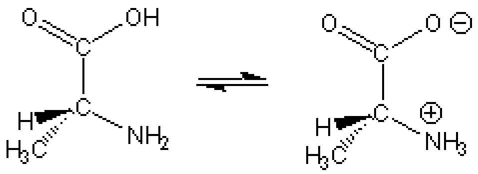


Figure 13.27: Alanine, an Amino Acid Note that the carbon atom in alanine that is connected to both the amine and carboxyl groups is a stereocenter. This is the case in almost all amino acids found in the human body. However, only one enantiomer is biologically active.

13.5 Introduction to Organic Reactions

Introduction

A good amount of organic chemistry can be understood with Lewis acid-base theory. Several mechanisms for different reactions are presented in this section, but all are Lewis acid-base reactions.

Prerequisites

- 5.6 Determining Lewis Structures (Draw Lewis structures.)
- 5.8 Formal Charge and Oxidation State (Determine formal charge.)
- 12.1-7 Curved Arrows in a Mechanism (Represent the mechanism of a Lewis acid-base reaction with curved arrows.)
- 12.1 Lewis Acids and Bases (Determine Lewis acidic and basic sites.)

Objectives

- Identify the Lewis acidic and basic sites involved in an organic reaction.
- Describe an addition reaction.
- Describe a condensation reaction and use curved arrows to show the mechanism for the reaction of a carboxylic acid and an alcohol.
- Use curved arrows to show the attack of an amine on an ester and predict the product of the reaction.

13.5-1. Addition Reactions of Alkenes

Addition reactions are reactions in which two reactants combine to form a single product. We use the addition of a hydrogen halide across a C=C double bond as an example.

A video or simulation is available online.

Alkenes are weak Lewis bases due to their pi electrons, and hydrogen halides are strong Brønsted acids. Hydrogen halides can add across the double bond in two Lewis acid-base reactions.

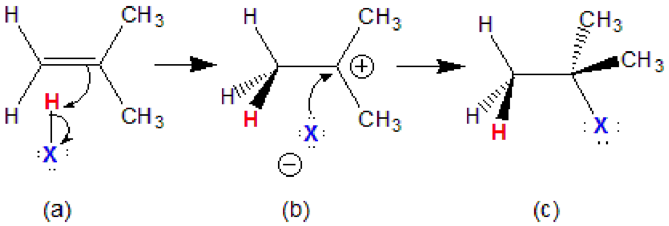


Figure 13.28: The Addition of a Hydrogen Halide Across a Double Bond

1. The pi electrons of the double bond attack the hydrogen of the hydrogen halide to produce a C–H bond, a halide ion, and a carbocation.
2. A lone pair on the halide ion attacks the strong Lewis acidic carbocation to form a C–X bond.

Note that the hybridization of each carbon changes from sp^2 (planar) to sp^3 (tetrahedral) as a result of the addition reaction.

13.5-2. Esterification

In ***condensation reactions***, two reactants combine to form two products (one of which is often a small molecule such as water). A carboxylic acid and an alcohol can undergo a condensation reaction called ***esterification*** to produce an ester and water.

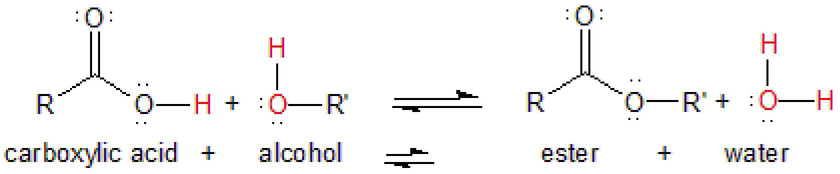


Figure 13.29: Esterification R and R' are usually two different alkyl groups.

The mechanism of esterification is very similar to the one we used to explain the reaction of SO_3 and H_2O in Chapter 12. Indeed, only the identities of the Lewis acid and base have changed.

A video or simulation is available online.

The reaction can be viewed as occurring in three steps.

1 In the first step, the lone pair on the oxygen of the alcohol (the Lewis base) attacks the carbonyl carbon of the acid (the Lewis acid) in a Lewis acid-base reaction. The lone pair becomes a C–O bond, and the pi electrons of the C=O double bond of the carbonyl become a lone pair on the oxygen.

2 A water molecule from the solvent (shown in green) assists in a proton transfer. It first accepts a proton from the oxygen with positive formal charge and then donates a proton to the oxygen involved in the O–H bond.

3 The proton transfer in the second step produces an OH_2 group with a positive formal charge on the oxygen. Electron density moves out onto the oxygen with positive formal charge to produce a water molecule. The water molecule is lost and the C–O pi bond reforms, resulting in a molecule with no formal charge. Loss of small molecules such as water is common in condensation reactions.

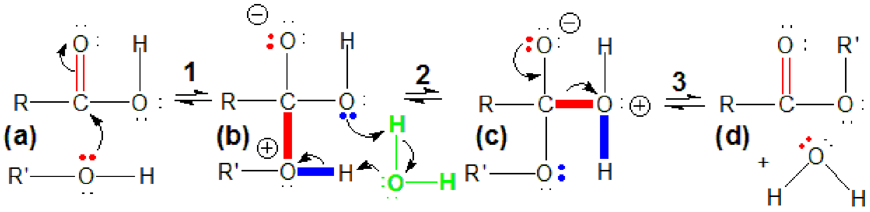


Figure 13.30: Esterification Mechanism

13.5-3. Amide Formation

Amides can be formed in a Lewis acid-base reaction of an amine (base) and an ester (acid). The other product of this condensation reaction is an alcohol.

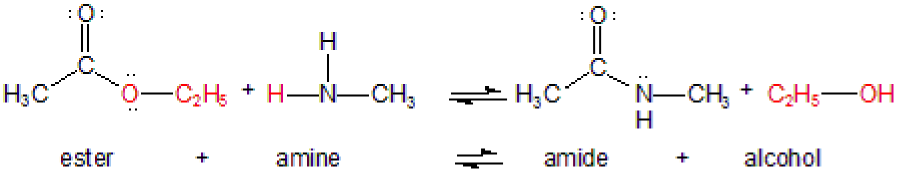


Figure 13.31: Amide Formation

The mechanism of the reaction is identical to esterification.

A video or simulation is available online.

The reaction can be viewed as occurring in three steps.

1 The lone pair on the nitrogen atom of the amine (the Lewis base) attacks the carbonyl carbon of the ester (the Lewis acid) in a Lewis acid-base reaction. The lone pair becomes a C–N bond, and the pi electrons of the C=O double bond of the carbonyl become a lone pair on the oxygen.

2 A water molecule from the solvent assists in a proton transfer. It first accepts a proton from the nitrogen with positive formal charge and then donates a proton to the oxygen involved in the O–R' bond.

3 The proton transfer in the second step produces a R'OH group with a positive formal charge on the oxygen. Electron density moves out onto the oxygen with positive formal charge to produce an alcohol molecule (R'OH), which is lost as the C–O pi bond reforms, resulting in a molecule with no formal charge. Loss of small molecules such as alcohols is common in condensation reactions.

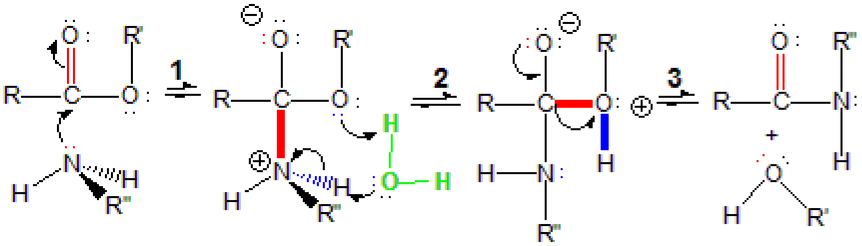


Figure 13.32: Amide Formation Mechanism

13.6 Polymers

Introduction

Natural polymers, such as carbohydrates, proteins, and nucleic acids, are part of living tissue and are responsible for increasing the rates of reactions and giving structural characteristics like strength and flexibility. Others store our genetic code. When most of us think of polymers, however, we think of man-made polymers like PVC, teflon, polyethylene, or polyesters. In this section, we examine both natural and man-made polymers.

Prerequisites

- 7.3-10 Hydrogen Bonding (Describe the hydrogen bond and state the requirement for it.)

Objectives

- Define monomer, dimer, trimer, and polymer.
- Identify the monomer upon which a polymer is based.
- Recognize some common polymers.
- State the requirement for the reactants used to produce a condensation polymer.
- Distinguish between a polyamide and a polypeptide.
- Explain why proteins frequently form α-helices.
- Describe a base pair, explain why they are important, and identify the hydrogen bonding sites in a base pair.
- Describe the double helix structure of DNA and explain its origin.

Addition

13.6-1. Polymers

Polymers are large molecules consisting of many single unit building blocks called ***monomers***.

"Mer" is used to indicate a building block. How the term mer is used is demonstrated in Figure 13.33, which shows a **mono**mer (single mer), a **di**mer (two mers), a **tri**mer (three mers), and a **poly**mer (many mers). The polymer grows as the result of successive reactions of the monomers that lengthen the polymer chain. They typically have many kinks and folds because the single bonds are flexible. Although polymers can be formed by several different mechanisms, we consider only those reactions that occur by mechanisms like those that we have already discussed. Synthetic polymers are classified as condensation or addition polymers depending on the type of reaction that is used to form them.

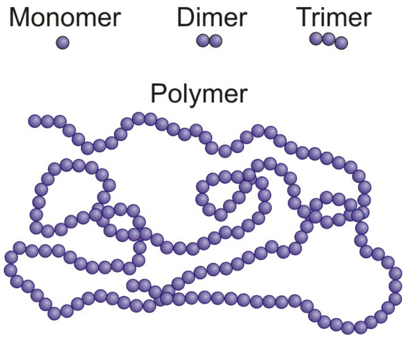


Figure 13.33: Several Mers

13.6-2. Addition Polymers

Addition polymers are formed in addition reactions.

Addition polymers based on alkenes include some of the most common polymers. The polymerization process is summarized in Figure 13.34. Note that the “x” in the figure is a large number typically in the thousands.

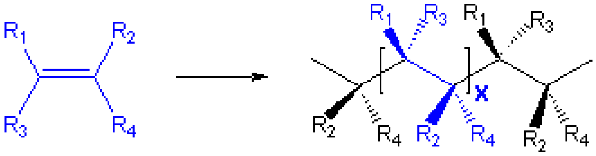


Figure 13.34: Alkene Polymerization

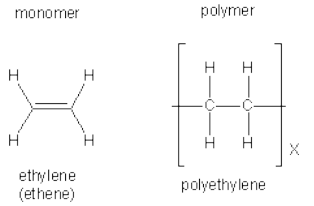
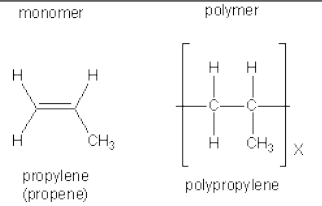
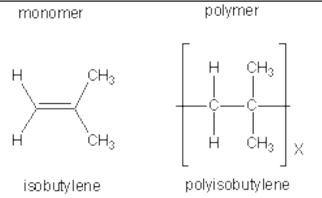
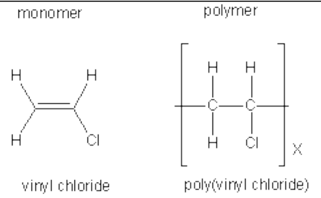
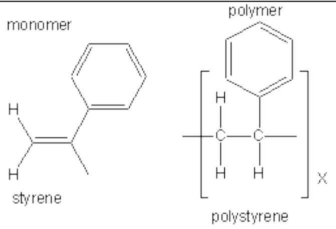
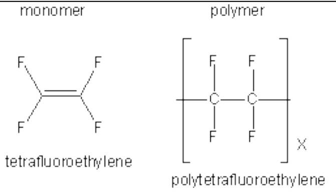
Polymer	Structure	Uses
polyethylene		plastic bottles and bags
propylene		carpets
isobutylene		tires
poly(vinyl chloride)(PVC)		plumbing and hoses
polystyrene		insulation
tetrafluoroethylene(teflon)		cooking utensils and nonstick cooking surfaces

Table 13.6: Structures and Uses of Some Common Polymers

13.6-3. Isobutylene

The reaction of isobutylene with hydrogen halides was used as an example of an addition reaction in the previous section. We now examine the mechanism of the reaction.

A video or simulation is available online.

In the first step of that reaction, the pi electrons attacked the hydrogen of HX to produce a C–H bond and a carbocation on the carbon (the carbon with more alkyl groups). The carbocation is a strong Lewis acid, which was immediately attacked by the strongest base in the vicinity, the halide ion. However, only trace amounts of HX are used in the polymerization, so there is no halide ion close to the carbocation. Consequently, the next strongest base (another isobutylene molecule) reacts with the cation. Reaction of an isobutylene molecule with the carbocation produces a dimer that still contains a carbocation. The dimer then reacts with a third isobutylene to form a trimer, and so on to produce poly(isobutylene). A typical poly(isobutylene) chain consists of from 2,000 to 20,000 monomer units.

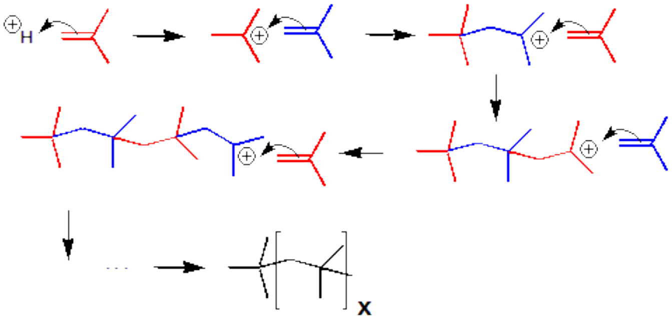


Figure 13.35: Polymerization of Isobutene into Isobutylene

Natural rubber is a polymer of isoprene (see Figure 13.36) that can now be made in the chemistry laboratory. Butyl rubber is a polymer made from isobutylene and isoprene. The United States produces over 500 million pounds of butyl rubber each year.

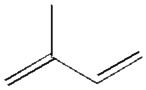


Figure 13.36: Isoprene

Condensation Polymers

13.6-4. Condensation Polymers

Condensation polymers are produced in condensation reactions.

The requirement for polymerization is that the reactants must each have two reacting centers. The formation of an ester from a carboxylic acid and an alcohol was used in the previous section as an example of a condensation reaction, and the formation of a **polyester** from a diacid and a diol (compounds with two carboxyl and two hydroxyl groups) is demonstrated in Figures 13.37a, 13.37b, and 13.37c.

$$\text{x diacid} + \text{x diol} \rightarrow \text{polyester}$$

The polyester poly(ethylene terephthalate) or PET is used in clothing, upholstery, tires, and other products. It is marketed as Mylar, Dacron, and Terylene. 4.5 billion pounds of PET are produced in the U.S. every year.

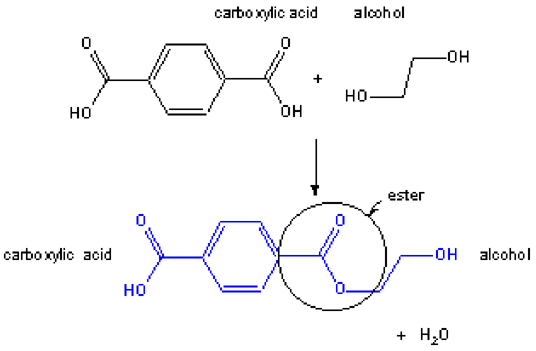


Figure 13.37a: Polyester Poly(ethylene terephthalate) or PET: Step 1 The reaction of a diacid and a diol produces an ester that contains a hydroxyl group at one end and a carboxyl group at the other.

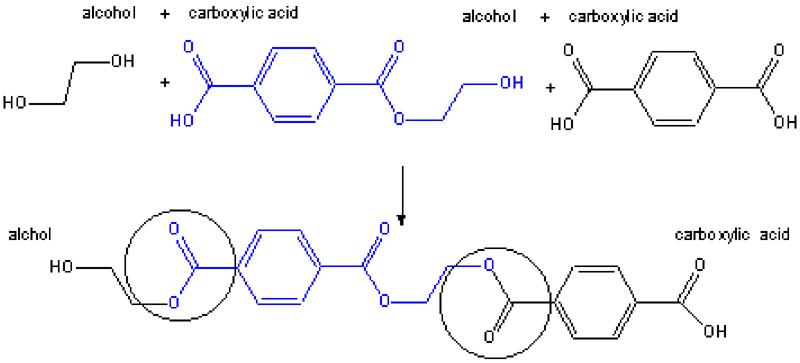
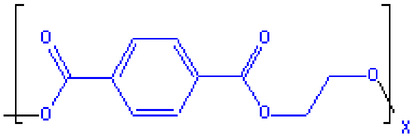


Figure 13.37b: Polyester Poly(ethylene terephthalate) or PET: Step 2 The ester formed in step 1 can react with another diacid molecule and another diol molecule to produce a compound with three ester linkages (the original one and two new ones, which are circled). The product still contains a hydroxyl group at one end and a carboxyl group at the other end, which can react with more diacid and diol molecules.



PET

Figure 13.37c: Polyester Poly(ethylene terephthalate) or PET: Product Continued reaction increases the number of ester linkages, but maintains one hydroxyl group and one carboxyl group that can react. The monomer unit of the PET polymer is shown.

13.6-5. Nylon 66

Nylons are polyamides formed from the reaction of a diester and a diamine.

Just as reacting an ester and an amine produces an amide, reacting a diester and a diamine produces a ***polyamide***. Polyamides produced in this manner are also called ***nylons***. Each step of the polymerization produces an amide bond, but the product always contains an amine or an ester at each end, so it can react with another diester and/or another diamide.

$$\text{x diamide} + \text{x diester} \rightarrow \text{polyamide (nylon)}$$

Mechanism:

1 Lone pairs on N atoms of diamines (red and blue in Figure 13.38a) attack carbonyl carbon of diester to form C–N bonds.

2 Proton transfers (shown in circles in Figure 13.38a) from diamine nitrogens to oxygens of diesters produce CH_3OH groups that leave as methanol molecules.

The produced amide also contains two amines, which can each attack another diester. The product of those reactions would contain four amide linkages and two ester groups, each of which could be attacked by another diamine. Each reaction lengthens the polymer chain.

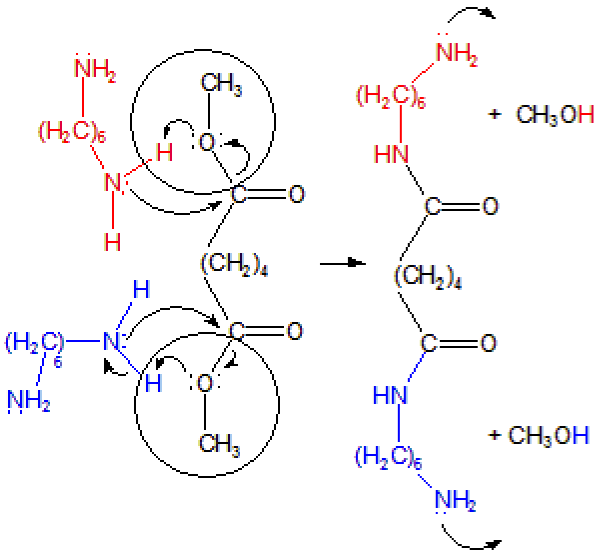


Figure 13.38a: Nylon

One monomer building block for a polyamide is shown in Figure 13.38b. Note that it contains six carbons from the diester between amide linkages (shown in blue) and six carbons from the diamine (shown in red), so the product is named Nylon 66.

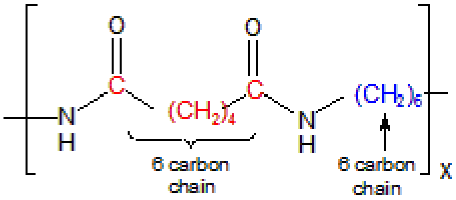


Figure 13.38b: Nylon 66

13.6-6. Polypeptides

Polypeptides are polyamides formed by the reaction of amino acids.

Polyamides can also form when each reactant contains both a carboxylic acid and an amine rather than two acids or two amines, i.e., polyamides can also be produced in the reaction of amino acids. Amides produced by the reaction of amino acids are called ***peptides***, and the polyamides made from amino acids are called ***polypeptides***. The resulting peptide always has two reactive sites, and continued reaction with other amino acids leads to a polypeptide or eventually a protein.

The structure of a polypeptide can be envisioned as a backbone of amide linkages, from which extend various side chains that characterize the various amino acids. Indeed, the amide backbone is frequently represented by thick bonds from which hang the side chains from the amino acids (methyl group from alanine and ethyl group from serine).

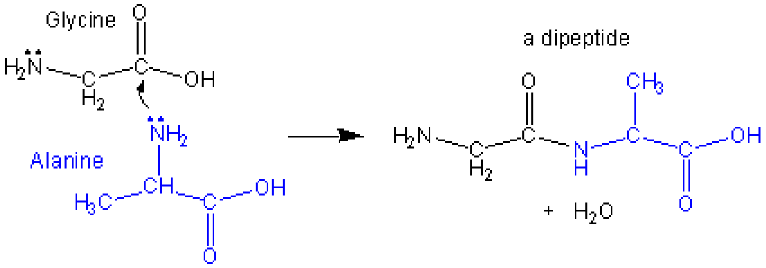


Figure 13.39a: Polypeptides: Dipeptide Two amino acids (glycine and alanine or GLY-ALA) combine to form a dipeptide. The resulting dipeptide still has a reactive site at each end (an amine and a carboxylic acid).

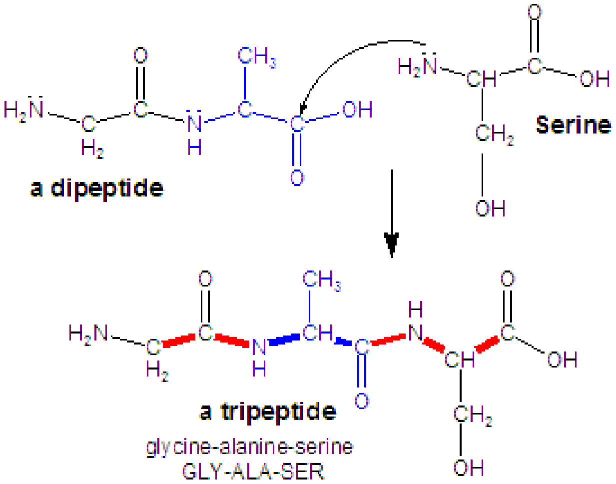


Figure 13.39b: Polypeptides: Tripeptide Three amino acids (glycine, alanine, and serine or GLY-ALA-SER) combine to form a tripeptide. Alternatively, a serine molecule reacts with the dipeptide formed in the first step.

13.6-7. H-Bonding in Proteins

Proteins are large polypeptides.

Proteins are high molecular weight polypeptides that often contain over 100 amino acids (called ***residues***). Hydrogen bonding and dipole-dipole interactions between groups within a polypeptide are responsible for the **secondary structure** of a polypeptide. The strongest interaction is hydrogen bonding between an N–H group and a C=O group that is four residues away.

This interaction results in the α-**helix** structure of proteins. The nature and position of the amino acids around the core of the α-helix are responsible for the specific function of the protein.

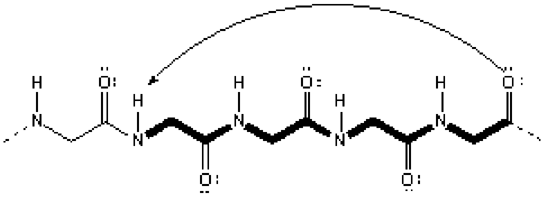


Figure 13.40: H-Bonds Responsible for the α-helix Structure

13.6-8. Protein Structure

An α-helix is shown in Figure 13.41. Color code: red = oxygen, blue = nitrogen, gray = carbon, white = hydrogen, and yellow = sulfur. Note only those hydrogen atoms involved in hydrogen bonding are shown.

(a) Space-filling model

(b) Ball-and-stick model with green ribbon to show polypeptide backbone

(c) Ball-and-stick model in which the side chains have been removed, and hydrogen bonds are shown as dashed lines

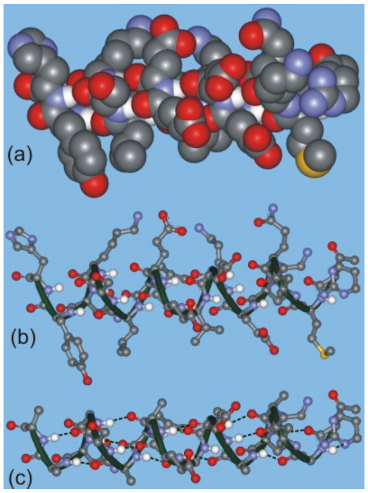


Figure 13.41: Representations of an α-Helix

DNA

13.6-9. Nucleotides

A ***nucleotide*** consists of a phosphate, a sugar, and an N-containing base.

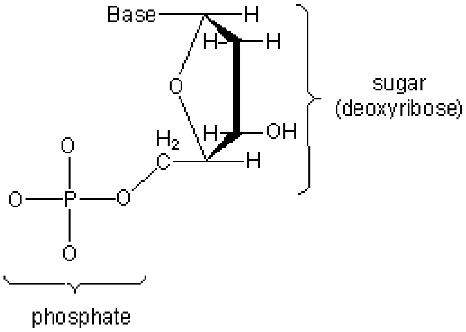


Figure 13.42 The sugar in this nucleotide is called deoxyribose.

Nucleic acids are polymers formed from nucleotide residues. If the sugar in the nucleotide is deoxyribose, then the nucleic acid is a **D**eoxyribo**N**ucleic **A**cid, or simply DNA.

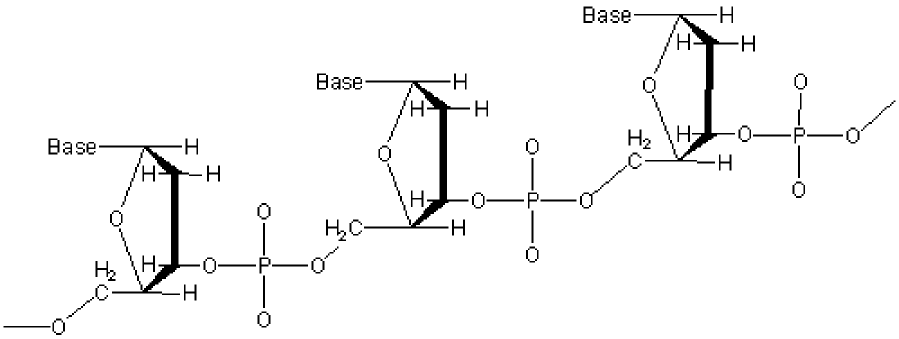
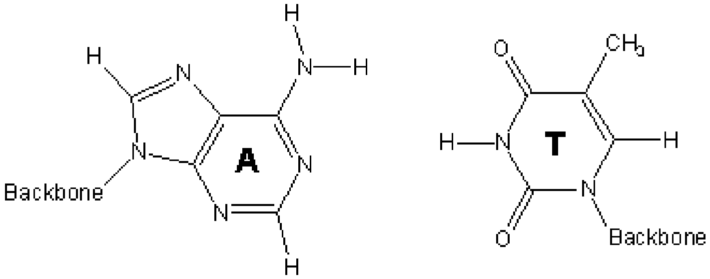


Figure 13.43: Three Residues of a DNA Molecule

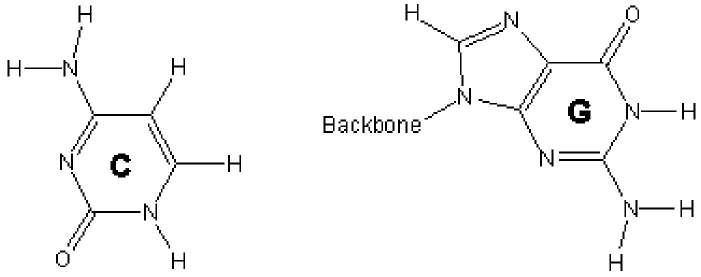
13.6-10. Bases

Only four bases, which exist in two base pairs, are found on the nucleotides that form DNA.

Each nucleotide of DNA contains one of the following four bases. The location marked “backbone” indicates the position where each base bonds to the sugar in the nucleotide.



adenine (A) thymine (T)



cytosine (C)

guanine (G)

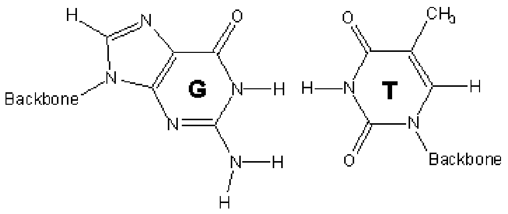
Figure 13.44

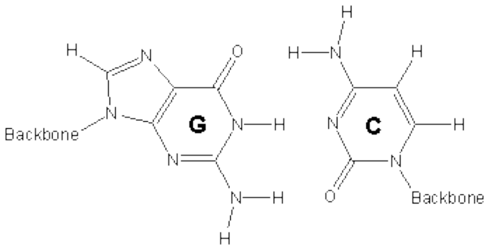
The above bases can be combined into two base pairs due to the strong hydrogen bonding that can exist between the members of each pair.

13.6-11. Determining Base-Pairs Exercise

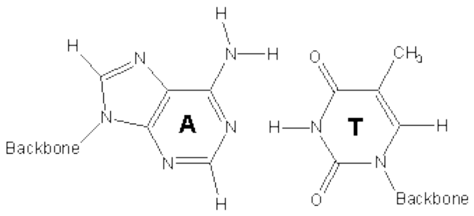
EXERCISE 13.11:

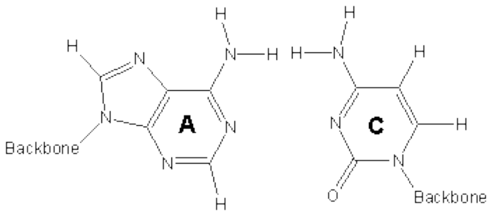
Adenine and guanine do not interact favorably, so they are not base pairs. Determine the base pair of each (T or C) based on how well each interacts with one of the other base pairs.





base pair of guanine (T or C) ________________





base pair of adenine (T or C) ______________

13.6-12. Base Pairs

Hydrogen bonding between base pairs results in the double helix structure of DNA.

There are favorable interactions in only two pairs of bases, which are called base pairs.

1 adenine (A) - thymine (T)

2 guanine (G) - cytosine (C)

In Figure 13.45, adenine and guanine are covalently bound to strand 1, and thymine and cytosine are covalently bound to strand 2. Hydrogen bonding of the adenine on strand 1 with the thymine on strand 2 and the guanine on strand 1 with the cytosine on strand 2 hold the two strands of DNA in this portion in a **double helix**.

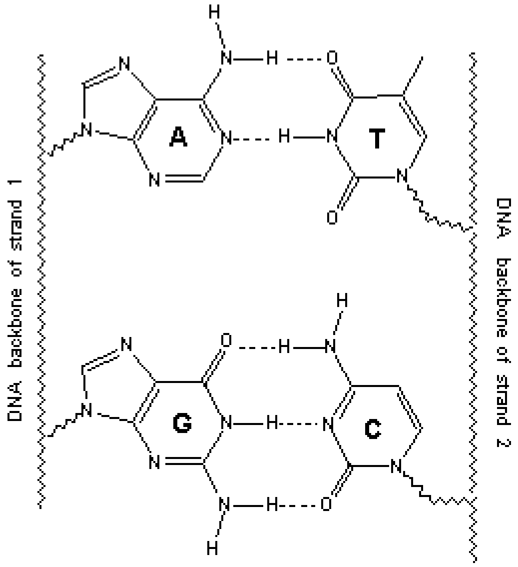


Figure 13.45: Base Pairs in DNA

13.6-13. Double Helix and Function of DNA

The structural unit of DNA is called the **double helix**. The double helix is a consequence of hydrogen bonding between base pairs on different strands. It is the sequence of the base pairs in the double helix that forms the genetic code. Thus, your genetic code requires only four different chemical letters: A, T, C, and G. However, the human cell contains about three billion base pairs.

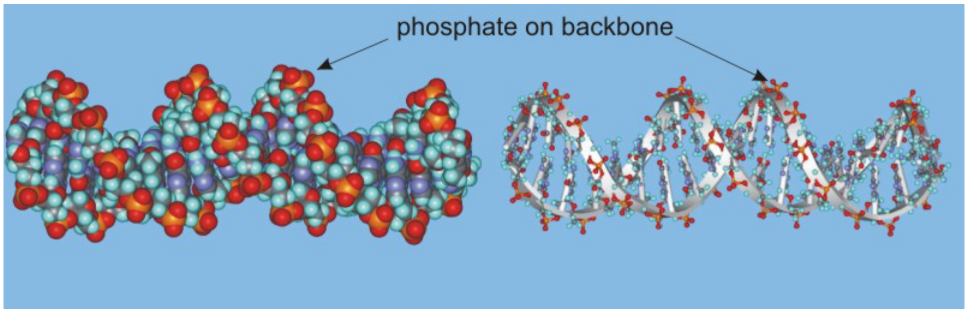


Figure 13.49: Double Helix of DNA

13.7 Exercises and Solutions

Links to view either the end-of-chapter exercises or the solutions to the odd exercises are available in the HTML version of the chapter.

Chapter 14 – Inorganic Chemistry

Introduction

Organic chemistry is based on the chemistry of carbon, so that leaves the chemistry of over 100 other elements to be characterized as inorganic chemistry. The chemistry of many of these elements is very rich. In this final chapter, we focus on only one segment of these elements, the transition elements, and introduce only some of their fascinating chemistry.

14.1 Ligands and Coordination

Introduction

The molecules and ions that are bound to metals are called ligands. The ligands are said to coordinate to the metal, and the compounds are called coordination compounds.

Prerequisites

- 5.6 Determining Lewis Structures
- 6.1 Molecular Shapes
- 12.1 Lewis Acids and Bases
- 2.1 The Nature of Light

Objectives

- Describe the common coordination geometries adopted by transition metals.
- Explain what a ligand is and give some examples.

14.1-1. Coordination

The number of donor atoms bound to the metal is called the **coordination number** of the metal, and the spatial arrangement of the ligands is called the metal's **coordination geometry**. The most common coordination numbers are 4, 5, and 6, and their common coordination geometries are described below. Octahedral coordination (coordination number = 6) is the most common coordination geometry in this chapter.

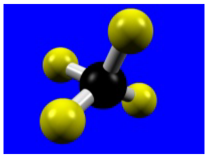
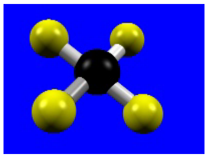
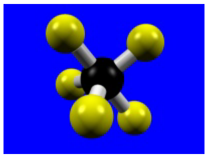
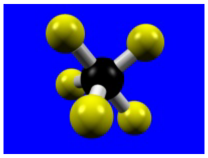
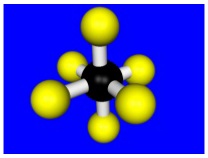
Coordination Number = 4	Tetrahedral 	Square Planar 
Coordination Number = 5	Trigonal Bipyramidal 	Square Pyramidal 
Coordination Number = 6	Octahedral 	

Table 14.1: Common Coordination Numbers

14.1-2. Ligands

Transition metals are frequently found in *complexes*, substances in which the metal is bound to several molecules and/or ions. The molecules or ions that bind to a metal are called ***ligands***. Ligands have lone pairs and function as Lewis bases, while metal ions have empty orbitals that can be used to share the lone pair; i.e., metals are Lewis acids.

Although most ligands use only one lone pair to bond to a metal, some ligands can use more than one. If such ligands bond to two different metals, they are called **bridging ligands**, because they form a bridge between the two metals. If more than one lone pair from a ligand binds to the same metal, the ligand is said to be a **chelating ligand**.

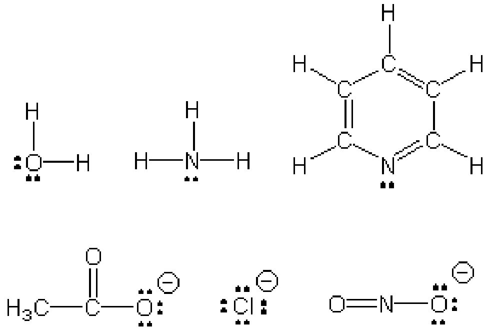
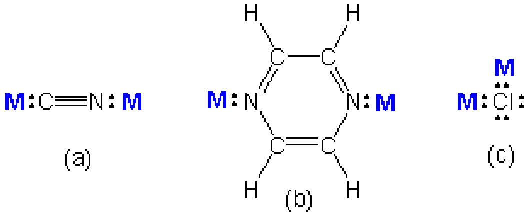
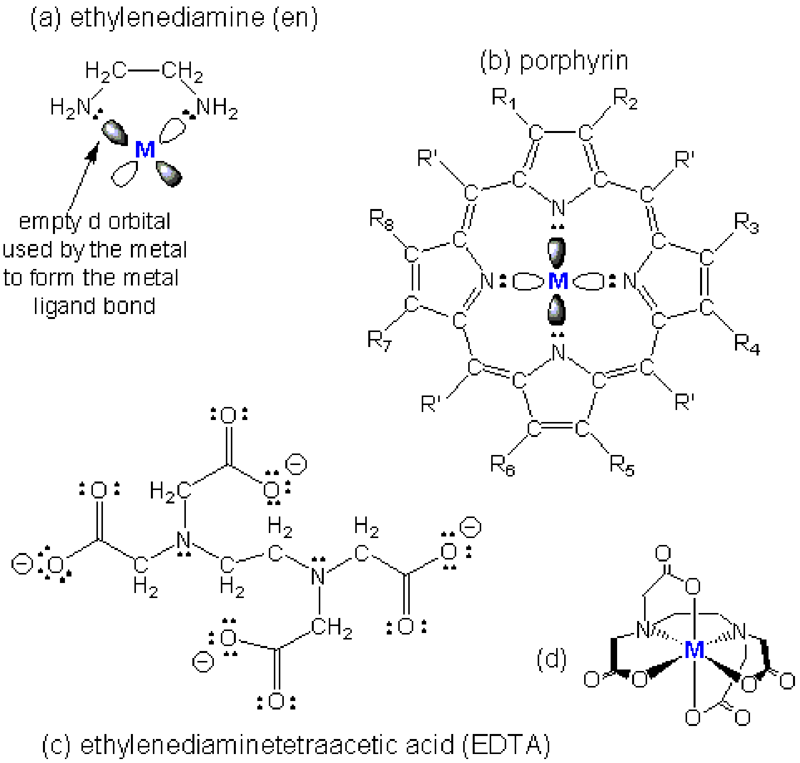


Figure 14.1a: Some Common Ligands Ligands contain lone pairs that are used to bond to the metal. Ligands can be molecules (top row) or ions (bottom row).



(a) (b) (c)

Figure 14.1b: Some Common Bridging Ligands Ligands that contain two lone pairs that can bond to two different metals are called **bridging ligands** because they can bridge two metals. Ligands (a) (cyanide ion) and (b) bridge with 180° bond angles, while ligand (c) (chloride ion) can bridge with ~109° bond angles. Note that these ligands can bridge, but they do not have to. For example, chloride forms bridges in only a small fraction of its compounds with transition elements.



(a) ethylenediamine (en)

(b) porphyrin

(c) ethylenediaminetetraacetic acid (EDTA)

(d)

Figure 14.1c: Some Common Chelating Ligands

Chelating ligands appear to “bite” the metal, and the term **dentate** is used to specify the number of places that a ligand “bites.” For example, consider the chelating ligands shown in Figure 14.1c. Ethylenediamine “bites” the metal in two locations, so it is said to be *bidentate*, porphyrin “bites” four locations and is a *tetra*dentate ligand, and EDTA bites in six locations and is a *hexadentate* ligand.

14.2 Ligand Fields

Introduction

The chemistry of the transition metals can be understood in terms of the interaction between the ligands and the metal’s d-orbitals. The ligands generate an electric field around the metal that alters the energy of the orbitals and strongly influences the properties of the metal.

Prerequisites

- 2.6 Orbital Shapes and Sizes
- 1.8 Electromagnetism and Coulomb’s Law
- 2.3 Bohr Model

Objectives

- Explain how the d-orbital energies are affected by their orientation to the ligands.
- Determine the total spin from the number of unpaired electrons.

14.2-1. d-orbitals

The five d-orbitals have the following electron distributions:

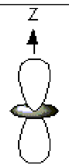
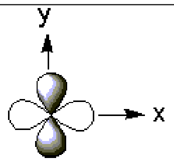
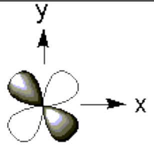
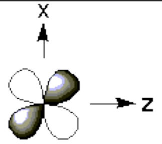
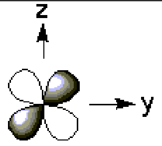
Name	Shape	Electron Distribution
z^2		along the z-axis and in a donut-shaped cloud in the xy plane
$x^2{-}y^2$		along the x and y axes
xy		in the xy plane but directed between the axes
xz		in the xz plane but directed between the axes
yz		in the yz plane but directed between the axes

Table 14.2: Electron Distributions in the d-Orbitals

14.2-2. The Coordinate System

As shown in Figure 14.2, the metal-ligand bonds in an octahedral coordination form the coordinate system for the d-orbitals. Thus, the z^2 and x^2-y^2 orbitals are directed along the axis of the metal-ligand bonds as they are directed along the z and the x and y axes, respectively.

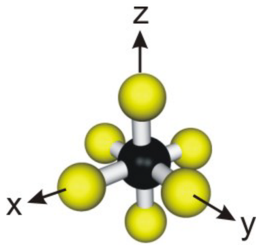


Figure 14.2: Coordinate System in Octahedral Coordination

14.2-3. d-Orbital Energies in Octahedral Fields

The energies of the d-orbitals change in the electric field produced by the ligands. The electric field is called a ligand field.

We saw in Section 2.7 that the orbitals in a d sublevel had the same energy, but that is only in a free atom. When the metal is bound to ligands, the relative energies of the d-orbitals change. The lone pairs on the ligands generate an electric field, known as the **ligand field**, and the energies of the d-orbitals rise in the presence of a ligand field. How much they rise depends upon the strength of the field (electron density on the ligand), the distance between the metal and the ligand, and the orientation of the d-orbital relative to the ligand. When the six ligands (octahedral field) all lie on the axes, the energies of those orbitals directed along the axes are higher than the energy of those directed between the axes.

Figure 14.3 compares the effect of ligands (grey spheres) lying along the x, y, and z axes on the five d-orbitals. The lobes of the z^2 and x^2-y^2 orbitals are directed along the bonding axes, so the ligands interact with them strongly and raise their energy. However, the ligands are directed at the nodes of the xy, xz, and yz orbitals. Consequently, the ligands do not interact as strongly with these orbitals, so their energy does not rise nearly as much.

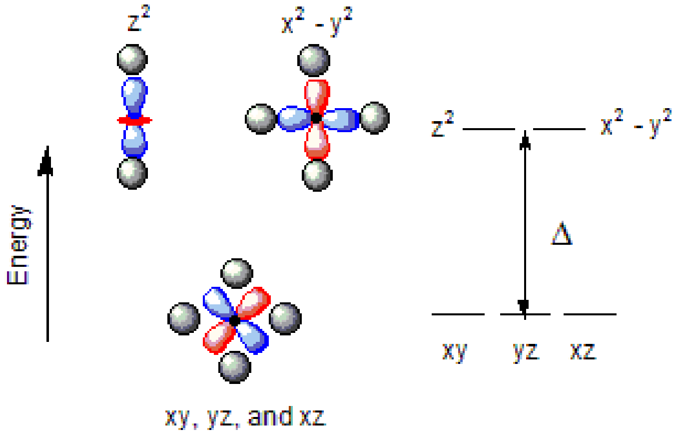


Figure 14.3: d-Orbital Energies in an Octahedral Ligand Field

The energy separation between the two groups of d-orbitals in an octahedral field is given the symbol Δ. A strong field ligand produces a large Δ, while a weak field ligand produces a small one.

CN^{1-} is a strong field ligand with a large Δ, while H_2O and Cl^{1-} are both weak field ligands with small Δs.

14.2-4. Color Complement

The color perceived for a substance is the complement of the one that is absorbed.

Substances are colored because they absorb visible light. However, the color perceived for a substance is that of the reflected light, not the absorbed light. The light that is reflected is the **complement** of the absorbed light. The sum of a color and its complement is black; i.e., the sum absorbs all colors. Thus, when white light (presence of all colors) strikes a substance, it absorbs a portion and reflects the remainder, which is the complement of the color that was absorbed. Two colors that are opposite one another on the **color wheel** (Figure 14.4) are complementary. For example, a substance appears violet when it absorbs photons in the yellow region because yellow is the complementary color of violet. Similarly, yellow compounds absorb violet photons. Similar conclusions can be drawn from the table.

Observed Color	Absorbed Color
green	red
blue	orange
violet	yellow
red	green
orange	blue
yellow	violet

Table 14.3: Complementary Colors

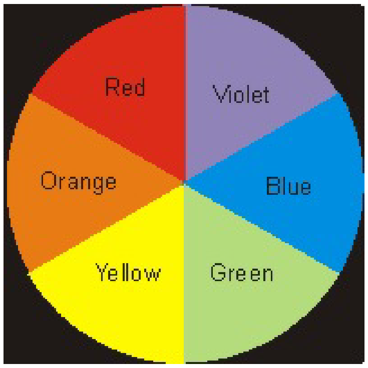


Figure 14.4: Color Wheel

14.2-5. Color and Energy

Recall from Section 2.2 that the energy of a photon (bundle of light energy) is proportional to its frequency:

$$E = h\nu$$

where h is Planck's constant (6.63×10^{-34} J/s) and ν is the frequency of the photon in s^{-1}. Thus, the energy of visible photons increases in the order red < orange < yellow < green < blue < violet.

Substances that are colored absorb photons in the visible region of the electromagnetic spectrum to promote an electron from one orbital to another that is higher in energy. The energy difference between the two orbitals (ΔE) can be determined from the frequency of the light that is absorbed by the following relationship:

$$\Delta E = h\nu$$

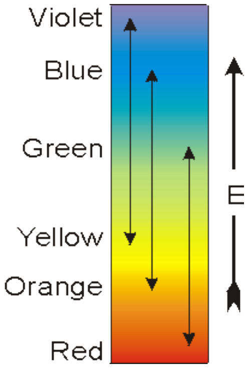


Figure 14.5: Energy and Color The double arrows connect complementary colors. Thus, if a substance appears the color at one end of the double arrow, then it absorbs light at the other end of the arrow.

Using the color wheel, we see that green grass actually absorbs red light, while an orange flower absorbs blue light, and using Figure 14.5, we conclude that the energy separation of the orbitals involved in the color is greater for the orange flower because the blue photons it absorbs have more energy than do the red photons absorbed by the grass.

14.2-6. Color in Transition Metal Ions

Many transition metal ions are colored because the energy separation between the d-orbitals lies in the visible region. The light that is absorbed in these transitions must obey the following relationship:

$$\Delta = h\nu$$

where Δ is the energy separation between the d-orbitals and ν is the frequency of the absorbed light. Thus, the relative field strengths of ligands can sometimes be determined from the color of the compounds they form with a metal.

EXERCISE 14.1:

Use the color wheel and relative energy figures and the fact that $CoBr_2$ is green while $CoCl_2$ is blue to determine the relative field strengths of the bromide and chloride ions.

$CoBr_2$ is green. What color does it absorb?	$CoCl_2$ is blue. What color does it absorb?
violet	violet
blue	blue
green	green
yellow	yellow
orange	orange
red	red

Which is the stronger field ligand?
chloride
bromide

14.2-7. Electron Spin

We now consider the effect of Δ on the spin of transition metal ions. The **spin** on an ion is the sum of the individual electron spins. Recall from Section 2.5 that the spin quantum number for an electron is either $+1/2$ or $-1/2$. The spin of two paired electrons is $+1/2 + (-1/2) = 0$. Therefore, only unpaired electrons contribute to the spin on a metal ion. In Chapter 2, we used Hund's Rule to determine the number of unpaired electrons in a d sublevel. Hund's Rule is based upon the fact that energy is required to pair two electrons in an orbital. This energy is called the **pairing energy (PE)**.

In the presence of an octahedral ligand field, the d-orbitals are in two groups separated by an energy Δ, so there are two ways in which four to seven electrons can occupy the five orbitals. Which way they actually fill the d-orbitals depends upon the relative sizes of Δ and the pairing energy. Remember that the electrons fill in such a way to minimize their energy.

- **high spin**: If $\Delta <$ PE, the electrons enter the higher energy set of orbitals before pairing. This is most likely in the presence of weak field ligands.
- **low spin**: If $\Delta >$ PE, the electrons pair before entering the higher energy set. This is most common when strong field ligands are present.

In the absence of any field, all of the d-orbitals have the same energy, so five electrons half-fill the d sublevel in accordance to Hund's Rule. This is the case in a free atom such as Mn as shown in Figure 14.6a.

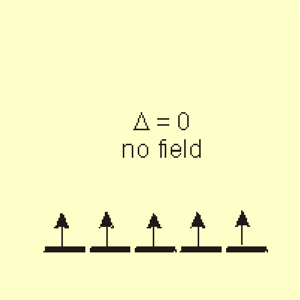


Figure 14.6a: Spin and Field Strength: No Field

In a weak field, the separation between the d-orbitals is less than the pairing energy, so the electrons occupy the higher energy orbitals before pairing. Since the electrons do not pair, this is called the high spin form of the ion.

As shown in Figure 14.6b, Mn^{2+} is high spin when surrounded by weak field ligands such as water molecules and chloride ions.

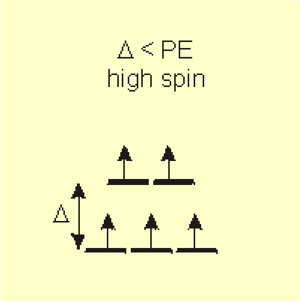


Figure 14.6b: Spin and Field Strength: Weak Field

In a strong field, the separation between the d-orbitals is greater than the pairing energy, so the electrons pair before occupying the higher energy orbitals. Since some of the electrons pair, this is called the low spin form of the ion. As shown in Figure 14.6c, Mn^{2+} is low spin when surrounded by strong field ligands, such as cyanide ion.

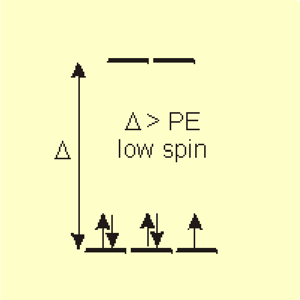


Figure 14.6c: Spin and Field Strength: Strong Field

14.3 Isomers

Introduction

Inorganic compounds can form geometrical isomers when the ligands can situate in different ways relative to one another. In this section, we consider the possible isomers of ML_2X_4 and ML_3X_3 in an octahedral coordination geometry.

Objectives

- Identify cis and trans isomers of ML_2X_4 and meridial and facial isomers of ML_3X_3.

14.3-1. Isomers

Two ligands in an octahedral geometry can be cis or trans, while three ligands can be meridial or facial.

Two ligands in an octahedral geometry can be situated in two different ways to produce two isomers. Ligands that are situated opposite to one another are said to be ***trans***, while two ligands that are adjacent to one another are said to be ***cis*** to one another.

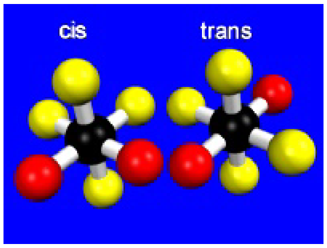


Figure 14.7: Cis and Trans Isomers Two cis ligands (red spheres) are adjacent to one another, while two trans ligands are opposite one another.

Three ligands in an octahedral geometry can also be situated in two different ways to produce two isomers. In ***mer or meridial*** isomers, the three ligands lie on a meridian of the octahedron, while the three ligands in a ***fac or facial*** isomer share a face of the octahedron.

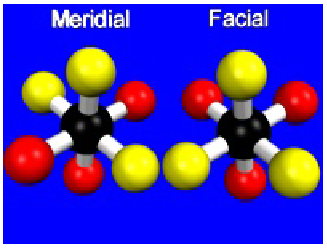


Figure 14.8: Ligand Placement in Facial and Meridial Isomers Three ligands in a meridial isomer lie on a meridian of the octahedron, while three ligands in a facial isomer share a face of the octahedron.

14.4 Metals in Biology

Introduction

Plants extract energy from the sun to synthesize carbohydrates ($C_n(H_2O)_n$) in a process called photosynthesis, and animals extract the energy from the carbohydrates in a process called respiration. Metals are key to both processes.

14.4-1. Photosynthesis

Photosynthesis involves a four-electron transfer reaction that is catalyzed by metals.

Plants produce carbohydrates from carbon dioxide and water. The process, which is called ***photosynthesis***, involves a four-electron transfer reaction. The two half-reactions are:

$$\begin{aligned} 2\mathrm{nH_2O} &\rightarrow \mathrm{nO_2} + 4\mathrm{ne}^{1-} + 4\mathrm{nH}^{1+} \\ \mathrm{nCO_2} + 4\mathrm{nH}^{1+} + 4\mathrm{ne}^{1-} &\rightarrow \mathrm{C_n(H_2O)_n} + \mathrm{nH_2O} \end{aligned}$$

Summing the two half-reaction yields the overall reaction:

$$\mathrm{nCO_2} + \mathrm{nH_2O} \rightarrow \mathrm{C_n(H_2O)_n} + \mathrm{nO_2}$$

The reaction is uphill in free energy, and plants use solar energy to carry it out. Photosynthesis is a source of carbohydrates and the only source of oxygen in the atmosphere. However, such reactions have very high activation energies, so nature uses a cluster of four Mn ions coordinated to proteins within the cells break the reaction down into four separate one-electron processes.

The light that drives the reaction is absorbed by chlorophyll (Figure 14.9) in the plants. Chlorophyll contains a Mg^{2+} ion in the center of a porphyrin derivative, which has an extended π system and the characteristic low energy separation between the highest filled π molecular orbital (HOMO) and lowest energy unfilled π^* orbital (LUMO). The extended π system absorbs red light. Plants appear green because green is the complement of red. The Mg^{2+} ion in the center of porphyrin alters the electronic states of the porphyrin slightly so that the excited electron moves away from the porphyrin rather than returning directly to the ground state. This high-energy electron is used to initiate photosynthesis.

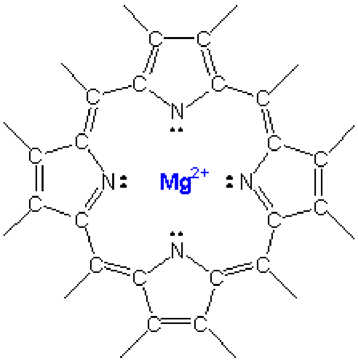


Figure 14.9: Chorophyll

14.4-2. Heme

Oxygen transport is carried out by binding O_2 to iron in a heme group.

Animals utilize other metal-containing proteins to reverse photosynthesis and extract energy from carbohydrates in a process called respiration. ***Respiration*** is the oxidative process that extracts chemical energy from organic molecules within living cells. These processes involve the consumption of O_2, which is transported to the cells by hemoglobin. The oxygen molecule attaches to a heme group, an iron(II) porphyrin, in a large protein. Thus, the heme group is the "active site" in hemoglobin. The oxygen is added or removed in the following equilibrium:

$$\text{deoxyheme} + O_2 \leftrightharpoons \text{oxyheme}$$

Whether the heme is in the oxy or deoxy form depends upon the pressure of O_2. Thus, the heme is oxygenated in the lungs where the O_2 pressure is high and comes off in oxygen-poor tissue.

O_2 is not a very strong Lewis base, so it binds weakly to the iron, which is essential for its delivery to the tissue. CO is a much stronger base and binds to the iron much more strongly and does not come off once it binds. When carbon monoxide is inhaled, it binds to the iron and ties up binding sites that would be used for O_2 transport. Asphyxiation results when so many of the heme sites are tied up with CO that O_2 can no longer be delivered to the cells.

Refer to Figure 14.10 in this discussion of the action of heme. Fe^{2+} has six coordination sites, but the porphyrin ligand coordinates to only four and one of the sites is used to bind to the protein. The occupation of the other site depends upon whether O_2 is bound to the iron. Figure 14.10a shows deoxyhemoglobin (no bound O_2). The sixth site is vacant, so the iron is five coordinate and adopts a square pyramidal geometry with the iron pulled out of the plane of the porphyrin. Figure 14.10b shows oxyhemoglobin (bound O_2). The iron is six coordinate and lies in the plane of the porphyrin molecule. The oxygen also hydrogen bonds to the protein.

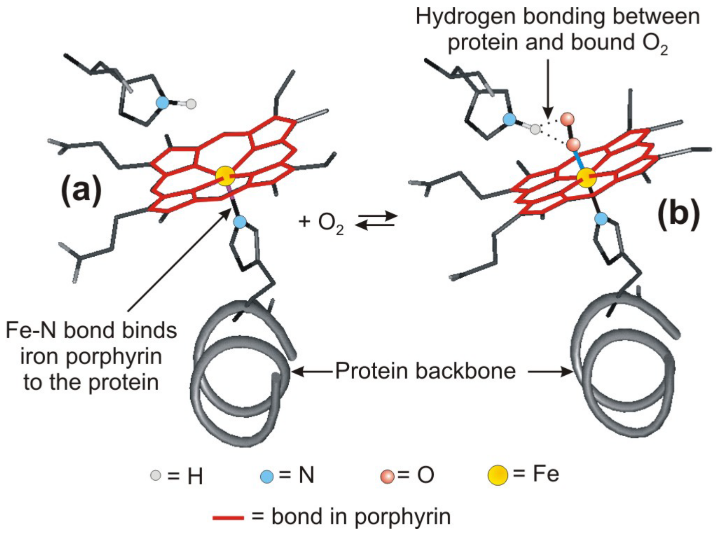


Figure 14.10: Action of Heme

14.4-3. Hemoglobin

Hemoglobin is comprised of 600 amino acids and consists of four similar units (Figure 14.11a). Each unit contains an active site. Although each active site (Figure 14.11b) is the center of the oxygen transport process, the polypeptide chains play critical roles in stabilizing the binding and release of four oxygen molecules.

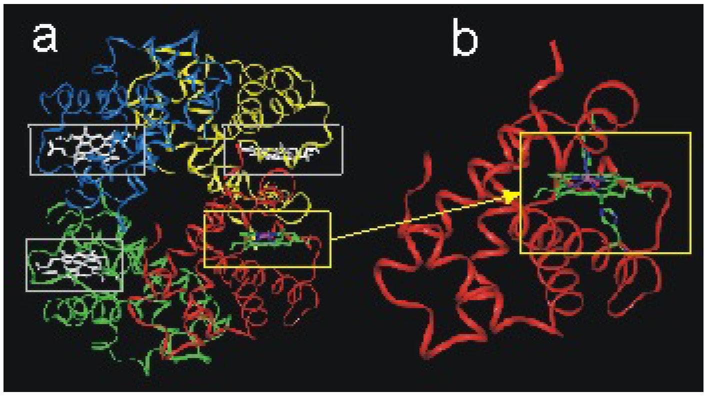


Figure 14.11: Hemoglobin

Only slight changes in that structure can have dramatic effects. For example, in people with sickle-cell anemia, two negatively-charged amino acids are replaced with two neutral amino acids. This small change causes the cell to adopt the sickle shape and greatly reduces the ability of the blood to transport oxygen.

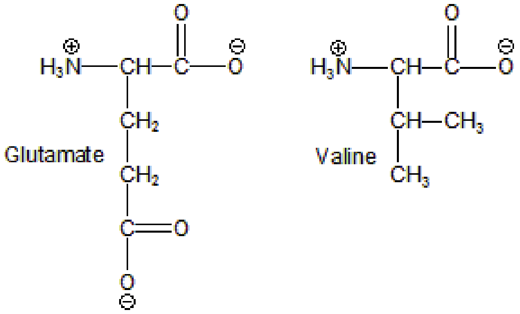


Figure 14.12: Amino Acids Involved in Sickle-Cell Anemia

14.4-4. Cisplatin — Drug Action

Cisplatin binds to DNA, which causes a shape modification in the DNA that hinders its function.

cis-$Pt(NH_3)_2Cl_2$ (cisplatin) is a square planar complex that is used as an antitumor drug to treat ovarian, testicular, and brain cancers. It functions by binding to DNA, which changes the shape of the DNA double helix and alters its function. Its action is described in the following.

Chlorides are displaced in the nucleus: The chloride ion concentration in the blood is quite high (∼0.1 M), so the chloride ions remain bound to the platinum, but, in the nucleus the chloride ion concentration is very low (∼0.003 M) and the chloride ions on cisplatin are replaced by water molecules. Water is a weak Lewis base and is easily displaced by a stronger base.

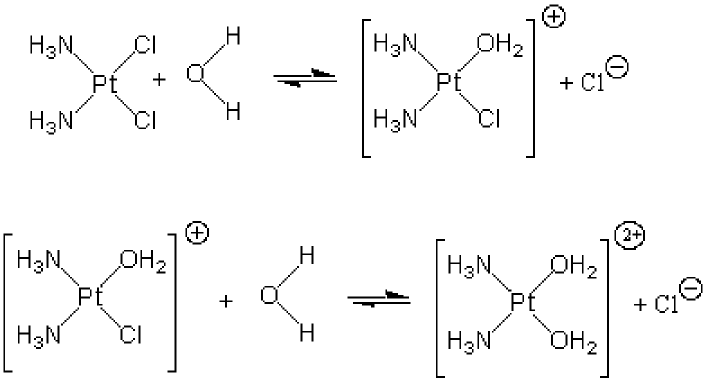


Figure 14.13: Replacement of Chloride with Water

Interaction of Cisplatin and DNA: The lone pairs on the nitrogen atoms make these DNA sites strong Lewis bases, so they displace the water molecules from the drug and bind to the platinum. However, in order for both basic sites to bind, the DNA must bend. The angle by which it bends (α) is 30–40°.

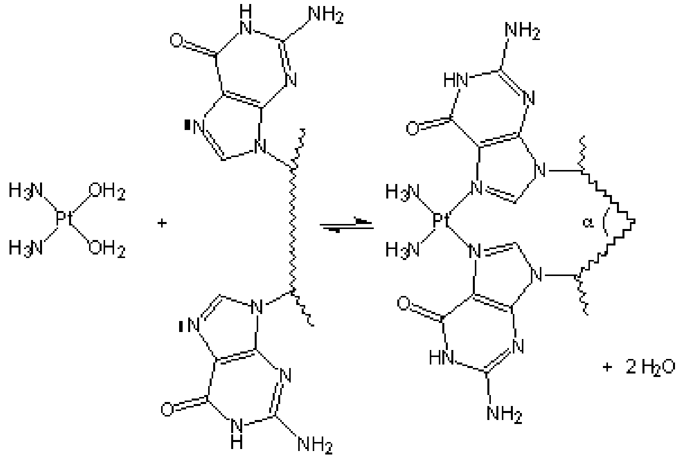


Figure 14.14: Cisplatin Bound to Two Sites of a DNA Strand

Drug Action: Many cellular events are initiated by interactions in which a protein "reads" a specific sequence on the DNA strand. The process is based almost entirely on the ability of the protein to conform its shape to that of the double helix. When the shape of the double helix is altered by the cisplatin, the interactions are modified and the protein can no longer function, which causes the cell to die.

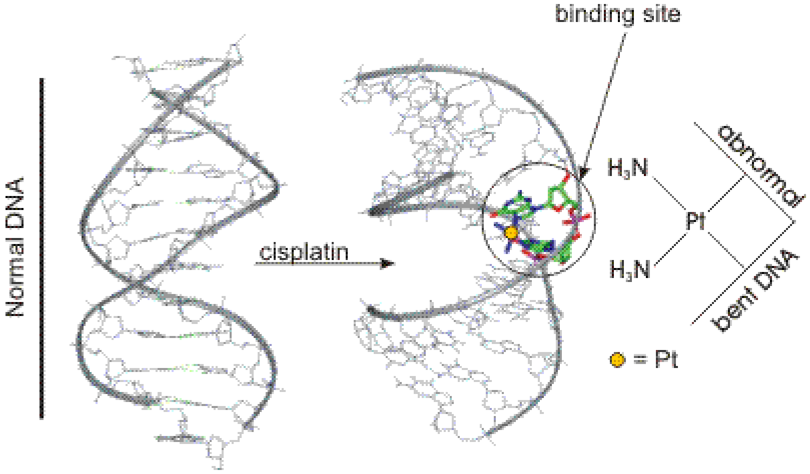


Figure 14.15: Changes in DNA Double Helix Due to Cisplatin Binding

14.5 Metals as Catalysts

Introduction

The interaction between a ligand and a metal can be used to provide new pathways for chemical reactions; i.e., metals catalyze some reactions. A catalyst is classified as either homogeneous (the catalyst is in the same phase as the reactants) or heterogeneous (the catalyst is in a different phase than the reactants).

Prerequisites

- 9.10 Rates of Reaction and the Rate Law

14.5-1. Heterogeneous Catalysts

Heterogeneous catalysts are solids that catalyze solution or gas phase reactions on their surfaces.

When a reactant adsorbs onto a solid surface, the reactant's bonds are weakened, which makes it more reactive.

Hydrogenation is an important reaction, but it has a high activation energy because it involves breaking H–H and C=C bonds. Thus, the reaction is very slow at normal conditions. However, in the presence of Ni, Pt, or Pd and a high pressure of hydrogen, the reaction proceeds rapidly by the mechanism shown for a platinum surface in Figure 14.16. The mechanism consists of the following steps:

1 H_2 adsorbs on the surface as H atoms.

2 H atoms migrate across the surface.

3 An ethylene molecule adsorbs on the surface by using its pi electrons.

4 H atoms and ethylene molecules migrate into one another.

5 C–H bonds form to produce an ethane molecule that desorbs from the surface.

Catalytic converters in automobiles are also heterogeneous catalysts that use Pt, Pd, and Rh to catalyze the complete combustion of CO and unspent hydrocarbons to CO_2 and H_2O.

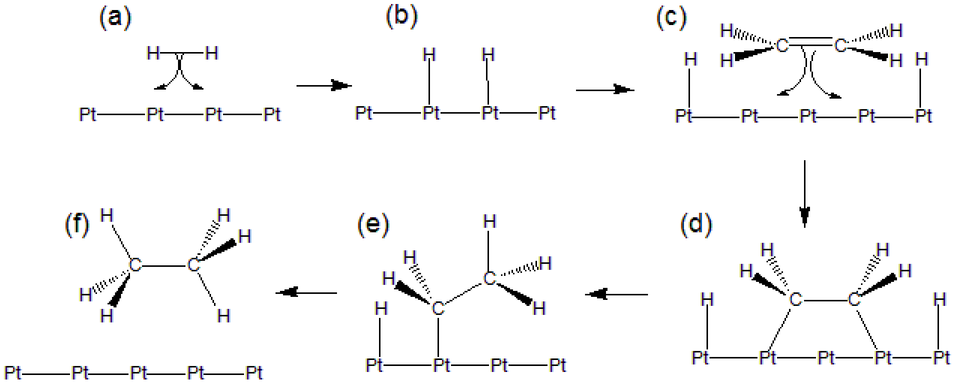


Figure 14.16: Mechanism for Metal Catalyzed Hydrogenation of Ethene Hydrogenation of ethene to ethane on a platinum surface.

14.5-2. Homogeneous Catalysts

Homogeneous catalysts function in the same phase as the reactants.

Consider the metal catalyzed polymerization of ethene into polyethylene. Titanocene, which is a catalyst for this reaction, is a four coordinate complex with one chloride ion, two ligands that do not directly affect the reaction, and an ethyl (C_2H_5) group that is the base upon which the polymer grows. The titanium is in a high oxidation state (+4) and its coordination number can readily be increased from four to five, so titanocene is a good Lewis acid, which is why it is a good catalyst for alkenes, which are weak Lewis bases. The steps of the mechanism, which is illustrated in Figure 14.17, are:

1 The pi bond is weakened by coordination to Ti and the Ti adopts a five coordinate geometry.

2 The pi electrons of the C=C bond are used to form a Ti–C bond

3 The electrons in the original Ti–C_2H_5 bond are used to form a C–C bond to the ethene.

4 The ethene is inserted between Ti and C_2H_5.

5 The process is repeated with each ethene being inserted between the Ti and the growing polymer chain.

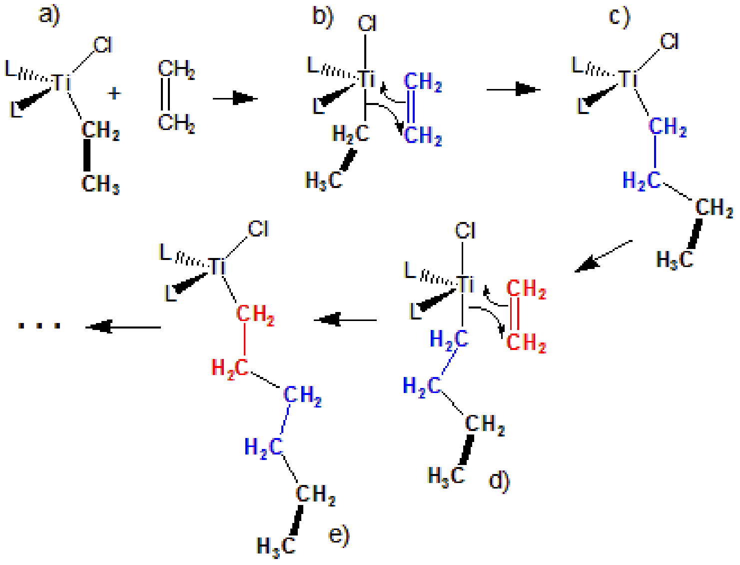


Figure 14.17: Mechanism for Titanocene Catalyzed Polymerization of Ethene

14.6 Transition Metals as Electronic and Magnetic Materials

Introduction

Thus far, we have focused on reactive complexes in solution, but transition metal complexes that are used in materials applications must be stable (ligands bound tightly) and they must be in their crystalline state.

Prerequisites

- 8.6-3 The Definition of a Band

14.6-1. Electronic Conductivity

Electrical conductivity in solids results from partially filled bands. Such bands can be produced by partially oxidizing or reducing a compound.

In order to make a transition metal complex that conducts electricity in the solid state, we must make one whose structure results in band formation and then find a way to make the band partially filled. One of the first conducting transition metal complexes was based on $[Pt(CN)_4]^{2+}$ ions.

$[Pt(CN)_4]^{2+}$ ions stack face-to-face to form one-dimensional chains in $K_2Pt(CN)_4$. Interaction of the z^2 orbitals produces a band.

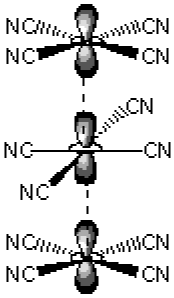


Figure 14.18: Linear Chains Formed from Face-to-Face Stacking of $[Pt(CN)_4]^{2+}$ Ions

The platinum atom in $K_2Pt(CN)_4$ is in the +2 oxidation state and has two electrons in the z^2. Since the z^2 is filled, the band formed from the interactions of the z^2 orbitals is also filled. Complete oxidation to the +4 state removes both electrons from the z^2, which would empty the band. However, conductors are characterized by partially filled bands, so neither the +2 nor +4 oxidation states leads to a conducting material. Thus, the material must be partially oxidized to produce the partially filled band required for conduction. A conducting material has been produced by reacting $K_2Pt(CN)_4$ with a limited amount of Br_2 (a good oxidizing agent) to produce a material with the stoichiometry of $K_2Pt(CN)_4Br_{0.3}$. The oxidation state of the Pt in this compound is 2.3; i.e., it has been partially oxidized. This is equivalent to removing about 15% of the electrons from the band to produce a partially filled band and a conductor.

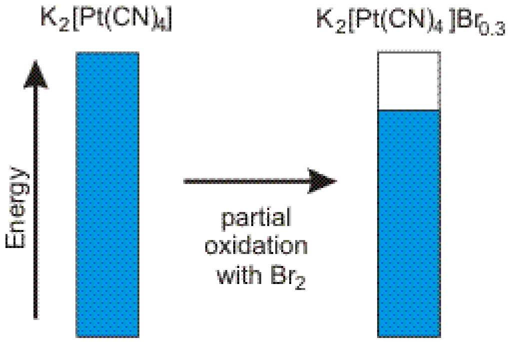


Figure 14.19: Band Occupancy Change due to Partial Oxidation of Platinum

14.6-2. Magnetic Materials

Magnetism is a bulk property that requires unpaired electrons to align in the same direction.

When many atoms that have unpaired electrons in the gas phase combine to form solids, the unpaired electrons pair to form bonds between the atoms. For example, a sodium atom has one unpaired electron, but sodium metal is not magnetic. However, other atoms, such as iron, are magnetic. The three most common magnetic classifications of materials with unpaired electrons are discussed below.

In ferromagnetic materials, the unpaired electrons on adjacent atoms align in the same direction to produce a magnetic field. Iron atoms have four unpaired, and some of them do pair to form the solid. However, not all pair and those that do not align so as to produce a magnetic material. The crystal structure plays a key role in the magnetism as it keeps the spins aligned. Thus, molten iron is not magnetic!

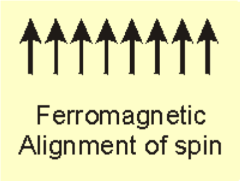


Figure 14.20a: Common Magnetic Classifications: *Ferromagnet*

Materials are not magnetic when the unpaired spins of adjacent atoms align in opposite directions and cancel their magnetic fields. Materials of this type are not magnetic. Sodium is antiferromagnetic.

Figure 14.20b: Common Magnetic Classifications: *Antiferromagnet*

Substances that have adjacent atoms with electron spins of unequal magnitude that are aligned in opposite directions are said to be ferrimagnetic. Although there is some cancellation of magnetic fields as a result of the opposite directions of the spins, these substances are magnetic because the opposite spins do not completely cancel one another because they have different magnitudes.

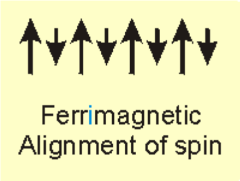


Figure 14.20c: Common Magnetic Classifications: *Ferrimagnet*

14.6-3. Ferrimagnet Example

The structure of $Cs_2Mn[V(CN)_6]$, which is a ferrimagnet in which the spins of the vanadium and manganese atoms are opposed, is shown in Figure 14.21. However, the vanadium atoms (red spheres), which are in the +2 oxidation state, have three unpaired electrons (S = 3/2), while the manganese atoms (yellow spheres), which are also in the +2 oxidation state, have five unpaired electrons (S = 5/2). Since the spin on Mn is almost twice that on V, a net magnetic field is produced even though the two spins oppose one another.

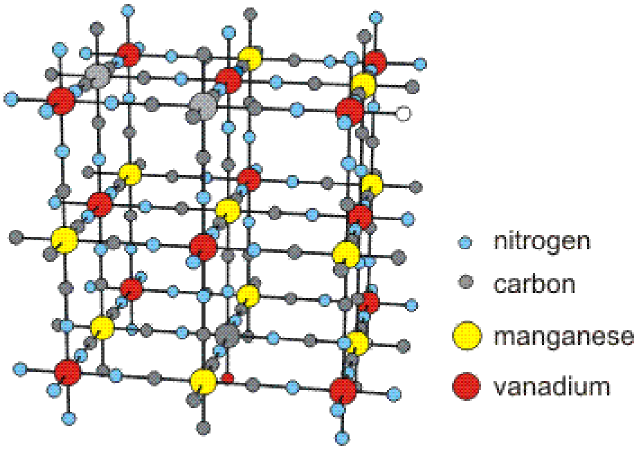


Figure 14.21: Structure of $Cs_2Mn[V(CN)_6]$

14.7 Exercises and Solutions

Links to view either the end-of-chapter exercises or the solutions to the odd exercises are available in the HTML version of the chapter.

Exercise 11.10 (Cont.)

EXERCISE 11.10: Continued

Use the Table of Standard Reduction Potentials to write the net equations for the processes described below and determine their standard cell potentials.

Metallic copper is placed in 1 M $AgNO_3$.

Oxidation half reaction:

________ $\rightleftharpoons$ ________ + ________ e^{1-}

Red. 1 Ox. 1

Reduction half reaction:

________ + ________ e^{1-} $\rightleftharpoons$ ________

Ox. 2 Red. 2

The number of electrons transferred (or the LCM) is: ________

Write the net equation (if any).

________ + ________ $\rightarrow$ ________ + ________

Red. 1 Ox. 2 Ox. 1 Red. 2

The standard cell potential in volts is: ________

Metallic chromium is placed in 1 M $CuSO_4$.

Oxidation half reaction:

________ $\rightleftharpoons$ ________ + ________ e^{1-}

Red. 1 Ox. 1

Reduction half reaction:

________ + ________ e^{1-} $\rightleftharpoons$ ________

Ox. 2 Red. 2

The number of electrons transferred (or the LCM) is: ________

Write the net equation (if any).

________ + ________ $\rightarrow$ ________ + ________

Red. 1 Ox. 2 Ox. 1 Red. 2

The standard cell potential in volts is: ________

Metallic iron is placed in 1 M $NiSO_4$.

Oxidation half reaction:

________ ⇌ ________ + ________ e^{1-}

Red. 1 Ox. 1

Reduction half reaction:

________ + ________ e^{1-} ⇌ ________

Ox. 2 Red. 2

The number of electrons transferred (or the LCM) is: ________

Write the net equation (if any).

________ + ________ → ________ + ________

Red. 1 Ox. 2 Ox. 1 Red. 2

The standard cell potential in volts is: ________

Metallic sodium is added to water.
Note: in some half reactions, there are substances present that are not involved in the electron transfer but are required for a balanced equations. These substances will be referred to as "other." Other substances are usually H_2O, OH^{1-}, or H^{1+} when they are not involved in the electron transfer. This example contains one "Other" substance.

Oxidation half reaction:

________ ⇌ ________ + ________ e^{1-}

Red. 1 Ox. 1

Reduction half reaction:

________ + ________ e^{1-} ⇌ ________ + ________

Ox. 2 Red. 2 Other

The number of electrons transferred (or the LCM) is: ________

Write the net equation (if any).

________ + ________ → ________ + ________ + ________

Red. 1 Ox. 2 Ox. 1 Red. 2 Other

The standard cell potential in volts is: ________

Metallic chromium is placed in 1 M $AgNO_3$.

Oxidation half reaction:

__________ $\rightleftharpoons$ __________ + __________ e^{1-}

Red. 1 Ox. 1

Reduction half reaction:

__________ + __________ e^{1-} $\rightleftharpoons$ __________

Ox. 2 Red. 2

The number of electrons transferred (or the LCM) is: __________

Write the net equation (if any).

__________ + __________ $\rightarrow$ __________ + __________

Red. 1 Ox. 2 Ox. 1 Red. 2

The standard cell potential in volts is: __________

Metallic copper is placed in 1 M nitric acid.

Oxidation half reaction:

__________ $\rightleftharpoons$ __________ + __________ e^{1-}

Red. 1 Ox. 1

Reduction half reaction:

__________ + __________ + __________ e^{1-} $\rightleftharpoons$ __________ + __________

Ox. 2 Other Red. 2 Other

The number of electrons transferred (or the LCM) is: __________

Write the net equation (if any).

__________ + __________ + __________ $\rightarrow$

Red. 1 Ox. 2 Other

__________ + __________ + __________

Ox. 1 Red. 2 Other

The standard cell potential in volts is: __________

Periodic Table

1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**
1A	**2A**	**3B**	**4B**	**5B**	**6B**	**7B**	**8B**	**8B**	**8B**	**1B**	**2B**	**3A**	**4A**	**5A**	**6A**	**7A**	**8A**
1 **H** 1.01																	2 **He** 4.00
3 **Li** 6.94	4 **Be** 9.01											5 **B** 10.81	6 **C** 12.01	7 **N** 14.01	8 **O** 16.00	9 **F** 19.00	10 **Ne** 20.18
11 **Na** 22.99	12 **Mg** 24.31											13 **Al** 26.98	14 **Si** 28.09	15 **P** 30.97	16 **S** 32.07	17 **Cl** 35.45	18 **Ar** 39.95
19 **K** 39.10	20 **Ca** 40.08	21 **Sc** 44.96	22 **Ti** 47.88	23 **V** 50.94	24 **Cr** 52.00	25 **Mn** 54.94	26 **Fe** 55.85	27 **Co** 58.93	28 **Ni** 58.69	29 **Cu** 63.55	30 **Zn** 65.39	31 **Ga** 69.72	32 **Ge** 72.61	33 **As** 74.92	34 **Se** 78.96	35 **Br** 79.90	36 **Kr** 83.80
37 **Rb** 85.48	38 **Sr** 87.62	39 **Y** 88.91	40 **Zr** 91.22	41 **Nb** 92.91	42 **Mo** 95.94	43 **Tc** (98)	44 **Ru** 101.07	45 **Rh** 102.91	46 **Pd** 106.42	47 **Ag** 107.87	48 **Cd** 112.41	49 **In** 114.82	50 **Sn** 118.71	51 **Sb** 121.75	52 **Te** 127.60	53 **I** 126.90	54 **Xe** 131.29
55 **Cs** 132.91	56 **Ba** 137.33	57 **La** 138.91	72 **Hf** 178.49	73 **Ta** 180.95	74 **W** 183.84	75 **Re** 186.21	76 **Os** 190.23	77 **Ir** 192.22	78 **Pt** 195.08	79 **Au** 196.97	80 **Hg** 200.59	81 **Tl** 204.38	82 **Pb** 207.2	83 **Bi** 208.98	84 **Po** (209)	85 **At** (210)	86 **Rn** (222)
87 **Fr** (223)	88 **Ra** 226.03	89 **Ac** 227.03	104 **Rf** (261)	105 **Db** (262)	106 **Sg** (263)	107 **Bh** (264)	108 **Hs** (265)	109 **Mt** (268)									

58 **Ce** 140.11	59 **Pr** 140.91	60 **Nd** 144.24	61 **Pm** (145)	62 **Sm** 150.36	63 **Eu** 151.97	64 **Gd** 157.25	65 **Tb** 158.93	66 **Dy** 162.5	67 **Ho** 164.93	68 **Er** 167.26	69 **Tm** 168.93	70 **Yb** 173.04	71 **Lu** 174.97
90 **Th** 232.04	91 **Pa** 231.04	92 **U** 238.03	93 **Np** 237.05	94 **Pu** (244)	95 **Am** (243)	96 **Cm** (247)	97 **Bk** (247)	98 **Cf** (251)	99 **Es** (252)	100 **Fm** (257)	101 **Md** (258)	102 **No** (259)	103 **Lr** (262)

Legend:					
	1 **H** 1.01	Atomic number **Symbol** Atomic mass	**Metals**	**Metalloids**	**Nonmetals**

Acid-Base Table

Acid	**K_a**	**Base**
$HClO_4$	$\gg 1$	ClO_4^{1-}
HX (X=I, Br, Cl)	$\gg 1$	X^{1-}
H_2SO_4	$\gg 1$	HSO_4^{1-}
HNO_3	$\gg 1$	NO_3^{1-}
H_3O^{1+}	1.0	H_2O
H_2SO_3	1.5×10^{-2}	HSO_3^{1-}
HSO_4^{1-}	1.2×10^{-2}	SO_4^{2-}
H_3PO_4	7.5×10^{-3}	$H_2PO_4^{1-}$
HF	7.2×10^{-4}	F^{1-}
HNO_2	4.0×10^{-4}	NO_2^{1-}
$HC_2H_3O_2$	1.8×10^{-5}	$C_2H_3O_2^{1-}$
H_2CO_3	4.3×10^{-7}	HCO_3^{1-}
HSO_3^{1-}	1.0×10^{-7}	SO_3^{2-}
H_2S	1.0×10^{-7}	HS^{1-}
$H_2PO_4^{1-}$	6.2×10^{-8}	HPO_4^{2-}
HClO	3.5×10^{-8}	ClO^{1-}
NH_4^{1+}	5.6×10^{-10}	NH_3
HCN	4.0×10^{-10}	CN^{1-}
HCO_3^{1-}	4.7×10^{-11}	CO_3^{2-}
HPO_4^{2-}	4.8×10^{-13}	PO_4^{3-}
HS^{1-}	1.3×10^{-13}	S^{2-}
H_2O	1.0×10^{-14}	OH^{1-}
NH_3	$\ll 10^{-14}$	NH_2^{1-}
OH^{1-}	$\ll 10^{-14}$	O^{2-}

An Acid-Base Table

Atomic Radii

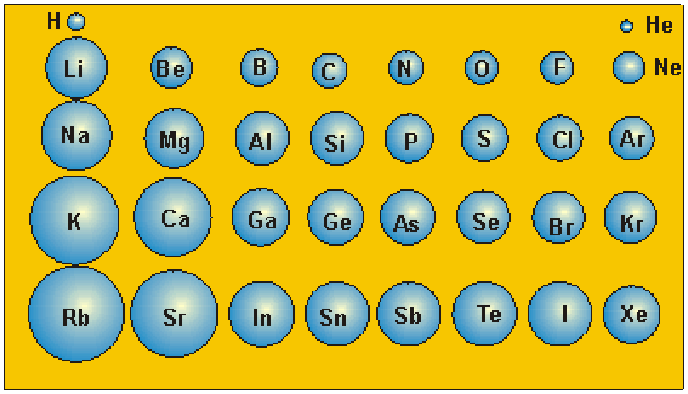


Figure: Atomic Radii

Li	1.52	Be	1.11	B	0.88	C	0.77	N	0.75	O	0.73	F	0.71
Na	1.86	Mg	1.60	Al	1.43	Si	1.17	P	1.10	S	1.04	Cl	0.99
K	2.27	Ca	1.97	Ga	1.22	Ge	1.22	As	1.21	Se	1.17	Br	1.14
Rb	2.48	Sr	2.15	In	1.63	Sn	1.41	Sb	1.40	Te	1.37	I	1.33

Atomic Radii (Å) of Some Main Group Elements

Bond Energies

C–H	413
C–F	485
C–Cl	328
C–Br	276
C–I	234

N–H	391
N–F	272
N–Cl	200
N–Br	243

O–H	463
O–F	190
O–Cl	203
O–Br	235
O–I	234

H–H	436
H–F	565
H–Cl	431
H–Br	366
H–I	299

F–F	159
Cl–Cl	243
Br–Br	193
I–I	151

C–C	347
C=C	612
C≡C	820

N–N	163
N=N	418
N≡N	941

N–O	201
N=O	607

C–N	293
C=N	615
C≡N	891

C–O	358
C=O	799
C≡O	1072

O–O	146
O=O	495

Common Bond Energies (kJ/mol)

Bond Lengths

Bond	Length (Å)
C–O	1.43
C=O	1.23
C≡O	1.13
C–C	1.54
C=C	1.33
C≡C	1.20

Bond	Length (Å)
C–N	1.47
C=N	1.27
C≡N	1.15
N–N	1.47
N=N	1.24
N≡N	1.10

Bond	Length (Å)
N–O	1.44
N=O	1.20
O–O	1.48
O=O	1.21

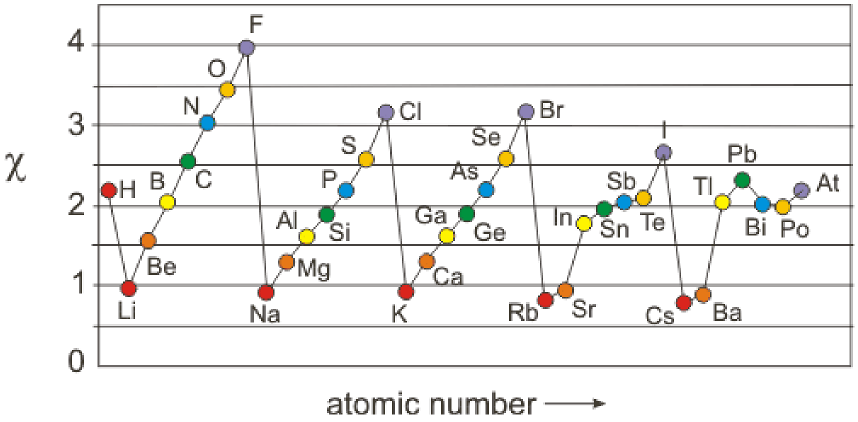
Average Bond Lengths of Bonds Involving C, N, and O

Bond Types

Note that δ is the value of δ in ${}^{\delta-}\mathbf{X}-\mathbf{Y}^{\delta+}$		
$\boldsymbol{\Delta\chi}$	**$\boldsymbol{\delta}$**	**Bond Type**
> 1.8	> 0.5	ionic
0.4 to 1.8	0.05 to 0.5	polar covalent
< 0.4	< 0.05	covalent

Approximate Bond Type Versus $\Delta\chi$

Electronegativities



H						
2.2						
Li	**Be**	**B**	**C**	**N**	**O**	**F**
1.0	1.6	2.0	2.6	3.0	3.4	4.0
Na	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**
0.9	1.3	1.6	1.9	2.2	2.6	3.2
K	**Ca**	**Ga**	**Ge**	**As**	**Se**	**Br**
0.9	1.0	1.8	2.0	2.2	2.6	3.2
Rb	**Sr**	**In**	**Sn**	**Sb**	**Te**	**I**
0.8	1.0	1.8	2.0	2.1	2.1	2.7
Cs	**Ba**	**Tl**	**Pb**	**Bi**	**Po**	**At**
0.8	0.9	2.0	2.3	2.0	2.0	2.2

Elements

List of Element Names, Symbols, Atomic Numbers and Masses

Elements	Symbol	Atomic Number	Atomic Mass
Actinium	Ac	89	227.03
Aluminum	Al	13	26.98
Americium	Am	95	(243)
Antimony	Sb	51	121.8
Argon	Ar	18	39.95
Arsenic	As	33	74.92
Astatine	At	85	(210)
Barium	Ba	56	137.3
Berkelium	Bk	97	(247)
Beryllium	Be	4	9.012
Bismuth	Bi	83	208.98
Bohrium	Bh	107	(264)
Boron	B	5	10.81
Bromine	Br	35	79.90
Cadmium	Cd	48	112.4
Calcium	Ca	20	40.08
Californium	Cf	98	(251)
Carbon	C	6	12.01
Cerium	Ce	58	140.1
Cesium	Cs	55	132.9
Chlorine	Cl	17	35.45
Chromium	Cr	24	52.00
Cobalt	Co	27	58.93
Copernicum	Cn	112	(277)
Copper	Cu	29	63.55
Curium	Cm	96	(247)
Dubnium	Db	105	(262)
Dysprosium	Dy	66	162.5
Einsteinium	Es	99	(252)
Erbium	Er	68	167.3
Europium	Eu	63	151.96
Fermium	Fm	100	(257)
Fluorine	F	9	18.99
Francium	Fr	87	(223)
Gadolinium	Gd	64	157.3
Gallium	Ga	31	69.72
Germanium	Ge	32	72.61
Gold	Au	79	196.97

Hafnium	Hf	72	178.5
Helium	He	2	4.003
Hessium	Hs	108	(265)
Holmium	Ho	67	164.9
Hydrogen	H	1	1.008
Indium	In	49	114.8
Iodine	I	53	126.9
Iridium	Ir	77	192.2
Iron	Fe	26	55.85
Krypton	Kr	36	83.8
Lanthanum	La	57	138.9
Lawrencium	Lr	103	(262)
Lead	Pb	82	207.2
Lithium	Li	3	6.941
Lutetium	Lu	71	174.97
Magnesium	Mg	12	24.31
Manganese	Mn	25	54.94
Meitnerium	Mt	109	(268)
Mendelevium	Md	101	(258)
Mercury	Hg	80	200.6
Molybdenum	Mo	42	95.94
Neodymium	Nd	60	144.2
Neon	Ne	10	20.18
Neptunium	Np	93	(237.05)
Nickel	Ni	28	58.69
Niobium	Nb	41	92.91
Nitrogen	N	7	14.01
Nobelium	No	102	(259)
Osmium	Os	76	190.2
Oxygen	O	8	15.99
Palladium	Pd	46	106.4
Phosphorus	P	15	30.97
Platinum	Pt	78	195.1
Plutonium	Pu	94	(244)
Polonium	Po	84	(209)
Potassium	K	19	39.09
Praseodymium	Pr	59	140.9

Promethium	Pm	61	(145)
Protactinium	Pa	91	(231.04)
Radium	Ra	88	(226.03)
Radon	Rn	86	(222)
Rhenium	Re	75	186.2
Rhodium	Rh	45	102.9
Rubidium	Rb	37	85.47
Ruthenium	Ru	44	101.1
Rutherfordium	Rf	104	(261)
Samarium	Sm	62	150.4
Scandium	Sc	21	44.96
Seaborgium	Sg	106	(263)
Selenium	Se	34	78.96
Silicon	Si	14	28.09
Silver	Ag	47	107.9
Sodium	Na	11	22.99
Strontium	Sr	38	87.62
Sulfur	S	16	32.07
Tantalum	Ta	73	180.9
Technetium	Tc	43	(98)
Tellurium	Te	52	127.6
Terbium	Tb	65	158.9
Thallium	Tl	81	204.4
Thorium	Th	90	232.04
Thulium	Tm	69	168.9
Tin	Sn	50	118.7
Titanium	Ti	22	47.88
Tungsten	W	74	183.9
Uranium	U	92	238.0
Ununnilium	Uun	110	(269)
Unununium	Uuu	111	(272)
Vanadium	V	23	50.94
Xenon	Xe	54	131.3
Ytterbium	Yb	70	173.0
Yttrium	Y	39	88.91
Zinc	Zn	30	65.39
Zirconium	Zr	40	91.22

Fundamental Constants

Energy

- 1 joule (J) = 1 kg $\cdot$ m^2 $\cdot$ s^{-2}
- 1 calorie (cal) = 4.184 J
- 1 V = 96.485 kJ/mol

Force

- 1 newton (N) = 1 kg $\cdot$ m/s^2

Length

- 1 meter (m) = 39.37 inches (in)
- 1 inch = 2.54 centimeters (cm)—exact
- 1 Å = 10^{-10} m

Mass

- 1 kilogram (kg) = 2.205 pounds (lb)
- 1 lb = 453.6 grams (g)
- 1 amu = 1.661×10^{-24} g

Pressure

- 1 atm = 760 mm Hg (torr) = 1.01325×10^5 Pa

Volume

- 1 liter (L) = 1000 mL = 1000 cm^3

Physical Constants

Avogadro's number	$N_\mathrm{A} = 6.0221 \times 10^{23}\ \mathrm{mol}^{-1}$
Electronic charge	$e = 1.6022 \times 10^{-19}$ coulomb (C)
Electron rest mass	$m_\mathrm{e} = 9.1094 \times 10^{-31}$ kg
Faraday constant	$\mathcal{F} = 9.6485 \times 10^4\ \mathrm{C} \cdot \mathrm{mol}^{-1}$
Gas constant	$R = 0.08206\ \mathrm{L} \cdot \mathrm{atm} \cdot \mathrm{mol}^{-1} \cdot \mathrm{K}^{-1}$
	$= 8.3145\ \mathrm{J} \cdot \mathrm{mol}^{-1} \cdot \mathrm{K}^{-1}$
	$= 1.9872\ \mathrm{cal} \cdot \mathrm{mol}^{-1} \cdot \mathrm{K}^{-1}$
Neutron rest mass	$m_\mathrm{n} = 1.675 \times 10^{-27}$ kg
Planck's constant	$h = 6.6261 \times 10^{-34}\ \mathrm{J} \cdot \mathrm{s}$
Proton rest mass	$m_p = 1.6726 \times 10^{-27}$ kg
Speed of light (in vacuum)	$c = 2.9979 \times 10^8\ \mathrm{m} \cdot \mathrm{s}^{-1}$

Physical Constants

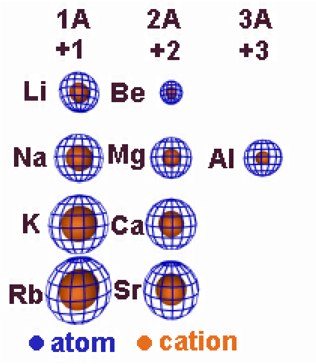
Temperature

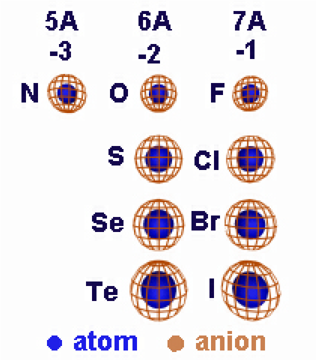
$$\begin{aligned}
0\ \mathrm{K} &= -273.15^\circ \text{ Celsius (C)} \\
&= -459.67^\circ \text{ Fahrenheit (F)} \\
{}^\circ\mathrm{F} &= (9/5)^\circ\mathrm{C} + 32^\circ \\
{}^\circ\mathrm{C} &= (5/9)(^\circ\mathrm{F} - 32^\circ) \\
\mathrm{K} &= {}^\circ\mathrm{C} + 273.15
\end{aligned}$$

SI Prefixes

- 10^{9} giga (G)
- 10^{6} mega (M)
- 10^{3} kilo (k)
- 10^{-1} deci (d)
- 10^{-2} centi (c)
- 10^{-3} milli (m)
- 10^{-6} micro (μ)
- 10^{-9} nano (n)
- 10^{-12} pico (p)

Ionic Radii





Cations are smaller than their atoms, and anions are larger than their atoms.

Li	1.52	Be	1.11			N	0.75	O	0.73	F	0.71
Li^{1+}	0.60	Be^{2+}	0.31			N^{3-}	1.71	O^{2-}	1.40	F^{1-}	1.36
Na	1.86	Mg	1.60	Al	1.43			S	1.04	Cl	0.99
Na^{1+}	0.95	Mg^{2+}	0.65	Al^{3+}	0.50			S^{2-}	1.84	Cl^{1-}	1.81
K	2.27	Ca	1.97					Se	1.17	Br	1.14
K^{1+}	1.33	Ca^{2+}	0.99					Se^{2-}	1.98	Br^{1-}	1.95
Rb	2.48	Sr	2.15					Te	1.37	I	1.33
Rb^{1+}	1.48	Sr^{2+}	1.13					Te^{2-}	2.21	I^{1-}	2.16

Atomic and Ionic Radii (Å) of Selected Main Group Elements

Ionization Energies

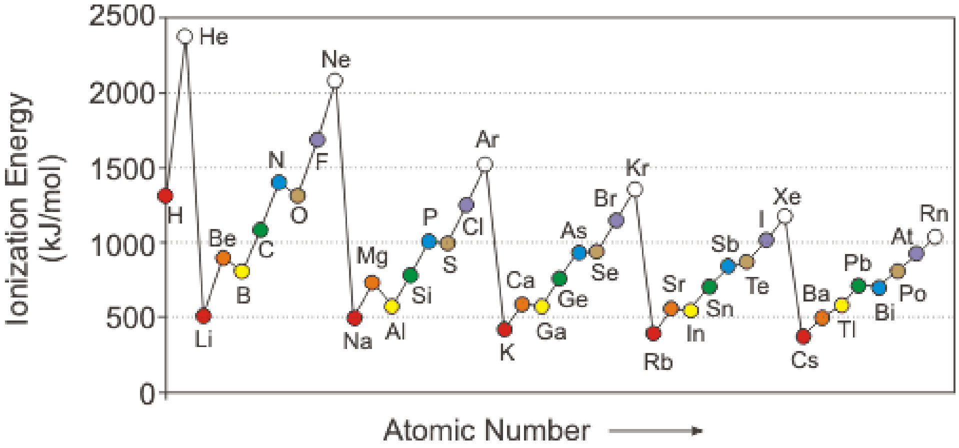


Figure: Ionization Energies

Polyatomic Ions

Cations			
NH_4^{1+}	ammonium ion	H_3O^{1+}	hydronium ion
Anions			
$C_2H_3O_2^{1-}$	acetate ion	OH^{1-}	hydroxide ion
CO_3^{2-}	carbonate ion	NO_3^{1-}	nitrate ion
ClO_4^{1-}	perchlorate ion	NO_2^{1-}	nitrite ion
ClO_3^{1-}	chlorate ion	MnO_4^{1-}	permanganate ion
ClO_2^{1-}	chlorite ion	O_2^{2-}	peroxide ion
ClO^{1-}	hypochlorite ion	PO_4^{3-}	phosphate ion
CrO_4^{2-}	chromate ion	SO_4^{2-}	sulfate ion
$Cr_2O_7^{2-}$	dichromate ion	SO_3^{2-}	sulfite ion
CN^{1-}	cyanide ion		

Some Common Polyatomic Ions

Standard Reduction Potentials

Ox + ne^{1-}		**Red**	**$\mathcal{E}^\circ$ (V)**
$K^{1+}(aq) + e^{1-}$	$\leftrightharpoons$	$K(s)$	−2.92
$Na^{1+}(aq) + e^{1-}$	$\leftrightharpoons$	$Na(s)$	−2.71
$Mg^{2+}(aq) + 2\ e^{1-}$	$\leftrightharpoons$	$Mg(s)$	−2.36
$Al^{3+}(aq) + 3\ e^{1-}$	$\leftrightharpoons$	$Al(s)$	−1.66
$2\ H_2O + 2\ e^{1-}$	$\leftrightharpoons$	$H_2(g) + 2\ OH^{1-}(aq)$	−0.83
$Zn^{2+}(aq) + 2\ e^{1-}$	$\leftrightharpoons$	$Zn(s)$	−0.76
$Cr^{3+}(aq) + 3\ e^{1-}$	$\leftrightharpoons$	$Cr(s)$	−0.74
$Fe^{2+}(aq) + 2\ e^{1-}$	$\leftrightharpoons$	$Fe(s)$	−0.44
$2\ H_2O + 2\ e^{1-}$	$\leftrightharpoons$	$H_2(g) + 2\ OH^{1-}(aq)$	−0.41*
$PbSO_4(s) + 2\ e^{1-}$	$\leftrightharpoons$	$Pb(s) + SO_4^{2-}(aq)$	−0.36
$Ni^{2+}(aq) + 2\ e^{1-}$	$\leftrightharpoons$	$Ni(s)$	−0.23
$Sn^{2+}(aq) + 2\ e^{1-}$	$\leftrightharpoons$	$Sn(s)$	−0.14
$Pb^{2+}(aq) + 2\ e^{1-}$	$\leftrightharpoons$	$Pb(s)$	−0.13
$2\ H^{1+}(aq) + 2\ e^{1-}$	$\leftrightharpoons$	$H_2(g)$	0.00
$Cu^{2+}(aq) + 2\ e^{1-}$	$\leftrightharpoons$	$Cu(s)$	+0.34
$O_2(g) + 2\ H_2O + 4\ e^{1-}$	$\leftrightharpoons$	$4\ OH^{1-}(aq)$	+0.40
$I_2(s) + 2\ e^{1-}$	$\leftrightharpoons$	$2\ I^{1-}(aq)$	+0.54
$Fe^{3+}(aq) + e^{1-}$	$\leftrightharpoons$	$Fe^{2+}(aq)$	+0.77
$Ag^{1+}(aq) + e^{1-}$	$\leftrightharpoons$	$Ag(s)$	+0.80
$O_2(g) + 4\ H^{1+}(aq) + 4\ e^{1-}$	$\leftrightharpoons$	$2\ H_2O$	+0.82*
$NO_3^{1-}(aq) + 4\ H^{1+}(aq) + 3\ e^{1-}$	$\leftrightharpoons$	$NO(g) + 2\ H_2O$	+0.96
$Br_2(l) + 2\ e^{1-}$	$\leftrightharpoons$	$2\ Br^{1-}(aq)$	+1.09
$O_2(g) + 4\ H^{1+}(aq) + 4\ e^{1-}$	$\leftrightharpoons$	$2\ H_2O$	+1.23
$Cr_2O_7^{2-}(aq) + 14\ H^{1+}(aq) + 6\ e^{1-}$	$\leftrightharpoons$	$2\ Cr^{3+}(aq) + 7\ H_2O$	+1.33
$Cl_2(g) + 2\ e^{1-}$	$\leftrightharpoons$	$2\ Cl^{1-}(aq)$	+1.36
$MnO_4^{1-}(aq) + 8\ H^{1+}(aq) + 5\ e^{1-}$	$\leftrightharpoons$	$Mn^{2+}(aq) + 4\ H_2O$	+1.51
$PbO_2(s) + 4\ H^{1+}(aq) + SO_4^{2-}(aq) + 2\ e^{1-}$	$\leftrightharpoons$	$PbSO_4(s) + 2\ H_2O$	+1.69
$F_2(g) + 2\ e^{1-}$	$\leftrightharpoons$	$2\ F^{1-}(aq)$	+2.87

Standard Reduction Potentials at 25 °C in volts

* The half-cell potentials for the O_2/H_2O and the H_2O/H_2 systems are for pure water and are not for standard reduction potentials where $[OH^{1-}]$ and $[H^{1+}] = 1.0\ M$.

Solubility Rules

Solubility Rules for Ionic Substances in Water

Rule 1 Compounds containing $NH_4{}^{1+}$ and group 1A metal ions are soluble.

Rule 2 Compounds containing $NO_3{}^{1-}$, $ClO_4{}^{1-}$, and $C_2H_3O_2{}^{1-}$ are soluble.

Rule 3 Compounds containing Cl^{1-}, Br^{1-}, and I^{1-} are soluble *except* those of Ag^{1+}, Tl^{1+}, $Hg_2{}^{2+}$, and Pb^{2+}.

Rule 4 Compounds containing $SO_4{}^{2-}$ are soluble *except* those of Ca^{2+}, Sr^{2+}, Ba^{2+}, and Pb^{2+}.

Rule 5 Most other ionic compounds are insoluble in water.